

The Handbook of Environmental Chemistry 104

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Manuel Jerold

Santhiagu Arockiasamy

Velmurugan Sivasubramanian *Editors*

Bioprocess Engineering for Bioremediation

Valorization and Management
Techniques



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Volume 104

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Bioprocess Engineering for Bioremediation

Valorization and Management Techniques

Volume Editors: Manuel Jerold · Santhiagu Arockiasamy ·
Velmurugan Sivasubramanian

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Series Preface

With remarkable vision, Prof. Otto Hutzinger initiated *The Handbook of Environmental Chemistry* in 1980 and became the founding Editor-in-Chief. At that time, environmental chemistry was an emerging field, aiming at a complete description of the Earth's environment, encompassing the physical, chemical, biological, and geological transformations of chemical substances occurring on a local as well as a global scale. Environmental chemistry was intended to provide an account of the impact of man's activities on the natural environment by describing observed changes.

While a considerable amount of knowledge has been accumulated over the last four decades, as reflected in the more than 150 volumes of *The Handbook of Environmental Chemistry*, there are still many scientific and policy challenges ahead due to the complexity and interdisciplinary nature of the field. The series will therefore continue to provide compilations of current knowledge. Contributions are written by leading experts with practical experience in their fields. *The Handbook of Environmental Chemistry* grows with the increases in our scientific understanding, and provides a valuable source not only for scientists but also for environmental managers and decision-makers. Today, the series covers a broad range of environmental topics from a chemical perspective, including methodological advances in environmental analytical chemistry.

In recent years, there has been a growing tendency to include subject matter of societal relevance in the broad view of environmental chemistry. Topics include life cycle analysis, environmental management, sustainable development, and socio-economic, legal and even political problems, among others. While these topics are of great importance for the development and acceptance of *The Handbook of Environmental Chemistry*, the publisher and Editors-in-Chief have decided to keep the handbook essentially a source of information on "hard sciences" with a particular emphasis on chemistry, but also covering biology, geology, hydrology and engineering as applied to environmental sciences.

The volumes of the series are written at an advanced level, addressing the needs of both researchers and graduate students, as well as of people outside the field of

“pure” chemistry, including those in industry, business, government, research establishments, and public interest groups. It would be very satisfying to see these volumes used as a basis for graduate courses in environmental chemistry. With its high standards of scientific quality and clarity, *The Handbook of Environmental Chemistry* provides a solid basis from which scientists can share their knowledge on the different aspects of environmental problems, presenting a wide spectrum of viewpoints and approaches.

The Handbook of Environmental Chemistry is available both in print and online via www.springerlink.com/content/110354/. Articles are published online as soon as they have been approved for publication. Authors, Volume Editors and Editors-in-Chief are rewarded by the broad acceptance of *The Handbook of Environmental Chemistry* by the scientific community, from whom suggestions for new topics to the Editors-in-Chief are always very welcome.

Damià Barceló
Andrey G. Kostianoy
Series Editors

Preface

The current generation society is moving ahead from the primordial conception of “take, make, and dispose of” to “reuse and recovery” of potentially available resources to attain a “healthy–wealthy environment” and “prospective socioeconomics.” Bioprocessing is a key platform in the establishment of circular bioeconomy through the valorization of biowaste, organic residuals, and bio-industrial side streams into value-added products of low cost and sustainable aspects. Waste biorefinery is gaining more attention nowadays because waste is used as the renewable feedstock for the recovery of bioproducts and bioenergy by means of sustainable biotechnology. The traditional approach of waste management is focused on the removal or reduction of pollutants to protect the environment and mammals from the harmful effects. However, scientific advancement has led to the remediation that can be pursued by using waste as an alternative feedstock toward refining the waste for the recovery of the valuable resource products. In a nutshell, all kinds of wastes including solid, liquid, and gas have inbuilt potential resources that can be valorized for the development of bio-based products and biofuels through an intensive bioprocess cascade system that enables the transformation toward a low-carbon circular bioeconomy. Therefore, circular bioeconomy paves way for the reuse, recycle, and remanufacture via the idea of utilizing the bio-based materials for the production of high-value products and fuels. The perception of biorefinery is similar to the petroleum refineries in which an array of bioproducts is derived from biomass feedstocks. Thereby, biorefinery is the integration of several components such as itinerary of bioconversion, bioprocess design, and equipment development for the sustainable processing of biomass into a spectrum of marketable value-added products like biomaterials, biochemicals, and bioenergy. Bioprocessing and biorefinery have gained a successful routine for the bioremediation. In order to enhance the proper utilization and recovery of value-added products from biowaste and organic waste products, there is a need for detailed and broad-spectrum technical knowledge. This book “Bioprocess Engineering for Bioremediation: Valorization and Management Techniques” conceived keeping view of the social importance to deliver the available up-to-date technical

information to the researchers and engineers working on bioremediation and pollution control. The content of the book is the net outcome of eminent researchers and academicians in the field of biotechnology and chemical engineering. Today, more focus is given to green techniques and technology to overcome the limitations of conventional methods and reduce the global level pollution.

This book contains 14 chapters related to bioprocess and biochemical engineering and its application in bioremediation. More focus is given to address the solid and liquid waste management. This book highlights the importance of waste valorization in a sustainable and eco-friendly approach. The readers would be able to gather more information on biomass valorization in a cost-effective method. Herein, in this book, algal biomass and its diversified value-added products such as biofuel, bioplastics, bioactive compounds, biosorbents, and nano biopolymer are reviewed in detail. Lignocellulosic biomass, a second-generation biofuel feedstock, is reviewed and explained to explore for the production of sustainable green fuels. Further, agricultural biomass valorization for organic acid production using microbial bioprocessing is reported in detail with recent advancements. Few other chapters related to biological wastewater treatment, bioleaching of e-waste, and phytoremediation of soil for metal and organic pollutant removal are added to give an outline about the green techniques in waste management. This book also gives information about the municipal solid waste supercritical water gasification technology. Hydrothermal liquefaction technology, considered as an emerging method in the conversion of biomass into fuels and fine chemicals and seen as green remediation, will also give a detailed knowledge on biomass valorization. In a nutshell, this book is an interdisciplinary work focused on green chemistry that will give essential information on R&D perspective to the readers working on sustainable bioremediation specialization. Moreover, this book is written by reputed authors from various technical institutions based on their expertise and research outcomes. So, we believe this book will be a driving force for the young budding engineers as well for the experts searching for the valorization and waste management techniques. Interestingly, this book will address the treatment of waste using advanced bioprocess techniques. Therefore, the readers would be happy to find the alternative approach to the conventional chemical methods in an eco-friendly route. It is assured that this book will be a handbook for students, researchers, academicians, and engineers who are involved in various scientific areas related to waste management. Today, waste management is a challengeable task for the public as well as for the private sectors. We ensure our book would provide an affordable and innovative method of bioremediation for the present scenario.

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Membrane Technology in Bioprocess Engineering



Randeep Singh, K. V. V. Satyannarayana, R. Vinoth Kumar,
and I. Ganesh Moorthy

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Abstract This chapter discusses about the role of membrane processes, namely, microfiltration, ultrafiltration, nanofiltration, and reverse osmosis in the field of bioprocess engineering. Membrane processes are widely accepted and used techniques in separation and filtration applications because of their unique and beneficial properties, such as low cost, environment friendliness, ease to scale up, ease to integrate with other processes, and compactness. Therefore, their use and implementation in various fields of bioprocess engineering helps in saving a lot of energy and resources. The basic concept and fundamentals along with the classification of different types of membranes and membrane systems are explained with suitable examples. The important applications of membrane technology in various fields of bioprocess engineering, such as food, pharmaceuticals, and biotechnology, are also discussed along with their advantages over other conventional separation techniques. The main applications where membrane processes proved their worth are virus purification, sterilization of heat labile products, concentration of food and dairy products, separation and filtration of racemic and azeotropic mixtures, fruit juice clarification, and beer and wine production. Hence, this chapter provides complete details about the importance, applications, and benefits of membrane technology in the field of bioprocess engineering.

Keywords Bioprocess engineering, Membrane separation processes, Membrane systems, Membrane technology, Separation and filtration

1 Introduction

The basic definition of a membrane states that a membrane is a thin barrier present between two phases that allow selective passage of components under the influence of an appropriate driving force [1]. Initially, membranes are employed on analytical scale; however, the advancements in the field of membrane science increase their use in commercial processes. These advancements and developments in membrane technology brought a dramatic change in the field of separation science due to the exceptional advantages associated with membrane separation processes. The conventional separation processes are failed by membrane separation processes due to their ease to use, no additional chemical requirements, exceptional product quality, energy efficiency, effectiveness, economical, and environment friendliness. Nowadays, membranes are widely used in various industries and processes, such as food,

pharmaceutical (pharma), biotechnology (biotech), desalination, and separation and purification of industrial effluents [1–3].

The reason behind the importance and integration of membranes in the field of bioprocess engineering lies in the fact that membranes are capable to carry out significant amount of work in different processes and applications under different capacities in fermenters and bioreactors, such as gas transport, transfer of selective nutrients, separation and purification of value-added products, as sensors to analyze the concentration of analyte, downstream processing of proteins and other products, and for sterilization of heat labile compounds. Downstream applications of membranes include sterile filtrations of buffer, gases, and end products. Membrane chromatography can be used for purification of raw materials and products. Further, upstream applications include sterile filtrations of fermenter media, pH controllable solutions, and gases, such as air and oxygen. Membrane filters with $0.1\text{ }\mu\text{m}$ pore size can provide retention of mycoplasma and larger organisms, and tangential flow microfiltration is used for medium exchange [4]. The different membrane separation processes, such as microfiltration, ultrafiltration, reverse osmosis, nanofiltration, pervaporation, and electrodialysis are playing important role in various capacities in different industrial and commercial applications [5]. Enantiomeric separations, artificial organs, hemodialysis, milk and fruit juice clarification, protein purification, beverage production, and drug delivery are few of the important applications where membrane separation processes are employed for effective and efficient operations [6].

This chapter discusses in detail about the role of membrane science in the field of bioprocess engineering by explaining various applications. Further, basics of membranes are discussed in the initial sections of the chapter, and emphasis is given on the types of membranes based on the driving force. Later, the membrane processes in different bioprocess industries by giving selective examples of various applications are explained for better understanding. Lastly, the future of membrane separation processes in the field of bioprocess engineering is explained with relative topics and examples.

2 Membrane Types and Their Importance in Bioprocesses

The membranes are classified mainly based upon their nature, structure, and separation principle or mechanism. Structurally, membranes are either symmetric or asymmetric [1]. Furthermore, symmetric membranes can be porous, dense, and charged. The porous membranes, as the name suggests, consist of voids and pores. The porous membranes follow size exclusion principle for separation of the feed components. Microfiltration and ultrafiltration are two common examples of membrane separation processes where porous membranes are used. Dense membranes, as the name suggests, are nonporous membranes. The separation of feed components takes place by diffusion mechanism in nonporous membranes. The driving force for the diffusion of the feed components may be pressure, concentration, temperature,

magnetic, or electrical potential gradient. Nanofiltration and gas separation are two commonly used membrane separation processes to employ dense membranes. On the other hand, charged membranes consist of a charge (negative or positive) and may be porous or dense depending upon the application. Again, the separation mechanism is diffusion and selectivity based upon the charges present on the membrane and feed particles. Electrodialysis is the most common example to use charged membranes.

Microfiltration membrane separations are mainly used for separation, removal, and concentration of cells and bacteria. Microfiltration membranes are being used for retains cells and cell debris while allowing proteins and other small solutes to pass into filtrate [4]. These are used for the removal of contaminants and particulates from solutions in advance of chromatographic processing and for the clarification of monoclonal antibody solutions. The microfiltration membranes are especially sterile filtrations, and they do not concern the quality of the product or solutions. Sterile membrane processes are the most important from an economical point of view [7]. Ultrafiltration is extensively applied in biopharmaceutical industries to concentrate and diafilter biological particles, commonly proteins. The membrane selection generally depends on the cleanability and compatibility. Ultrafiltration membranes are typically used in cross-flow filtration devices. Membranes are used extensively throughout the production, purification, and formulating biotechnological products. Ultrafiltration membranes are used when there is requirement of high retention of protein and other big size molecules (macromolecules) and used for high-performance tangential flow filtrations (HPTFF) [4]. Membrane chromatography modules are the new technology in the field of pharmaceuticals. Membrane chromatography can be used for purification of products and materials, e.g., the separation of endotoxins from raw materials before using them in downstream processing. The removal rates of these membranes depend on adsorptive and size-based retention mechanism [8]. Diafiltration and ultrafiltration are used for removal of thymidine and glycine. Virus filtrations used to protect cell cultures and introduction of viral contaminants into medical raw materials [4].

Asymmetric membranes consist of two layers of different thickness, pore sizes, and porosity [1]. The top layer is a dense membrane with thickness in the range of 0.1–0.5 μm . In contrast, the bottom layer consists of a porous membrane of thickness in the range of 50–150 μm . The top dense layer offers selectivity, and strength is given by the porous bottom layer [6, 9]. The bottom layer is kept porous so as to reduce the flux resistance. The asymmetric membranes are named differently based upon their constituents. For example, layers formed of two different materials are known as composite membranes. Furthermore, the layers can be optimized independently based upon the requirements. Asymmetric membranes are the most commonly used membranes in various membrane separation processes due to their advantages of selectivity, productivity, and life span.

Furthermore, membrane processes are classified based upon their mechanism of separation as reported in Table 1. The different categories are explained below.

Table 1 Membrane processes are classified based upon their mechanism of separation

Membrane process	Feed phase-permeate phase	Driving force	Size of retained compounds	Type of retained compounds
Microfiltration (MF)	L-L	ΔP	0.1–100 μm	Fine solids, bacteria
Ultrafiltration (UF)	L-L	ΔP	5 nm to 100 μm	Suspended solids, viruses, natural organic matter
Nanofiltration (NF)	L-L	ΔP	1 nm to 100 μm	Surfactants, dyes, sugars, inorganics
Reverse osmosis (RO)	L-L	ΔP	0.1 nm to 100 μm	Minerals, metal ions salts
Pervaporation	L-G	ΔP	0.5 nm to 100 μm	Liquids
Dialysis	L-L	ΔC	—	—
Electrodialysis	L-L	$\Delta \phi$	—	Ions
Membrane distillation	L-L	ΔT	—	Liquids

L-L liquid-liquid, G-G gas-gas, L-G liquid-gas, ΔP pressure difference, ΔC concentration difference, $\Delta \phi$ electric potential difference, ΔT temperature difference

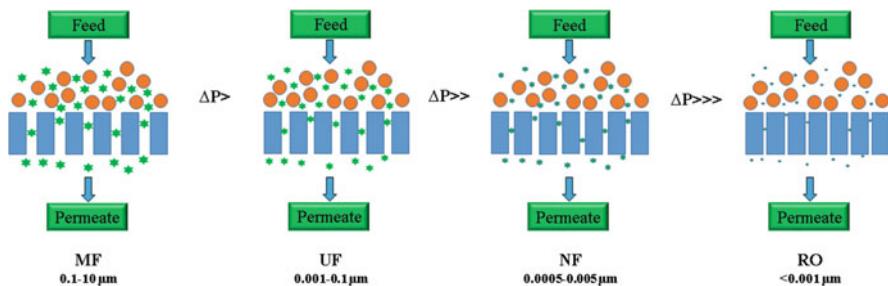


Fig. 1 Schematic representation of pressure-driven membrane separation processes [1] (Reproduced with permission from Taylor and Francis)

2.1 Pressure-Driven Membrane Separation Processes

The membrane separation processes where pressure acts as the driving force are known as pressure-driven membrane separation processes [1]. The common examples of pressure-driven membrane separation processes are microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. Figure 1 shows a representative pressure-driven membrane separation process. These membrane separation processes are commonly used in various bioprocess-associated industries, such as biotechnology, chemical, pharmaceutical, food, and dairy. The membranes used in these membrane separation processes are either polymeric, ceramic, or metallic. Furthermore, these processes are classified based upon the pore size, charge, or pressure range used. The overall membrane separation efficiency (MS_e) depends upon various factors, such as feed and membrane type, feed particle size, and

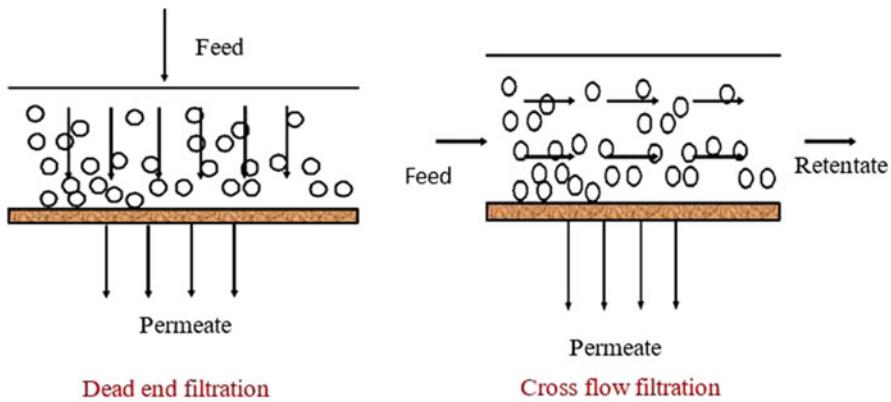


Fig. 2 Schematic representation of flow pattern of membrane separation processes

physicochemical process parameters. These factors give rise to total membrane resistance (R_t). Further, it can be calculated by using the following relation.

$$MS_e = 1 - \frac{P_c}{F_c} \quad (1)$$

where MS_e represents the membrane separation efficiency (%), P_c the permeate concentration (mg/L), and F_c the feed concentration (mg/L).

The membrane separation efficiency lies in between 50 and 90% for various industrial processes. The total membrane resistance can be calculated by using the following relation.

$$R_t = R_r + R_{ir} \quad (2)$$

where R_r represents the reversible membrane resistance and R_{ir} the irreversible resistance. The reversible and irreversible resistances are also due to the reversible and irreversible membrane fouling, respectively. The reversible fouling as can be deciphered from the name is removable by simple hydraulic washings. However, irreversible fouling, as the name suggests, is difficult to get rid of from the membranes and lastingly adds to the total membrane resistance.

There are two types of flow patterns and filtration arrangements in UF and MF membranes as shown in Fig. 2 [1]:

Dead-End Filtration In a dead-end filtration system, the feed flow is perpendicular to the membrane surface. The solute or the rejected particles remain on the membrane, forming a gel or cake layer. This phenomenon enhances the accumulation of particles on the membrane surface and causes increase in membrane resistance. The resistance can only be minimized by applying pressure to maintain the flow.

Cross-Flow Filtration In the cross-flow filtration arrangement, feed flows in the parallel direction to the membrane surface. Most of the retained particles or the solutes are swept away with the flowing feed side liquid. Recirculation of the retentate to enhance the concentration can be achieved in this arrangement. This flow pattern involves less or negligible accumulation of solid particles on the membrane and is favored.

2.2 Concentration-Driven Membrane Separation Processes

Concentration-driven membrane separation processes are the membrane separation processes where concentration is the driving force [1]. The concentration and pressure-driven membrane separation processes are similar in function with only difference that in concentration-driven membrane separation processes the permeant's chemical activity remains the same on the feed side and decreases drastically on the permeate side. However, in case of pressure-driven membrane separation processes, the chemical activity of the permeant increases on the feed side on application of increased pressure. Gas separation, pervaporation, and dialysis are some of the common examples of concentration-driven membrane separation processes [1, 2]. Figure 3 represents a concentration-driven membrane separation process.

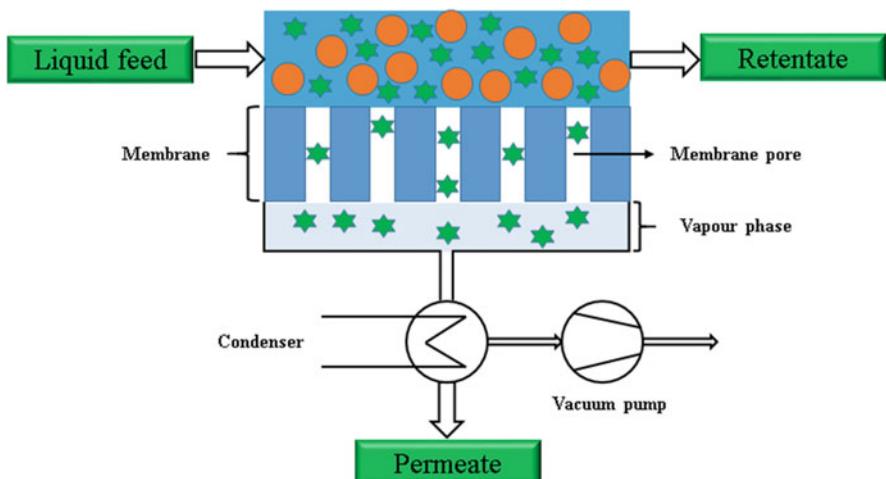


Fig. 3 Schematic representation of concentration-driven membrane separation process (Pervaporation) [1] (Reproduced with permission from Taylor and Francis)

3 Membrane Processes for Pharmaceutical and Biotechnology

The pharmaceutical and biotechnology industries are major users of membrane science due to their specific requirements and advantages associated with membranes. In this section, some of the applications of membranes in the field of pharma and biotech industries are discussed for better insights into the use and advantages of membranes. Major applications of membranes in pharma and biotech sector are based on the filtration and separation of heat labile compounds and purification of blood and other liquids. In addition to biotechnological industry, membranes can also be used in biomedicine. Further, biotechnological products can be produced with recombinant DNA technology. Transgenic animals and plants are produced with the recombinant DNA technology. These animals and plants are modern alternatives of common animals and plants to produce quality animal and plant products, such as milk, eggs, corn, and tobacco [4].

3.1 Virus Purification

Centrifugation and ultrafiltration techniques were frequently employed techniques for the virus purification in the bioprocesses; however; both techniques are labor intensive, time taking, and expensive. In the last decade, membrane chromatography was widely utilized for the purification of viruses due to several limitations on using the traditional resin chromatography. The separation can be achieved owing to distinctive chemical/physical properties of defective/inactive and bioactive virus particles in the membrane chromatography technique. It was reported that the binding capacity of membrane adsorber is strongly influenced by the size of the biomolecules, which demonstrated using thyroglobulin (MW 660 kDa, ~20 nm), Aedes aegyptidensonucleosis virus (AeDNV, ~20 nm), lysozyme (MW 14 kDa), and bovine serum albumin (MW 67 kDa) [10]. The membrane ligand density can also be related by the effect of biomolecule size on ligand accessibility within the pores of the membrane. In order to achieve the enhanced purification of the recovered virus, ligand density can be reduced appropriately [11]. In the membrane chromatography, specific factors related to viruses, including point of zero charge (PZC) and affinity, may decide the separation characteristics and type of the ligand and capture. Bioactivity of separated viruses and mobile phase conditions may be altered while using chemicals to remove the virus particles from the membrane adsorbers [12]. The decrement in the ion strength (pH) of the mobile phase results in the infection of baculovirus. Most importantly, virus purification required proper protections of virus structure and production of attenuated viral vaccine [13].

3.1.1 Purification of Biologicals

Membrane filtrations are preferred because of low costs and increased process performance in case of large-scale productions and thickening of bacterial toxins. In the direction of keeping production costs, the following two filtration steps are needed [7]:

1. Fermentation broth is required to be clarified by using microfilterable membranes.
2. Toxins should be concentrated by ultrafiltration.

In comparison to organic membranes, inorganic membranes have high chemical, mechanical, biological, and thermal resistances. Also, they have a long life, low membrane friction, and high performance of filtration [14]. Bacterial toxins must be purified and detoxified by formalin or heat to get toxoid as product. High flux, regeneration capacity, and along life cycle are needed to reduce necessary membrane area, which further reduces the overall process costs. Regarding these requirements, ceramic membranes are well suitable for biologicals. Apart from this membrane fouling is a major problem.

Stationary phases for purification of big molecules have designed as membranes and monoliths. Their advantages lie in their ability to be used at high flowrates, while exceeding the conventional flow rates. Adsorptive and monoliths are disposable and scalable, which eliminates the needs for cleaning and sterilization. ATMPs (advanced therapy medicinal products) are upcoming class of biologicals for gene therapy and tissue paper repair including cancer treatment. All these molecules, cells, and VLPs (virus-like particles) require extensive purification to meet regulatory standards. Therefore, this membrane-based technology is promising, especially for its efficiency in downstream processes [14].

3.2 Sterilization

The reagents and compounds, such as antigens, antibodies, enzymes, human plasma fractions, parenteral drugs, vaccines, and culture medias, are required to be sterilized in the field of bioprocess engineering. Additionally, these reagents and compounds are generally heat and pressure sensitive. Therefore, conventional sterilization methods, such as heat sterilization, are not suitable for their sterilization. Henceforth, membrane separation technique proves to be the best sterilization solution for such reagents and compounds. However, the separation and purification indirectly the sterilization via membrane separation process should be perfect because in case single microorganism or impurity may spoil the whole compound completely. For example, if a single microorganism is permeated across the membranes, then overnight it can grow into thousands. Furthermore, the clinical data shows that particulate matter present in IV solutions points to severe health risks, such as clotting resulting in the direct blood vessel blocking or partial arteries occlusion.

Thus, US Food and Drug Administration (FDA) strictly regulated the conditions of mean porosity ($0.45\text{ }\mu\text{m}$) of the membranes for the sterilization of parenteral drugs.

Additionally, membranes are also used to sterilize the air and gases used for various applications in the health care industry. The harmful microorganisms and particulate matter are removed from the air or gas to make it deemed to be fit for use. Furthermore, FDA also recommended the installation of air vents and filters at places where microorganisms are handled or controlled environment is required, which is the requirement of bioprocess engineering in various processing and manufacturing processes of different products. Similarly, this explains the use of vent filters as retentive filters in case of bioreactors and fermenters.

The sterilization of the membranes is also important and should have capabilities to be installed aseptically. Otherwise, they can infect the feed to be sterilized. Further, the membranes should be tested for their cleanliness and sanitization prior to use. This demand gives rise to the development of autoclavable and sterilizable membranes for their continuous use and reuse. It is also important to note that for gas and liquid separations, hydrophobic and hydrophilic membranes are recommended, respectively. However, the hydrophobicity and hydrophilicity of the membranes depend upon the nature of the feed.

3.3 Racemic and Azeotropic Separations

Sugars and amino acids are important part of bioprocess engineering. They are key components and starting material for many important products of bioprocess industry. Therefore, there separation and purification are important as they are required to be in their purest of form for the product formation. There are several separation processes, including membrane separation processes, that can be used for their separation and purification. However, the problem arises when they are present in their chiral form. This means that the sugars or amino acids are present in their two different enantiomer forms. Further, these enantiomers of a material consist of similar crystalline states and chemical qualities. Thus, it is difficult to separate such compounds with conventional separation processes. Also, only one of the enantiomer of the compound is useful toward a particular function, and the other might have weak functionality or would be toxic. For example, thalidomide is a racemic drug used during pregnancy for the cure of nausea. The dexter (D) form of thalidomide being a safe sedative is useful. However, its laevis (L) form results in birth defects and deformities.

Membrane separation processes, such as pervaporation, ultrafiltration, and liquid membranes are suitable for the separation of racemic and azeotropic mixtures [1, 2]. The membranes used for this purpose are either enantioselective or non-enantioselective. The difference between the two types of membranes is that the enantioselective membranes are made up of enantioselector components, such as antibodies, antigens, and enzymes. On the other hand, non-enantioselective membranes are normal membranes integrated with other chiral separation processes.

Further, the enantioselective membranes are either inherent or functionalized chiral. The difference lies in the fact that chiral materials, such as diphenylacetylenes, disubstituted acetylene, and norbornadiene, are used to synthesize the inherent chiral membranes and functionalized chiral membranes, as the name suggests are functionalized with chiral materials. The enantioselector components show affinity toward a selective enantiomer. Therefore, the enantioselective membranes are capable of selectively separating enantiomers effectively and efficiently without any outside assistance. The enantioselectors are incorporated into the membranes by grafting, in case of pervaporation or ultrafiltration membranes and immobilization, in case of liquid membranes. Further, the enantioselective membranes based on their mechanism of separation can be categorized into diffusion enantioselective and adsorption enantioselective membranes. The inherent chiral and functionalized chiral membranes come under diffusion and adsorption enantioselective membranes category, respectively. The chiral materials present in the inherent membranes support the diffusion enantioselective mechanism of separation, and on the other hand, the chiral materials present on the functionalized chiral membranes aids in adsorption enantioselective mechanism.

3.4 Filtration of Valuable Products

Membrane technology is capable of extracting all the available reserves from a source in an efficient and effective manner. Therefore, the use of membranes for the filtration and separation of value-added products from different sources is highly recommended. The best example is the separation of whey protein from milk during cheese production [1]. Whey which is a byproduct of cheese production due to its high oxygen demand is used to create a huge disposal problem. However, with the use of membrane science, this waste is used for the extraction of whey protein which is an energy-rich nutrient and widely used for its nutrient values. Additionally, lactose is produced from the whey permeate by using different membrane separation processes, such as reverse osmosis. Similarly, in beverages industry membrane processes are used for the recovery of microorganisms (e.g., yeast) from the bottom of the fermenters for their reuse. In case of beer industry, this process of yeast recovery also revives 1% of the total beer produced in a year, which used to get wasted at the bottom of the fermenters. Therefore, not only the microorganisms used for fermentation of the beverages are recovered but also the remaining beverages left at the bottom of the fermenters. Thus, membrane processes are important for the filtration, separation, and recovery of the valuable products.

Furthermore, the membrane separation processes are efficient in the separation of heat labile products. Therefore, the valuable products will not be denatured or harmed during their filtration and separation. Thus, the valuable products will be available in their natural form and flavor. This is one of the important advantages of using membrane separation processes for the filtration, separation, and recovery of valuable products from different processes and source. These are some of the reasons

that membrane separation processes are nowadays widely used in different bioprocess engineering applications. Further, the use of membrane science will increase many folds in coming years due to the fast growth, advancement, and development in the field of membrane science.

3.5 *Hemodialysis*

Hemodialysis, as the name suggests, is the dialysis of blood. This procedure is required in case kidney failure occurs in a person. Membranes imitating physiological functions and superior hemocompatibility are desirable. Additionally, enhanced flux and selectivity along with better antifouling nature are the prerequisites. These membrane properties improve the efficiency and effectiveness of the membranes in a hemodialysis process. Therefore, novel membranes with improved hemocompatibility, self-cleaning, and flux are required to be developed. Similarly, there is a need to develop membrane materials with desired properties because these materials are solely responsible for the prerequisite membrane properties.

In early stages of development, hydrophobic membranes of polymers, such as polyamide, polyacrylonitrile, polyarylethersulfone, and polysulfone, are used [1]. These membranes are researched for enhancing the permeability for better purification rate. However, with time and progress in the field of membrane science, focus is given to the development of hemocompatible membranes with improved flux and antifouling behavior. Presently, main focus is on the development of living membranes that can imitate complete functions of the natural organs. Researchers working on this domain developed renal tubule cell assist device (RAD) that can imitate functions of a natural kidney. Membranes are used to adhere human renal cells to mimic a kidney and carry out other physiological functions of a kidney, such as managing metabolic activities and endocrine processes, including separation and purification. Hemofilter along with the RAD device is used as an artificial kidney performing separation, purification, metabolic and endocrine activities, and reabsorption of useful nutrients [1].

Membrane technology is advancing at a very good pace; therefore, membrane-based techniques are both safe and secure. Henceforth, hemodialysis a membrane-based procedure is also in its advanced stages. Mainly because of the developments in the ancillary equipments and the inclusion of automation in the devices responsible for safety. Therefore, the improvements in the membranes, water quality, dialysate, and computer controls makes hemodialysis a fully automatic and safe to operate procedure. The progress and growth in hemodialysis procedure help to improve the survival rate. Therefore, there is immense scope of development in the field of membrane science for the betterment of health and life.

4 Membrane Processes for Food Industries

This section discusses about the importance and use of membranes in different applications of food industry. Membranes are employed for the separation and purification of food products, such as proteins, fruit juice, milk, and other beverages. In this section, the role and use of membranes for the separation and purification of these food products are discussed in detail.

4.1 Protein Purification and Concentration

The membrane separation processes, especially ultrafiltration, are widely used for the protein separation, purification, and concentration [1]. This section is divided into following subsections for better understanding of the topic.

Protein Concentration

Membrane processes separate proteins from a feed, and the resultant remains is the protein concentrate. This helps in recovering of protein in its intact form and from any dilute feed. Additionally, protein content is adjusted with the help of membranes in pharmaceutical formulations. The conventional processes of protein purification, such as chromatography, crystallization, and precipitation, can be employed after the step consisting of membrane processes. This will help in keeping the natural form and composition of the proteins intact. In addition to this, it also makes the whole process economical.

Protein Desalting

The solution containing proteins also contains salts and some impurities. Therefore, membrane separation processes are also employed for the desalting of the protein solution. This results in the protein of pure quality. Membrane separation processes can also be used in combination with other salt removal techniques, such as salt-induced precipitation in case the salt concentration is very high. This combination is useful as high salt concentrations result in fouling of the membranes.

Protein Purification

Proteins are separated from other impurities, such as bacteria, viruses, salts, and other unwanted compounds; this results in proteins with high quality and quantity in their intact form. Nowadays, ultrafiltration membranes are commonly used for the separation of prions.

Protein Fractionation

In case two or more numbers of proteins are present in a solution, then membrane separation processes are used for the separation of one protein from other. This process of protein separation from each other is known as protein fractionation. The major factors playing important role in protein fractionation are pH and ionic

strength of the solution, protein-protein and protein-membrane interactions, and flux and mass transfer across the membrane.

The protein purification and concentration are carried out in the above mentioned steps by using membrane separation processes. The major advantages of using membranes in protein purification and concentration are that they are efficient, effective, economical, and consume low energy.

4.2 *Fruit Juice Clarification*

Fruit juices are rich in cellulose, protein, fibers, pectin, polysaccharides, lignin, gum, and starch including many other constituents. The fruit juice is very cloudy and viscous due to the presence of these compositions. The processed fruit juices should have the following requirements for consumer satisfactoriness: (1) fruit juice with low viscosity and higher clarity, (2) should have natural flavor, (3) and long shelf life of the juice. Several separation and conservation methods have been in use to make the treated fruit juice more concentrative for the consumers [1].

Membrane separation techniques are one of the most profitable methods, as they do not require addition of any chemical agents and it is a room temperature process. Additionally, they need low maintenance to maintain the original flavor, taste, smell, and nutritional parameters of the fruit juice. However, they have a limitation of fouling, as the accumulation of fouling layer on the membrane surface reduces the permeability flux [15]. Consider that pectin is one of the key gel forming agent in the presence of Ca^{2+} ions at low pH, which is present in fruits. Pectin is mostly found in citrus fruits and enzymatic treatment of guava juice at 45 °C with various enzyme concentrations [16]. Among these bananas has high content of pectin. Pectins are polysaccharides which are rich in galacturonic acid. The molecular weight of pectin is in the range of 30,000–130,000 Da, based on separation conditions. In the extraction process, the juices are viscous because of the presence of pectin, thus affecting the flux of the filtration process. Therefore, it needs depectinization to give long shelf life to the fruit juice as well as the membranes.

Clarification/Depectinization

Amylase and pectinase enzymes are used for the clarification of fruit juices conventionally to reduce the high pectin concentrations as shown in Table 2. Membrane-based separation processes are used for clarification of fruit juices because they are high-pressure resistant, operated at high temperatures, and resistant to highly corrosive fluids. In 1991, Chamchang et al. reported that by using pectinase enzyme at constant temperature tangerine juice had been depectinized [18]. Rai et al. (2004) stated that mosambi fruit juice clarification varies with concentration of enzyme (pectinase) and temperature [19]. Apple juice clarification is reported by Onsekizoglu et al. (2010) that a series of membrane processes ultrafiltration, membrane distillation, and osmotic distillation were employed, with combined application of bentonite and gelatin (fining agents) that gives high permeability flux,

Table 2 Depectinization of fruit juices with membrane-based processes [17]

Fruit juice	Enzyme	Filtration process	Transmembrane pressure (kPa)
Lemon	Novozym 33,095	Filter paper	By gravity
Pomegranate	Fungus (<i>F. fomentarius</i>)	Carbosep M2	200
Kiwifruit	Pectinex ultra SP - L	PVDF UF membrane process	85

Table 3 Membrane distillation applications in fruit juice processing [17]

Membrane type	MD configuration	Fruit juice
Hollow fiber, polypropylene	DCMD	Apple
MFK3, flat sheet, polyvinylidene fluoride	DCMD	Apple
K150, flat sheet, polytetrafluoroethylene	VMD	Blackcurrant
Millipore, flat sheet	DCMD	Orange juice
Enka Microdyn, hollow fiber, polypropylene	DCMD	Apple

recovered the nutritional and physicochemical properties after integrated membrane separation processes [20]. K.S. Youn et al. (2004) developed a series of microfiltration and ultrafiltration membrane processes for clarification of apple juice concentrate (cloudy, 45° Brix). Permeability flux increases with filter aid (bentonite) pre-treatment and produced good quality of apple juice with lower membrane fouling [21]. B. K. Nandi et al. (2009) studied the microfiltration membrane processes for mosambi juice with low cost kaolin-based ceramic membranes. Various pore blocking models had been used to analyze the decline in permeate flux [22]. Membrane distillation (MD) employs microporous hydrophobic membrane to separate two liquids which are at different temperatures; it is temperature-driven process and operated at atmospheric pressure, since MD keeps a good potential as an alternative to the pressure-driven processes [23]. A few of the major issues hindering the development of membrane operations for juice clarification, such as microfiltration and ultrafiltration in the fruit juices clarification, are primarily related to the membrane fouling. Fouling can affect membrane life span and results in decrease of permeate flux. Novelty in cleaning methods can benefit in extensive applicability of these methods in the juice industry. Some applications of membrane distillation processes are given in Table 3.

4.3 Skim Milk and Cheese Production

Skim milk production is nowadays carried out by using various membrane separation processes, such as ultrafiltration. The skim milk is standardized, concentrated, and fractionated as per need by using membrane separation processes while keeping the natural milk flavor and contents intact. This enhances the customer satisfaction

and provides profit to the producer. The standardization of milk is carried out by using ultrafiltration membrane separation process, whereas microfiltration, nanofiltration, and reverse osmosis membrane separation processes are commonly used for the concentration and fractionation of the milk. These membrane-based processes are alternative of conventional energy-intensive processes, such as heating and evaporation. The output of these processes are used for the production of various other milk products, such as concentration of milk results in the production of milk concentrate that is used in the production of milk proteins of various concentrations and other milk products; milk fractionation results in various products that are used in the production of ice cream, cheese, and other milk proteins [1]. For example, the outcome of the ultrafiltration membrane separation process for concentrating the milk is used for the production of different types of cheese, namely, cream cheese, feta cheese, and quark. Furthermore, the permeate part of this process is given to reverse osmosis membrane separation process for lactose recovery, and the permeate of this process is further used for flushing the whole system. Therefore, membrane separation processes make it possible to use single fraction of milk to produce various products, and the waste generated is negligible. Additionally, the advantage of membrane separation processes is that they conserve the original taste, texture, composition, and flavor of milk during all these processing of milk, which was not possible with conventional techniques. Hence, membrane separation processes are highly recommended in milk industry due to their efficiency, effectiveness, and economy.

4.4 Milk Sterilization

Milk sterilization is an important task so as to preserve milk for longer duration. Also, it is important to remove any foreign particles, agents, and microorganisms from milk as they are responsible for its fouling and quality degradation. The milk composition changes due to the presence of such impurities and use of conventional sterilization techniques, such as heating that alters its taste and smell. Membrane separation processes provide unaltered sterilization of milk without using any energy-intensive process and degeneration of the milk quality [1]. This helps in consumption and production of direct milk and milk products with original taste and flavor. Therefore, membrane-based separation, purification, and sterilization of milk are recommended.

4.5 Beer and Wine Production

Beer and wine are two alcoholic drinks used worldwide on a very large scale. That is why they play an important role in the economy of any country. Further, there use depends upon their quality and flavor. These two factors depend upon the production

procedure and steps followed. The separation and purification of unwanted compounds from beer and wine play an important role as any type of impurity may hamper the overall quality and flavor of the beverages. Therefore, membrane separation processes play an important role in beer and wine industry as they are capable of separation of unwanted compounds from the beverages without hampering their original flavors [1].

The beer production starts with heating the malt with fermented water, which results in the production of wort. This wort has to be clarified, before keeping it for fermentation process, to remove the hot trub (mixture of precipitated hops, malt, and proteins). The membrane separation processes, such as microfiltration, are employed for the clarification of wort. This results in better fermentation and production of flavored beer. Further, cross-flow microfiltration is used after the secondary fermentation process of beer production. In this stage, the beer is clarified of biomass and other unwanted solid compounds. Presently, hollow fiber membranes in continuous microfiltration process are used in beer industry for the separation of yeast and other microorganisms, haze, and hot trub while keeping the quality and flavor intact. The use of membrane separation processes in beer industry is useful not only in terms of flavor and quality but also reduces health associated risks and waste disposal problems. Thus, membrane separation processes are better than the conventional kieselguhr filtration used. Thereafter, the alcohol concentration in the beer is regulated by using reverse osmosis membrane separation process. Lastly, the beer pasteurization process is used for the sterilization of the beer, but here also membrane separation processes can be used. The membrane separation processes will help to store the beer flavor, freshness, and quality for a longer period of time. The beer sterilized by using the membrane separation processes is known as “cold beer” due to the nonuse of any heat treatment process. Furthermore, it costs the same as a pasteurized beer and appreciated by the consumers. Additionally, the remaining beer and yeast mixture at the bottom of the fermenters can be separated by using microfiltration. This may result in better output and utilization of the resources. Membrane processes, such as pervaporation and membrane contactors, are finding use in beer industry due to the advantages associated with them [2]. Pervaporation is used for the extraction of beer flavors so that they can be added to nonalcoholic drinks and can be sold as beer with no alcoholic content for profit. On the other hand, membrane contactors are used for the removal of carbon dioxide and oxygen for better life expectancy of the product [1, 2]. Membrane contactors are also used for the deoxygenation of water used for the high-gravity brewed beer dilution.

Grapes are crushed, pressed, and centrifuged to make grape must from which wine is produced. The alcohol content plays an important role in the quality of the wine, and alcohol production directly depends upon the sugar content present in the grape must. For example, grapes with high sugar content will produce high alcohol quantities during the fermentation process. This increased alcohol content will mask the taste of other flavors present in the wine. Therefore, it is important to regulate the sugar content, and this can be done by using reverse osmosis membrane separation process. Furthermore, in case of high sugar content, both ultrafiltration and microfiltration membrane separation processes can be used together. Additionally,

nanofiltration membrane separation process can be used for the acid enrichment. This product is then fed to the fermenter.

Wine is required to be filtered after primary fermentation, and microfiltration or diafiltration is commonly used for this purpose. Thereafter, the wine is kept for secondary fermentation in wood barrels or stainless steel tanks. The wine is again filtered after the completion of the secondary fermentation process by using conventional kieselguhr filtration or microfiltration. However, microfiltration due to its advantages is recommended for better results. Microfiltration membrane separation process is carried out by using polymeric hollow fiber or ceramic tubular membranes with pore size in the range of 0.2–0.65 μm . Thus, the wine is successfully separated, purified, and sterilized by using membrane separation processes. Moreover, electrodialysis is also employed before the bottling of wines so as to remove the tartrate salts that affect the wine quality. Electrodialysis is better and efficient method than the conventional method of tartrate salts removal. Conventionally, the wine is cooled to remove the tartrate salts, but this method is not efficient enough. Therefore, electrodialysis is recommended for better wine production. Furthermore, membrane contactors can also be used for the direct removal of alcohol from the wine and for the production of dealcoholized water. This water can be used for different purposes in the wine industry. Likewise, pervaporation membrane separation process is also effective and efficient for alcohol removal from wine, but it is not recommended as higher chances are there of the loss of characteristic flavors of the wine. In addition, microfiltration membrane separation process can also be used for the wine recovery from wine lees, the left out sediments (yeast, fining agents, seeds, and little amount of wine) at the bottom of the storage tanks making the whole process of wine making effective and efficient. Lastly, the membrane separation processes are also used for either rejuvenating or adding extra colors, flavors, and antioxidants to the produced wine. This will aid in enhancing the overall quality and flavor of the produced wine which results in its high demand and profit.

5 Future Perspectives of Membranes in Bioprocess Engineering

This section discusses about the role of membranes in the future of bioprocess engineering. Including, the areas where expertise of membrane science will be useful and appropriate for the growth and development of bioprocess engineering. Some of the main areas in this field, namely, development of artificial organs, selective drug delivery, and responsiveness to an external stimulus, are discussed. Membranes play an important role in the sustainable development of these areas and help in the advancement of the bioprocess engineering in the future.

5.1 Artificial Organs

Artificial organs, as the name suggests, are man-made organs for the patients requiring an organ transplant. Worldwide there are numerous patients who are in the waitlist of an organ transplant due to the unavailability of a suitable organ. Therefore, this situation demands the development of devices that can replicate the function of natural organs. Additionally, these artificial organs need to be developed in way such that they should not be having any compatibility issues. In the recent years, membranes are successfully used for the development of artificial organs, namely, the kidney, pancreas, lung, and liver. Moreover, research is also going on in the development of an artificial heart. Many breakthroughs were achieved in the recent past in this mission of development of an artificial heart [1]. However, still a lot of research and development are required to be successful due to the complexity and vitality associated with this organ. Anyhow, great success is achieved in case of other stated artificial organs. Some of the important artificial organs where membranes have proved their mettle are discussed below.

Artificial Kidney

Human beings are creatures with very efficient and complex machinery. This machinery consists of various organs and vessels that take care of the organism. Kidneys are one of the vital organs that sustain the organism by regulating its fluid and salts. Humans are so efficient that they can sustain with only single kidney on failure of one out of the two kidneys. However, in case of failure of both the kidneys, artificial kidneys are required due to the unavailability of a suitable donor. Nevertheless, dialysis is the commonly used procedure before the development of artificial kidneys. Dialysis is also a membrane-based device. The blood coming from the body is permeated across a membrane, and the waste and excessive fluids are rejected. The treated blood then again infused back to the body. Abel et al. were the first to demonstrate the process of dialysis in early twentieth century [24]. They carried out blood purification by using handmade collodium tubes of cellulose. Dialysis was first used on a patient in the year 1925 by Haas [25]. It was the year 1943, when the first artificial kidney was developed by Kolff et al. [26]. Rotating drum dialyzer using cellophane tubing membrane was used to develop the first artificial kidney. The cellophane membrane wrapped wooden drum rotates in a dialysate solution, and the blood arrives in it from the patient's body for purification. It was a simple device, but now dialysis is a well-developed blood purification procedure used across the world.

Artificial Liver

Human body depends upon many organs for its various functions. Liver is one of the important organs out of many in a human body. The main function of the liver in a human body is to keep it safe and free from various toxins. This function depends on hepatocytes, the mature cells of the liver. Hepatocytes are parenchymal cells that maintain contact with the body via other nonparenchymal cells, namely, Kupffer, pit, sinusoidal endothelial, and stellate cells and bile duct. Liver failure occurs in case of the autoimmune disease, hepatocellular cancer, long exposure to toxins, and viral

hepatitis. The only way to sustain an acute or chronic liver failure is a liver transplant. Liver transplant faces same problems as other organ transplants, such as organ shortage or suitable donor availability. Therefore, in this case too, there is a need of development of artificial liver that may help in rejuvenating the life of a patient with acute or chronic liver failure.

Nowadays, with the advancements in membrane science, the development of an artificial liver is made possible. The previously used blood purification techniques, like hemofiltration, hemodialysis, hemoperfusion, and plasmapheresis, are seldom used alone. Initially, cellophane and polyacrylonitrile membranes, with high rejection of lower molecular weight toxins, were used to detoxify the body. However, recently with the advancements and developments in the field of membrane science, various advanced processes and devices are into use, namely, molecular adsorbent recirculation system (MARS), single-pass albumin dialysis (SPAD), and the Prometheus system [1, 27]. These advanced systems employ novel materials made up of charcoal and polymers for the detoxification process. Hollow fiber membranes with high flux are the choice for said processes and devices. For example, polysulfone hollow fiber membranes with molecular weight cutoff of 50 kDa are used in MARS and SPAD along with albumin dialysis. However, the Prometheus system employs a 250 kDa molecular weight cutoff albumin permeable polysulfone membrane. These systems and processes show effective and efficient results over a short period of time. Therefore, these membrane-based systems play an important role and provide a patient time to arrange an organ or suitable donor in case of an acute or chronic liver failure. Nevertheless, these systems are not able to carry out other functions of the liver; therefore, there is a need to develop bioartificial liver.

Recently, the bioartificial liver system based on the hepatoma cells (primary hepatocytes) attached over the surface of a flat or hollow fiber membrane is developed. This system is termed as bioartificial liver support (BALS) system. Polyether ether ketone, polyethersulfone, and polytetrafluoroethylene are some of the commonly used membrane materials for culturing the hepatoma cells. The membranes are fundamental part of the BALS system. Hydrophilic and hydrophobic membranes are employed for better mass and gas transport, respectively, in the system to successfully carry out the function of a liver. However, there is still scope for further improvement and development to make the artificial liver truly a natural liver.

Similarly, membrane-based systems are used to develop other important organs, namely, lungs and pancreas as reported by Purkait and Singh [1].

5.2 Drug Delivery

The effective and efficient treatment of a disease depends upon the proficient delivery of the required drug dose. The conventional methods use oral or intravenous administration. This method offers drug delivery only at a particular time. This results in high drug usage, and the patient has to take the drug regularly over a

period of time until the disease persists. Therefore, there is a need of a capable and effective drug delivery system that can provide the drug on specific time in required dosage at a given site. Nowadays, membrane separation processes are used for the development of an efficient and effective drug delivery system [1–3]. Mainly, there are two types of membrane systems based on the mechanism of drug delivery, namely, diffusion and osmotic drug delivery systems. These membrane-based drug delivery systems are discussed below.

Diffusion Drug Delivery System

This system works on the Fick's law of diffusion. The drug diffuses across the membrane, and thus the membrane thickness plays an important role in its effective and efficient delivery. This system is widely used on commercial scale due to its advantages. Commonly, it uses drugs in any of the available forms, such as tablets, implants, and patches.

The drug delivery system is developed based on the interactions and feasibility between the materials of the systems, consisting of the drug and delivery mechanism. In membrane-based drug delivery systems, the effectiveness and efficiency of the drug delivery depend upon the diffusion of the drug across the polymeric membrane. Predictive methods, such as Hildebrand's and Flory-Huggins theories, are used for the prediction of drug diffusion across the membrane. The Hildebrand's theory helps in predicting the drug's solubility in a solvent, and Flory-Huggins theory is used to predict the drug's solubility in a polymer [1]. These predictive membranes help in predicting the course of the drug in the drug delivery system ranging from its melting to permeation across the membrane by formulating a relation between these two processes, thereby, facilitating the effective and efficient controlled delivery of the drug.

Osmotic Drug Delivery System

This drug delivery system, as suggested by the name, is similar to osmosis. In this system, a membrane is used as a drug reservoir as it allows permeation of water but not of the drug. However, when the reservoir is filled with water, it releases the drug, thereby, making it an efficient drug delivery system that delivers drugs at a higher rate. The system is generally in the form of a capsule made from a hydrophilic polymeric membrane. These systems are various osmotic drug delivery systems developed over the time, namely, Rose-Nelson (1955), Higuchi-Leeper and Higuchi-Theeuwes (1970), and Theeuwes (1987) system [28].

In these systems, as discussed, membranes are employed in different forms for drug delivery, such as reservoirs or matrix. Both active and passive modes of diffusion are used under these systems. Under active diffusion, a driving force, such as pH or electric potential, regulates the drug delivery. On the other hand, under passive diffusion, generally concentration difference is the only driving force responsible for the drug delivery. Furthermore, the development in stimuli-responsive membranes allows better use of membranes for the effective and efficient drug deliveries. The detailed discussion on stimuli-responsive membranes is presented in Sect. 1.6.3.

5.3 *Stimuli-Responsive Membranes*

The stimuli-responsive membranes are the most advanced membranes with response to an external stimulus, such as pH [29], temperature [30], light [31], biological [32], magnetic [33], or electrical [34] by inducing changes to their structural or functional properties [1, 35]. Stimuli-responsive membranes can be synthesized by either direct blending or grafting of compounds containing stimuli-responsive groups [3]. These groups show responsiveness to a specific external stimulus, thereby making the membranes stimuli-responsive in nature. Therefore, these membranes get capabilities to these open various domains of fascinating applications for membrane separation processes, such as controlled drug delivery, wastewater treatment, sensor development, gas separations, antifouling, and artificial organ development.

The development and advancement in this field of stimuli-responsive membranes come from the better understanding of the fundamentals of stimuli-responsiveness in terms of concept and mechanisms. Generally, the external stimulus works as a bulk stimulus that is the stimulus will be present on the whole system and not at a particular area or point. This is both good and bad in terms of efficiency and effectiveness, good in terms of area governed and bad as it results in the wastage of energy as well as resources. For example, a particular drug is to be delivered on arrival of a particular cell type in the body, but the bulk stimulus, such as pH, will make the whole process inefficient in a way that it will trigger the delivery of the drug even when the said cell type is not present. Therefore, there is need of development of more accurate, efficient, and effective local stimulus for the betterment of stimuli-responsive membrane separation processes. Furthermore, the external stimuli are categories into three categories, viz., direct, indirect, and field stimulation, and are shown in Fig. 4. In case of direct stimulation, the external stimuli come in direct contact with the membranes. Consequently, in indirect stimulation, the membranes respond to the external stimuli, where the stimulus is pressure or temperature making a thermodynamic environment. On the other hand, membranes respond to an external stimuli field, like electromagnetic.

Presently, the applications of stimuli-responsive membranes make them fascinating in the field of bioprocess engineering. The major applications are in the field of food, pharmaceutical, and biotechnology industries. The applications, such as protein separation, sterilization, acidification or deacidification of beverages, fruit juice clarifications, antibiotic and other valuable products separation and purification, and whey protein and cheese production [1–3]. The stimuli-responsive membranes show better flux, antifouling, and separation efficiencies under the required external stimulus. For example, Sinha and Purkait showed that the dual, pH and temperature, responsive polysulfone polymeric ultrafiltration membranes show better antifouling nature, increased pure water flux, and enhanced bovine serum albumin flux ($3.37\text{ L/m}^2\text{ h}$) and rejection (90%) with change in external stimuli (pH and temperature) [36]. Further, Singh et al. showed that the photoresponsive Cu_2O -modified polysulfone mixed matrix membranes successfully removed ibuprofen from the feed under the influence of visible light at a rate of $32.63 \times 10^{-3}\text{ min}^{-1}$.

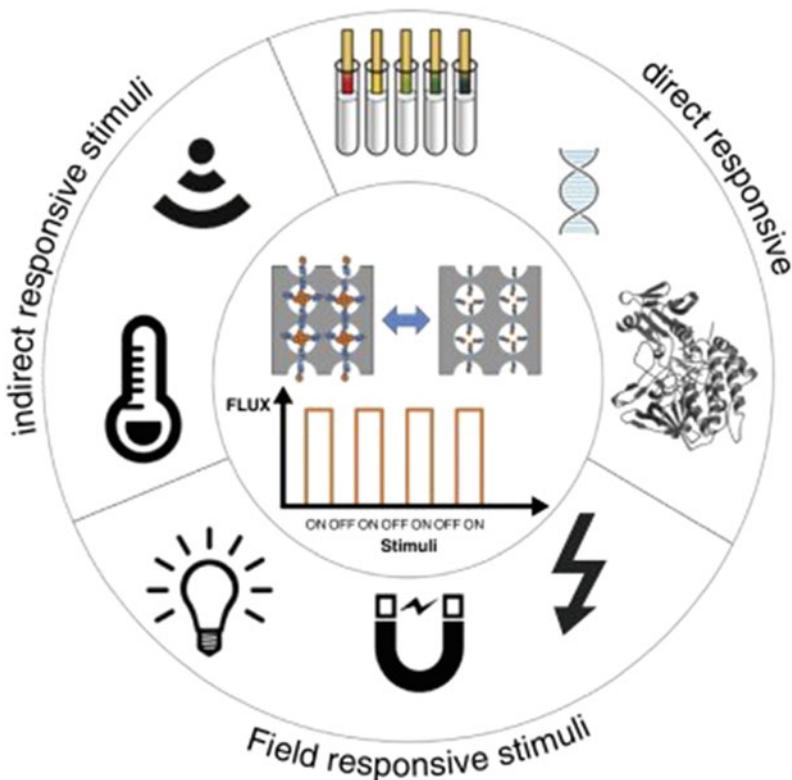


Fig. 4 Schematic representation of three types of external stimuli [13] (Reproduced from S. Daryishmanesh, X. Qian, and S. R. Wickramasinghe, Responsive membranes for advanced separations, Current Opinion in Chemical Engineering, 8 (2015) 98–104 with permission from Elsevier)

[35]. Additionally, the membranes show better flux and antifouling profile with pure water flux enhanced from $34.24 \text{ L/m}^2 \text{ h}^{-1}$ to $179.54 \text{ L/m}^2 \text{ h}^{-1}$ and static water contact angle improved from 71.5° to 45.3° . Figure 5 interprets these results for better clarity.

The above discussion illustrates the importance and benefits of stimuli-responsive membranes in the present-day bioprocess engineering field. These membranes not only make the downstream processing easy, fast, and effective but also bring novelty to the domain, which can further be used for the betterment and rise of new ideas and processes.

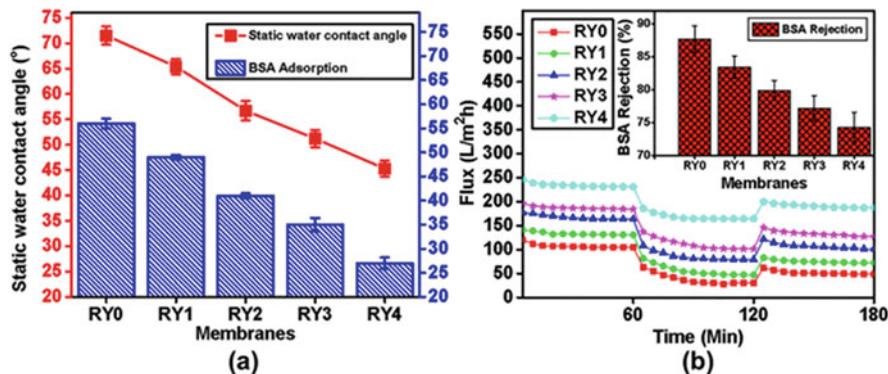


Fig. 5 (a.i) SWCA and (a.ii) BSA adsorption; (b) antifouling profile and BSA rejection (inset) results of the membranes [35] (Reproduced from R. Singh, V. S. K. Yadav, and M. K. Purkait, Cu₂O photocatalyst-modified polysulfone mixed matrix membrane for ultrafiltration of protein and visible light-driven photocatalytic pharmaceutical removal, Separation and Purification Technology, 212 (2019) 191–204with permission from Elsevier)

6 Summary

The chapter discussed about the basics and advancements of membrane science in the field of bioprocess engineering. The advantages of using membranes in the field of bioprocess engineering are discussed in detail, while evaluating the need and role played by membranes. The role of membranes in pharma and biotech sector, importance of membranes in the food industry, and significance of membrane science in the development and advancements in the future of bioprocess engineering discussed extensively. Membranes show better, effective, and efficient performance compared to other conventional separation processes in the field of bioprocess engineering. This strives the demand for further development and advancement in the field of membrane science for the betterment of not only bioprocess engineering but other fields associated with the field of membrane science.

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Process Engineering Aspects in Bioleaching of Metals from Electronic Waste



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Abstract Obsolete electronic devices and their components majorly contributed by the computer and mobile phone printed circuit boards (PCBs) constitute the electronic waste (e-waste). The e-wastes pose an environmental threat due to their eco-toxicological characteristics, thus making its management a mandate through an ecologically sustainable process. Further, the high concentration of metals in the e-waste makes it a secondary ore for metal recovery. Bioleaching is a bio-hydrometallurgical process, which is microbe-mediated dissolution of metals. Different nutritional classes of microorganisms like autotrophs and heterotrophs are active bioleaching agents of e-wastes. The mode of action of microbes for bioleaching of metals is obscure and is believed to ensue through redox reactions, protonic attack, or chelation. The process of bioleaching is influenced by biotic factors like the group and class of microorganism, growth rate, metabolic activity, etc. However, there are several abiotic factors that strongly affect the bioleaching efficiency.

Development of a bioleaching process would need the study of various biological, nutritional, and engineering factors that influence the process. This chapter

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presents the critical analysis of various process engineering aspects in the bioleaching of metals from e-waste. To engineer a bioleaching process, (1) various biological, nutritional, and physicochemical factors, such as media composition, pH, e-waste loading, particle size, oxygen requirement, inoculum size, etc., should be optimized and (2) suitable bioreactor choice considering the microbial type, phases to be contacted, and the pattern of contacting followed by optimization of bioreactor operational parameters. This paper brings out a critical review of these bioprocess engineering aspects in bioleaching of metals from e-waste, directing the reader to the future scope of research on bioleaching, a bioremediation strategy to save and conserve environment for sustainable development.

Keywords Abiotic factors, Bioleaching, Bioreactors, Biotic factors, E-waste, Optimization

1 E-Waste Management

Rapid evolution in the quality of living has imparted several technological innovations, especially in the use of electronic gadgets. Consequently, these gadgets have a short life span, and the obsolete ones are disposed of as e-wastes. The composition of e-wastes includes non-hazardous and hazardous constituents like plastics, glass, ceramics, and metals. Informal handling of these constituents causes environmental issues by the release of noxious gases, toxic leachate, and effluents posing health risks to the ecological niche [1]. Vaccari et al. [2] has presented a detailed statistics on the generation and collection of both electrical and electronic wastes, according to which Asia produces the highest amount of e-waste. Only one-third of the waste generated is collected for recycling. The challenges in e-waste treatment are due to the lack of infrastructure to recycle the large quantities of waste generated, the flow of e-wastes from the developed to the developing countries, inadequate knowledge about the toxicity and impact of the e-waste, improper segregation of e-waste from municipal solid waste, etc.

A major portion of the computer and mobile phone e-wastes are printed circuit boards (PCBs). The metallic fraction of PCBs contains substantial quantities of precious metals, base metals, and heavy metals, making it a suitable secondary ore for urban mining. The most common strategies for the recovery of these metals is through (1) mechanical separation by dismantling, pulverization followed by magnetic or electrostatic separation techniques resulting in a poor quality yield [3], (2) pyrolysis at high temperatures which releases hazardous emissions and is not an economically feasible technique [4, 5], and (3) hydrometallurgical methods by the use of chemical leaching agents with complete dissolution of metals [6]. The drawbacks of these techniques, like natural resource pollution, low purity, and the use of high-cost operations and energy, necessitate an eco-friendly and cost-efficient recovery strategy [7]. A green technology to confront the shortcomings of the conventional strategies is the alternative use of biological leaching agents in

hydrometallurgy termed as “biohydrometallurgy.” The benefits of this technique are the flexibility of the organism to acclimatize to extreme conditions, being inexpensive, easier, and environmental friendly [8], though a relatively slow process. The different mechanisms involved in biohydrometallurgy for metal recovery are bioaccumulation, bio-oxidation, reduction, bioleaching, bioprecipitation, biosorption, bioflocculation, etc. These processes occur individually or in combinations or can be employed as one of the steps in extraction of metals from e-wastes [9].

2 Bioleaching of E-Waste for Metal Recovery

Bioleaching is the microbe-mediated transformation or mobilization of metals from the ores or metal wastes into the lixiviant [10]. The abiotic factors that affect bioleaching are pH, temperature, substrate concentration, oxygen requirements, etc. The microbial genera, its nutritional type, inoculum size, metal resistance, and adaptability contribute to the biotic factors of bioleaching [11].

A primary requirement for the microbe is to acclimatize itself to the metal-containing e-waste. To establish this, the organisms express the cryptic metal-resistant gene clusters present in the plasmids or chromosomal DNA [12]. Further, metal resistance is also attained through an active efflux of metal ions or entrapment by metal chaperones [13]. Three main principles [14] that govern the microbial leaching of metals from e-waste are:

1. *Redoxolysis* accounts for metal solubilization through oxidation and reduction reactions. Under aerobic and acidic conditions, the microorganism oxidizes ferrous to ferric ions that act as oxidants for the insoluble metal forms. Additionally, ferric ion catalyzed sulfuric acid formation in case of metal sulfides and dissimilatory reduction of ferric to ferrous ion result. This takes part in the next cycle of reaction [15, 16].
2. *Complexolysis* is a consequence of the secretome of the organism complexing with the metals. The extracellular metabolites of the microbial cells either act as ligands, aid in chelation, or directly complex with the metals. Siderophore-mediated iron chelation, peptides binding the metals, and carboxylate anions from the carboxylic acids complexing with the metals churn out soluble forms of metal complexes [17].
3. *Acidolysis* is the generation of inorganic and organic acids and dissolution of metals from the surface. The inorganic acid produced by the microorganisms is usually sulfuric acid that plays a role in solubilizing metal sulfides. Another group of organisms excretes organic acids like citric, glutamic, and oxalic acids. The metals are displaced from their surfaces by the protons from these carboxylic acids [15].

Bioleaching of metals from the solid substrate is accomplished by contact mode through chemotaxis and cell attachment to preferred sites of imperfection on the

metal surface forming biofilm [15]. The bacterial cells form a biofilm, by the production of extracellular polymeric substances (slime) on the material. The metals bind to the functional groups of the carbohydrates and proteins that constitute the proteinaceous surface layers [18, 19]. On the contrary, the presence of metals in the environment of the planktonic state cells triggers the production of various secondary metabolites including organic acids, enzymes, etc., for non-contact mode of bioleaching [20]. The release of CO_2 leads to carbonic acid attack on solid surfaces [21]. The increase in Fe^{2+} to Fe^{3+} conversion and vice versa in the solution is expected to increase the redox potential and in turn bioleaching [22].

3 Process Engineering Aspects in Bioleaching

Bioleaching like other bioprocesses can be efficiently applied to recover metals from e-waste in various scales of application. Bioleaching involves the use of microbes, and hence the biotic factors to be considered for its implication include the type of microorganism, the inoculum concentration, its growth rate, the cell genotype, the ability of the organism to resist the heterogeneity and toxicity of the e-waste, etc. Various abiotic factors like the physicochemical conditions, the e-waste loading, its size and composition, nutrients required by the microorganism, etc. also affect the bioleaching [11]. Better mixing and process control may be achieved in contained systems such as bioreactors. Industrial scale bioleaching processes are carried out in bioreactors which are better equipped with the phase contact mechanisms and control systems. Based on the complete understanding of the principles and modes of bioleaching by a suitable microbe and bioreactor design, the process can be established by opting for either batch or continuous mode of operation.

One-step bioleaching [23] is where the microorganism and the e-waste metal concentrates are simultaneously added and incubated for solubilization [24]. In this method, (1) the microbial growth may be inhibited by the presence of leached metals in solution, thus reducing the leaching rate; (2) microbes may take longer time for acclimatization in the media containing leached metals, and thus lag phase would be longer; and (3) the leached metals may get adsorbed/utilized or accumulated in the cells, thus reducing the metal recovery [25].

Two-step bioleaching [23, 26] is the addition of metal-containing solids after the precultured microorganism has attained the late exponential phase of growth [27, 28]. This process would reduce the inhibitory effect of the metals on growth, however, and may still lead to adsorption/accumulation of leached metals in the cells, thus reducing recoverability. The lag phase of growth (first step) may also be lesser.

Spent medium bioleaching [26] is the dissolution of metals from the solids in cell-free supernatant that contains the extracellular proteins and secondary metabolites [29]. In this process, the extracellular metabolites and proteins which tend to be secreted only in the presence of metals would not be available for any leaching action. However, this process can also prevent the toxic or inhibitory effect of metals

on microbial growth. The time required for growth may be lower during the production of spent medium, owing to lower lag phase period and higher growth rate in the absence of metal-containing wastes.

Choice of these modes of bioleaching process operation depends on the type of microbes chosen, inhibitory nature of the metals, and metal-microbe interaction involved. The bioleaching efficiency can be maximized by adequate optimized process conditions.

3.1 Biotic Factors Involved in Bioleaching

3.1.1 Nutritional Type of Microorganism

Microorganisms are classified into four major groups based on their electron, carbon, and energy source requirements [30] as presented in Table 1. These comprise both bacteria including actinomycetes and fungi (yeasts and molds). The chemotrophs are well studied for their bioleaching abilities. Chemolithoautotrophs have the potential to survive extreme environmental conditions. They are metal resistant and oxidize metals into solution using oxygen from air as the final electron acceptor. Chemolithoautotrophs derive energy from reduced inorganic chemicals (sulfides), using atmospheric carbon dioxide as carbon source and inorganic hydrogen serve to donate electrons. Most of the bioleaching members of the lithotrophs are sulfur and iron oxidizers. The genera of bacteria effective for bioleaching of metals from their surfaces are *Acidithiobacillus* [8, 22, 27], *Leptospirillum* [31], *Acidianus*, *Sulfolobus*, etc. [15, 32]. Though lithotrophs are the preferred organisms for bioleaching due to their low nutrient requirements, it can be applied only for sulfur-containing compounds [20].

The contribution to the mode of nutrition for heterotrophs is provided by organic compounds which serve as the source of carbon, energy, and electrons. The glycolytic pathway and the tricarboxylic acid cycle in the metabolism of organic compounds generate different types of organic acids that occupy a central position in the heterotrophic bioleaching [33]. These organisms also have the ability to produce

Table 1 Nutritional classification of microorganisms

Nutritional type of microorganisms	Energy source	Electron donor	Carbon source
<i>Photolithoautotrophy</i>	Light	Inorganic hydrogen	Carbon dioxide
<i>Photoorganoheterotrophy</i>	Light	Organic hydrogen	Organic carbon
<i>Chemolithoautotrophy</i>	Inorganic chemicals	Inorganic hydrogen	Carbon dioxide
<i>Chemoorganoheterotrophy</i>	Organic chemicals	Organic hydrogen	Organic carbon

amino acids, proteins, and exopolysaccharides which facilitate metal solubilization. Heterotrophs contribute to metal leaching of non-sulfur containing solids and sustain higher pH. The use of fungi has a drawback since the metals would be entrapped in the mycelial network or adsorbed in the cells [7]. Fungi such as *Aspergillus* sp. [24, 34], *Penicillium* sp. [29, 35], etc. have been reported for the bioleaching of metals. The bacterial genera majorly exploited for the bioleaching of metals from e-waste are cyanogenic and include *Pseudomonas* sp. [36–38], *Chromobacterium violaceum* [39–41], and *Bacillus* sp. [12, 42].

3.1.2 Inoculum Size and Growth

The inoculum size has a vital role in the bioleaching of metals from e-waste by influencing the substrate utilization rate and consequently the metabolites released. The increase in size of inoculum was found to increase the production of organic acids to leach metals [24], increase bioleaching of heavy metal [43], and enhance copper recovery [25] from e-waste. Inoculum size beyond a certain limit results in turbidity and clogging in the bioreactor, which limits the contact between the solids and cells and thus the time provided for bioleaching would not be sufficient and incomplete bioleaching of metals would result [25]. The advantage of optimizing inoculum size is to shorten the lag phase and obtain higher growth rate while preventing clogging. The growth rate indirectly triggers the process, analogous to natural biogeochemical pathways at a faster rate and hence bioleaching [44]. Pham and Ting [45] have found that, in the presence of e-waste, *Pseudomonas fluorescens* has higher cyanide production as a result of higher growth rate to achieve better bioleaching efficiency [45].

3.1.3 Omics of Bioleaching Microorganisms

A detailed study on the genome, proteome, and the metabolome of the organism signifies its use in the bioleaching of metals from e-waste. At present the omics approach has revealed the population dynamics in the natural leaching environments and laboratory scale operations using a consortium. Next-generation sequencing technologies will help improve the design and operational control of bioleaching with respect to the organism involved in the process [46]. Additional information on the genotype of the cell including the genomic islands (GI) of metal resistance will give insights into the ability of the organism to adapt to the metal-containing environment, understand the cryptic passive or active regulatory networks for enzyme production, etc. One such example is the discovery of ATPases of *Sulfolobus solfataricus* for copper resistance [47]. Few attempts have been made to identify specific genes that express for bioleaching of metals, by knockout studies. Further, the genes are subjected to heterologous expression for bioleaching, but the limitation with releasing the engineered strains into the natural environment is inevitable, and hence a natural selection is endorsed [13]. The gene expression is

based on cell density and coordinated by the *N*-acylhomoserinelactone (AHL) as the quorum-sensing molecule and results in the formation of biofilms. The formation of biofilms is noteworthy in bioleaching, as the contact mechanism is vital in the recovery of metals [18, 48, 49]. The interphase between the bacteria and the cell comprises of the secretory compounds like the metabolites, membrane-associated compounds, organic acids, and extracellular proteins. These compounds facilitate the process by complex formation, protonation, or electrochemical reactions. Investigation on the biochemistry of iron oxidation is valuable in the construction of bioleaching systems for large-scale applications. The energy conserving genes function to regulate the respiratory pathway resulting in ATP synthesis followed by the expression of *rus* operon for copper bioleaching [16, 50]. Other examples include the organic acid production by fungi to leach metals [51]; licanatase, a lipoprotein contributes to bioleaching in *Acidithiobacillus thiooxidans* [52]; etc.

3.2 Abiotic Factors that Influence Bioleaching of E-Waste

3.2.1 Physicochemical Properties for Bioleaching

The properties like pH, temperature, oxygen requirement, and bioleaching medium composition are organism specific and based on the bioleaching system to be employed in the process. The initial pH and the temperature to be maintained during the bioprocess solely depend on the natural habitat of selection. Most of the well-studied autotrophic strains are mesophilic, thermophilic, and acidophilic [53]. At higher initial pH, the availability of protons is less and inhibits the microbial oxidation process. Most of the acidophiles require low pH to grow and in the process solubilize metals. A pH below the optimum values may cause static effects. Most of the heterotrophs require approximate physiological pH/temperature for growth and bioleaching. The leaching rate is proportional to the temperature but depends on whether it is a thermophile or mesophile [11]. Reports on the effect of Fe^{2+} concentration, pH [54], temperature, carbon source, energy source [55], and additional supplement [42] optimization for bioleaching of metals from e-waste demonstrate each of its role in the process. Supplementing the media with precursors of cyanide synthesis, where cyanogenic strains are employed, enhances the bioleaching of precious metals from e-waste [27, 40]. Oxygen is the terminal electron acceptor in most of the strains involved in bioleaching and contributes in the redox reactions. In open systems like heaps, the oxygen requirement is met by a network of pipes and not homogeneously distributed. This limits the oxygen mass transfer and anaerobic conditions persist in the interior of the heaps [56]. In engineered systems, the aeration rate can be controlled desirably to achieve effective oxygen transfer for bioleaching [31].

3.2.2 E-Waste Loading and Particle Size

An e-waste loading up to the optimum has a positive effect on the bioleaching efficiency, whereas higher loading will limit the contact between the phases. Further, the available cell concentration will not be sufficient for the bioleaching of the entire loading [25]. An increased loading of e-waste for bioleaching would also result in the increase in pH, toxic metals, and hazardous compounds (above MIC), causing a decrease in the bioleaching rate [27, 57]. To overcome this inhibitory effect on specific growth rate of the organism and the production of organic acids, the bioleaching process can be accomplished by a two-step or spent medium bioleaching process [34]. E-waste loading also affects specific metal dissolution like the increased loading increases copper leaching by non-cyanide leaching agents, whereas gold removal is minimal, attributed to the inhibition of cyanide production [45]. The e-waste loading and particle size to be chosen also depend on the type of bioleaching system operated.

Particle size of the solid is another crucial factor in the hydrodynamics of bioleaching, phase contact for efficient mass transfer, contact surface area, and the collision between the solids and the cells. Coarse particles have lesser surface area for contact, and the fine particles cause collision of particles and attrition on the microbial cells which are detrimental, thereby decreasing the bioleaching efficiency. The metal leaching rate increases with the decrease in the size of e-waste [8, 58, 59]. A study by Li et al. [60] reveals that the set range of particle size was least significant for bioleaching and was not considered for the pretreatment process. The order of significance of the biotic and abiotic factors in their study reports to be pH > e-waste loading > inoculum size > temperature > particle size. However, the significance of parameters may vary with different bioreactor systems.

3.3 Bioreactor Design and Its Operational Parameters

Development of a large-scale bioleaching process necessitates the use of contained systems such as bioreactors. The use of bioreactors like stirred tank reactors, column reactors, etc. improves the efficiency of the bioleaching process. Adequately designed bioreactors allow good mixing conditions and enhance the mass transfer rate which is essential for any multiphase contacting processes such as bioleaching. Bioreactors can be easily operated under controlled environment, and optimized conditions can be maintained to maximize the recovery of metals. The material to be used to construct the reactor should be carefully chosen, as the walls or the internal components of the reactor might be subjected to biocorrosion by the microorganism used for bioleaching. Bioreactor design, physical components, material used, its capacity, and operational parameters affect the efficiency of the bioleaching. Bioleaching rate varies in different reactors. Some of the commonly used bioreactors include column reactors like mechanically agitated stirred tank reactors, rotating drum bioreactor, packed bed reactors, pulsed plate bioreactor, bubble column

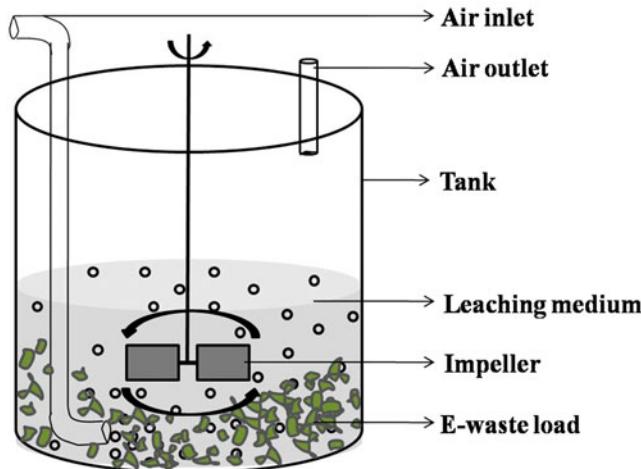


Fig. 1 Stirred tank bioreactor

reactors, and airlift bioreactors. The operational factors like pattern of mixing, air distribution, packing of solids, etc. are specific to each type of reactor.

3.3.1 Mechanically Agitated Stirred Tank Reactors

In mechanically agitated stirred tank reactors, the internal moving components as illustrated in Fig. 1 bring about contact between the phases [31, 61]. In this type of reactors, the air distribution is provided from the bottom of the cylindrical vessel [62]. The speed (as revolutions per minute) of the mechanical stirrer plays a significant role in homogeneous mixing of the phases. The temperature is maintained by suitable heat regulatory system [61, 63]. E-waste loaded and the particle size used is relatively high, as the mixing is brought about by an external stirrer and can be controlled for its efficient bioleaching. The reactor can be employed by itself or in combination with other type of reactors for leaching and growth separately [64]. One of the major limitations in the bioreactor is the moving components causing cell disintegration due to attrition of the cells with moving parts in one-step or two-step bioleaching process. The colonization of the organism in the baffles may also occur.

3.3.2 Rotating Drum Bioreactor

Limited studies exist on the efficiency of rotating drum contactors for bioleaching of metals. The rotating drum bioreactor as a whole rotates in the leaching liquor wherein the perforations in the solid containing drum allow solid-liquid contact as shown in Fig. 2. The rotations of the drum establish uniform mixing. It is an efficient alternative to stirred tank reactors with the advantages of using high solid loading,

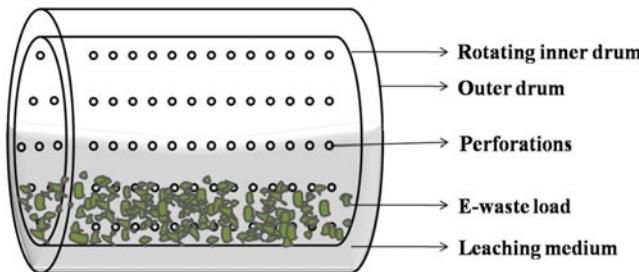


Fig. 2 Rotating drum bioreactor

higher particle size, lower energy requirement and reduced physical stress on the microbial cells. In view of eliminating the crushing step to achieve size reduction, coarsely ground e-waste can be used in this type of bioreactor [65].

3.3.3 Packed Bed Column

Most of the column bioreactors are set up in series to achieve growth in one column followed by bioleaching in another column/any other reactor. Packed bed reactors have a packed bed of e-waste material providing higher e-waste loading capacities as illustrated in Fig. 3. Ilyas et al. [66] have reported a load of 10 kg e-waste for bioleaching in a packed bed reactor. The temperature control is maintained by water jackets. The efficiency of packed bed reactor in bioleaching depends on the temperature, redox potential, pH, and $\text{Fe}^{2+}/\text{Fe}^{3+}$ concentrations and allows the leaching media to pass through the bed of solids which limits the mass transfer in the system [22]. The major limitation with the packed bed column for multiphase bioprocess is the bed loading wherein the gaseous and liquid phases contact the solids only through the void spaces. These spaces may be clogged by the growing biomass (cell aggregates or biofilms). This might hinder the air and liquid flow through the packed bed, and a uniform mixing of the solid, liquid, and gaseous phases would not be achieved [67].

3.3.4 Pulsed Plate Bioreactor

In pulsed plate column, the solids are loaded between the reciprocating perforated plates as represented in Fig. 4. The liquid and gas phases contact the solids through the perforations in the plates. Our previous studies have found that in pulsed plate column, higher particle loading resembles the tightly packed bed and consequently reduced the recovery. Lower particle loading has resulted in movement of the particles in the bed and thus improving the phase contacts resulting in higher metal recovery. The significant functional parameters to be considered in this bioreactor are the frequency of pulsation, amplitude, number of plates, and space

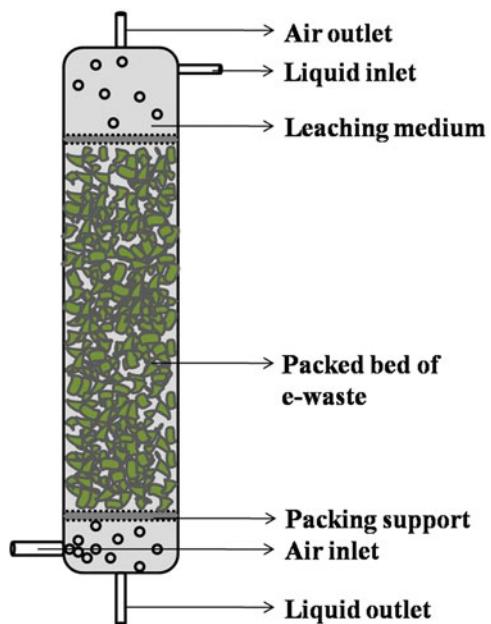
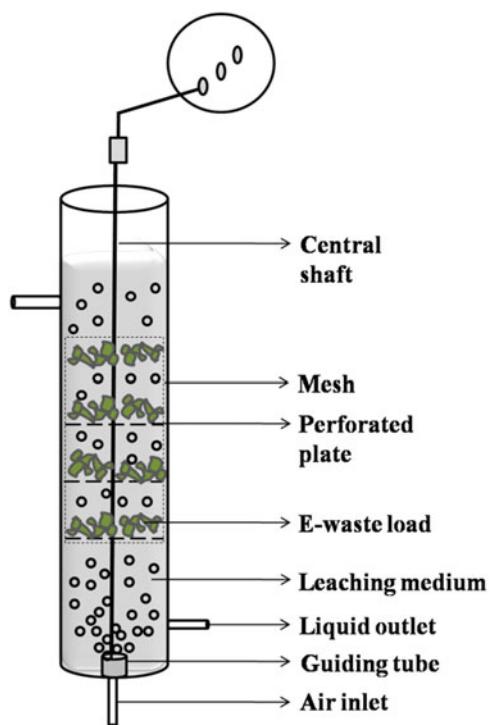
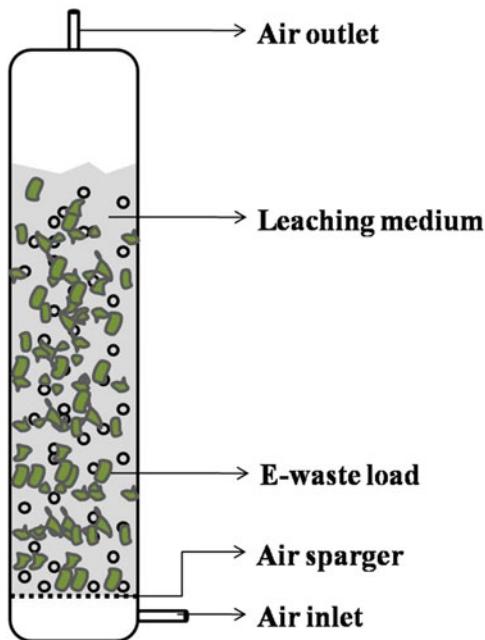
Fig. 3 Packed bed column**Fig. 4** Pulsed plate bioreactor

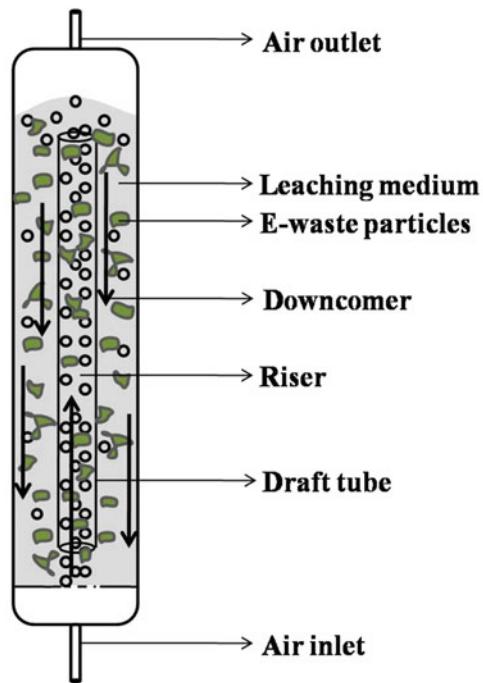
Fig. 5 Bubble column reactor



between the plates, packing per stage. Aeration is provided from the bottom of the column and mixing achieved by the reciprocating plates fixed on the central shaft [25].

3.3.5 Bubble Column Reactors

In bubble column reactor, the aeration and mixing are brought about by air flow from the bottom of the column. These are cylindrical columns that are aerated at the bottom where the air produces a random flow pattern and thus similar to pneumatically agitated reactors as shown in Fig. 5 [68]. The desired temperature is controlled by passing water from the bath into the jacket around the column. Air flow rate is the most important factor to be considered in this reactor [24]. Bubble columns in series are reported for continuous generation of biogenic Fe^{3+} to be used as lixiviant in the first column and for the spent medium bioleaching process in the second [69]. The e-waste loading to be used in this reactor should be optimized such that the air can homogeneously pass through the liquid and solid phases. The particle size range should be selected to reduce pressure drop. A comparative study on the stirred tank reactor with the bubble column suggests that the column reactor is closely efficient as the mechanically stirred reactor [31].

Fig. 6 Airlift bioreactor

3.3.6 Airlift Reactors

Airlift reactors [68, 70] are pneumatically agitated reactors. Airlift reactors are distinguished from bubble column reactors by fluid circulation. They provide well-defined fluid circulation with a cyclic pattern that provide a loop liquid recycle. These reactors consist of (1) riser, to which the gas is injected at the bottom and upward flow of the gas and liquid occurs in this section, (2) gas separator wherein gas disengages from the liquid, and (3) downcomer in which the liquid flows down from the top to the reactor bottom [71, 72]. The liquid circulation is determined by a pressure difference created between the riser and downcomer due to difference in the gas volumes retained in them. Conventional airlift reactors may provide internal loop configuration as in the concentric (draft) tube and the split vessel reactors or external loop configuration [71, 73]. A schematic of the airlift reactor that can be used for bioleaching of metals from e-waste is shown in Fig. 6.

Airlift reactors have been used in the bacterial leaching of metals from sewage sludge [74, 75], bioleaching of heavy metals from the sediment by sulfur-oxidizing bacteria [76], and copper recovery from chalcopyrite by *Acidithiobacillus ferrooxidans* [77].

These reactors provide high gas dispersion, good mixing efficiency, better heat transfer characteristics, simple in construction, and easier control over sterility [70, 71, 78, 79]. In stirred tank or bubble column reactors, energy dissipation is localized producing heterogeneous shear field, whereas airlift reactors are advantageous as

they provide homogeneity of the stress forces [80–83]. The hydrodynamic environment in stirred tank reactors, bubble column reactors, or pulsed plate reactors may lead to physical damage of the cells caused by moving mechanical parts or fluid turbulence. But the hydrodynamic environment developed in ALR is favorable to prevent such cells damage by agitation or turbulence [71]. Shear stress being lower in airlift reactors, biofilm growth is facilitated [71], and thus rate of reaction occurring during leaching process can be improved [84].

ALRs require less power than STRs to attain a given rate of gas-liquid mass transfer. The investment costs are lower, and operation cost is lower or similar compared to STRs [85]. The ALRs provide better heat and mass transfer characteristics, lower energy consumption for mixing [86] compared to BCRs.

However, ALRs are less flexible to changes in process requirements [86], as they do not have such modifiable features [71]. ALRs offer limitations in handling high-viscosity fluids because wall friction causes high energy dissipation leading to low circulation velocity and reduced mixing [72].

4 Conclusion

To apply bioleaching in an industrial scale for the recovery of metals from e-waste, (a) a suitable microorganism may be chosen; (b) a suitable reactor may be chosen based on (1) the type of microorganism, its oxygen requirements, its shear sensitivity considering the rheological behavior of the media during the growth; (2) number of phases to be contacted, mixing and mass transfer characteristics; (3) ease of control of temperature, sterility, etc.; and (4) simplicity of construction, operating costs involved along with ease of maintenance; and (c) a suitable mode of operation such as one step, two-step, or spent medium bioleaching may be chosen.

The bioleaching efficiency can be maximized by adequate optimization of the process conditions. Thus, the bioreactor type, its components, and operational parameters play a significant role in the process engineering of e-waste bioleaching. All biotic and abiotic factors based on the bioreactor type should be considered. The operational parameters vary with reactor type. An optimization of all these features will give an effective implication of bioprocess engineering in bioleaching of metals from electronic wastes. The benefits of engineered systems for bioleaching reduce energy and cost, operational conditions can be controlled, and recovery is efficient. On selection of appropriate systems, the bioleaching can be established as a bioremediation strategy in an eco-friendly manner.

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Phytoremediation of Soil for Metal and Organic Pollutant Removal



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Abstract In the recent decades, industrialization and urbanization have increased the concentration of heavy metals, hydrocarbons, and other contaminants in soil. Among the various strategies to tackle the environmental issues, phytoremediation may be applied to combat pollution or recover the contaminated site or limit the degradation of such entities. It is relatively cost-efficient and environmental-friendly and also provides easy public acceptance. Mechanisms for degradation and removal of contaminants, i.e., rhizofiltration, phytoextraction, phytovolatilization, phytostimulation, phytostabilization, and phytotransformation, are available. However, the condition of the soil, microbes residing in the rhizosphere, and the plants to be employed are the important factors to be considered and assessed before implementing the techniques. A wide understanding and appreciation are required to interpret the interactions between the microorganisms, plants, and contaminants involved. Genetic manipulation can also be implemented for better removal and contaminant uptake.

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Keywords Hyperaccumulators, Phytoremediation, Plants, Soil remediation

1 Introduction

1.1 Environmental Toxins and Contaminants

For a functional and a balanced ecosystem, the protection of the environment is a chief factor. Huge number of environmental toxins and pollutants can lead to high-level degradation impact on the ecosystem, especially soil [1]. About 25% of the global soil is reported to be highly degraded and 44% to be significantly degraded. Various anthropogenic and natural causes lead to degradation of the soil quality by both the organic and inorganic pollutants [2]. Human activities in metalliferous mining, smelting, sewage sludge treatment, agricultural fertilizers, military training and warfare, landfills, electronic industries, electroplating, energy and fuel production [3], etc. lead to an ineluctable release of the pollutants (metals, organic compounds, etc.) to the ecosystem causing a threat to human health [4]. Therefore, the land and water availability, where these pollutants are expected to be localized, is minimalized for agricultural activity or human habitat [5].

1.2 Contaminants in the Soil and Its Risks

Soil is mainly contaminated by metals such as arsenic, lead, and cadmium and organic pollutants such as polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) and pharmaceuticals. The soil quality deteriorates by the presence of heavy metals and adversely affects the normal metabolism, prevents the vegetation, and interferes the functioning of both the soil and plant biota [6]. The mobility and the toxicity of such metals and organic pollutants in soil depend on many factors like pH; total concentration; soil composition or chemical properties of the soil; soil texture like sand, clay, and silt; soil structure which refers to the arrangement of particles; permeability; specific chemical form of the pollutants; binding state; properties of the pollutant; soil salinity; etc. [7].

Heavy metals are highly persistent which makes the remediation of heavy metal-contaminated soil complex. The inception of soil-borne heavy metals to the ecosystem food chain is dependent on the source and the amount of the metal input, rate and magnitude of uptake, properties of the soil, and the extent of absorption level by the animals [1]. The most common metals found in the soil are chromium, iron, arsenic, lead, nickel, zinc, copper, cadmium, and mercury. The accumulation of heavy metals is found in various forms of its geochemical property, e.g., bound in carbonate phase, sulfides, Fe/Mn oxides, or residual forms [8]. The exposure of heavy metals to human may occur through inhalation of air or by ingestion of food and water. It may lead to chronic accumulation of metals in human kidneys and liver (bioaccumulation). Such contaminants have been observed to affect the biochemical

pathways and lead to diseases related to human cardiovascular, nervous, kidney, and bone [9].

Other classes of pollutants present in soil are organic pollutants. Organic pollutants may be hydrocarbons characterized by saturated, unsaturated, linear, or open-chain structures and aromatic hydrocarbon or derivative compounds such as pesticides. Some pesticides are non-biodegradable and are persistent organic pollutants. Their behavior in soil can affect their fate, degree of removal, sequestration, and potential intervention to the microflora [10]. Studies show that most of the polycyclic aromatic hydrocarbons are mutagenic, toxic, and carcinogenic. Their high solubility in lipids facilitates the absorption to the mammalian body. Naphthalene and pyrene can adhere to the kidney, liver, and lung cells [11]. Other organic contaminants like PAH and PCB are found to contaminate the soil too [12]. The degree of retention of pesticides and their transformation products depend on soil-pesticide interactions which in turn depend on the soil characteristics and pesticide properties. The organic matter content, pH, and surface charges of the soil influence the adsorption of pesticides and transformation products [13, 14]. They can harm beneficial soil microorganisms and reduce soil fertility. Pesticides can reach surface water or groundwater through runoff or percolation from treated soil. Many pesticides are highly toxic to fish and cause the death of fish in waterways near treated fields [13]. Organochlorine or organophosphate or carbamate pesticides are considered as endocrine disrupters.

The non-biodegradable organic pollutants and heavy metals present in the soil accumulate in the environment. This leads to the risk to the environment by making the soil unsuitable for agricultural activities. The runoff waters from the soil contaminate the surface water and groundwater, making water unsuitable for drinking. Contaminants in the soil and water enter into the plant bodies or aquatic animals and accumulate in the living tissues of an organism which ascend to a higher living organism through food chain. Thus, remediation of contaminated soil is essential.

1.3 Soil Remediation

Physical, chemical, or biological methods are used to remediate the contaminated soil. The treatment methods may be in situ or ex situ. In in situ methods, contaminated soil is treated at the site of its occurrence [15]. In ex situ methods, the contaminated soil is excavated and taken to the place of treatment for remediation [16]. Chemical and physical treatments of contaminated soil are excavation and removal, extraction, electrochemical treatment, soil washing to remove the contaminants, thermal treatment, oxidation, and reduction [17, 18] However, physical and chemical treatments could potentially [19] cause a deleterious impact on the soil properties. Besides, extraction of contaminants from the soil is laborious because it contains a number of heavy metals like lead, chromium, and mercury; other inorganic ions such as arsenic, cesium, and strontium; organic compounds like trichloroethylene; radioactive materials like uranium; explosives such as 1,3,5-trinitro-

1,3,5-hexahydrotriazine (RDX); hydrocarbons such as benzene, toluene, and xylene (BTX); and pesticides such as atrazine [20].

The use of bioremediation as a treatment strategy for contaminated environments has gained a lot of interest due to its viability and low cost [17, 21, 22]. In bioremediation microorganisms (fungi, bacteria) and plants (phytoremediation) are used for the removal of contaminants from the soil [23, 24]. Microorganisms may mineralize or neutralize the hazardous contaminants. Microbial-based bioremediation uses specialized strains of bacteria with capability of consuming the targeted contaminants [25]. Plants can also be used to consume CO₂ and other gaseous industrial effluents [26]. Remediation using plants is termed as phytoremediation, and it has already received significant scientific and commercial attention.

1.4 The Emergence of Phytoremediation

The employment of the plants alone or in association with microorganism to remediate the soil, water, and air by degradation or stabilization of various environmental contaminants present in them is known as phytoremediation [27]. It is a non-intrusive, effective, and inexpensive means to remediate the soil. The technology is cost-effective than the mechanical or chemical methods for removal or degradation of hazardous compounds from the soil [12]. Every plant extracts the essential nutrients from the soil and water including metals. Plants which have the ability to store huge amount of metals are known as hyperaccumulators. They can uptake even metals that do not appear to be required for their physiological functioning processes [28]. However, the applicability of phytoremediation can be flashed up to low to moderate concentration of contaminant, so as to allow the plant to survive, germinate, and grow at the same time. In regard to plant biological system, there are essential heavy metals which are required by the plant in minute quantities, and they play a vital role in physiological and biochemical function. Essential heavy metals such as Fe, Ni, Mn, Cu, and Zn are essential, whereas the heavy metals which are not needed by the plant for its physiological and biochemical process like As, Hg, Cr, Cd, Pb, etc. are known as non-essential metals. If uptake of such metals becomes higher than its threshold, it may interfere to its normal plant functions [29]. In addition, genetic engineering is now being conducted for the improvement in plant natural capabilities to perform the remediation process better. Advantages of phytoremediation are the following: (1) it is an aesthetically solar-driven cleanup technology; (2) minimal disruption to the environment which preserves the top soil in in situ treatment; (3) cost-effectiveness, i.e., 60–80% lesser than conventional methods; (4) suitable, where the contaminants are at low level and shallow sites; and (5) broad-spectrum treatment of environmental contaminants. However, one of the drawbacks is that it is a time-consuming process because the plant may take a lot of time to grow [27].

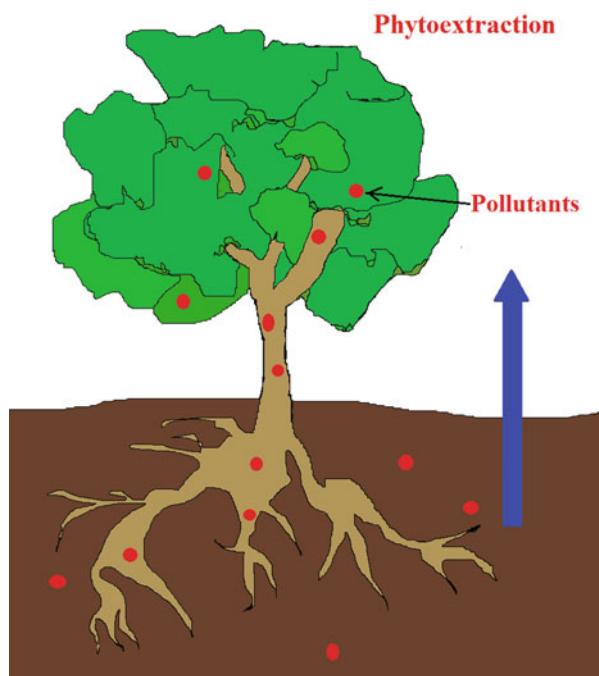
1.5 Mechanisms of Phytoremediation [30, 31]

The mechanism by which phytoremediation takes place depends on the type of the contaminant being treated. The mechanisms may be broadly classified as phytoextraction, phytodegradation, rhizofiltration, phytostabilization, and phytovolatilization.

1.5.1 Phytoextraction

Phytoextraction is also called as phytoabsorption, phytoaccumulation, and phytosequestration. It removes metals or organics from soils and accumulates them in the biomass of harvestable plants by root and surface shoots. It is the uptake of the contaminant from the soil by the plant roots and can be concentrated and translocated from the soil into the harvestable part [32] of the roots or shoots and above the soil surface [29]. The contaminants are not destroyed but are accumulated in various parts of plant such as shoots, leaves, etc. [33]. Figure 1 presents the schematic representation of phytoextraction. Phytoextraction has been basically divided into two strategies: induced phytoextraction and long term-continuous phytoextraction.

Fig. 1 Phytoextraction



A. Induced phytoextraction is also known as chelate-assisted phytoextraction. Chelating agent can make the pollutant bioavailable. The chelating agents like ethylene di-amine tetraacetic acid (EDTA) enhance the biosorption and the accumulation ability of non-hyperaccumulating plant. Plants gain affinity toward the metal by the chelate agent, and thus metal accumulation efficiency of the plants gets enhanced. An outline of chelate-assisted phytoextraction of contaminated site is as follows:

- Evaluation of the site to be treated and determination of chelate and crop combination.
- Preparation of the site by planting the plants.
- After the optimal biomass is reached, the soil is subjected to the metal chelate.
- After the metal accumulation phase starts, the crop can be harvested.

Depending on the plant and its seasons, the plant can be planted in the contaminated or treatment site [34]. Kos and Leštan [35] had investigated the effect of citric acid, EDTA, diethylene-tri-amine-penta-acetate (DTPA), and [S-S]-stereoisomer of ethylenediamine disuccinate (EDDS) on phytoextraction of copper from vineyard soil using *Brassica rapa* var. *pekinensis*. It was found that EDDS showed better result of removal of Cu than the other chelates. Another study showed that EDDS was effective than EDTA in terms of stimulation in translocating metals to the shoots [36]. Metal-chelate complex is transported through the xylem of the plant in the shoots. Water is found to evaporate; however, metal-chelate complex remains. Water evaporates, leaving behind the metal-chelate complex. Thus, the plant acts like a wick that transports the metal ions from the soil into the leaves [34].

B. Continuous phytoextraction

Continuous phytoextraction is the utilization of a metal hyperaccumulating plant which can accumulate, translocate, and also tolerate the high metal concentration over the complete operation cycle. Phytoextraction of organic pollutant depends on the absorption, translocation, and metabolism of organic pollutants in plants [37]. Some organic compounds penetrate through the cell membrane easily and enter into plant cells. *Medicago sativa* and *Tagetes patula* are suitable for the phytoremediation of soils contaminated with phthalic esters and polycyclic aromatic hydrocarbons (PAHs) [38–40]. Transformation and sequestration of organic pollutants in plants are aided by several detoxification enzymes such as cytochrome P450 enzymes (CYP) which catalyze the emulsification of hydrophobic pollutants [41, 42] and glutathione S-transferases (GSTs) which catalyze conjugation of sulphydryl (-SH) group of glutathione (GSH) and the organic pollutant [43].

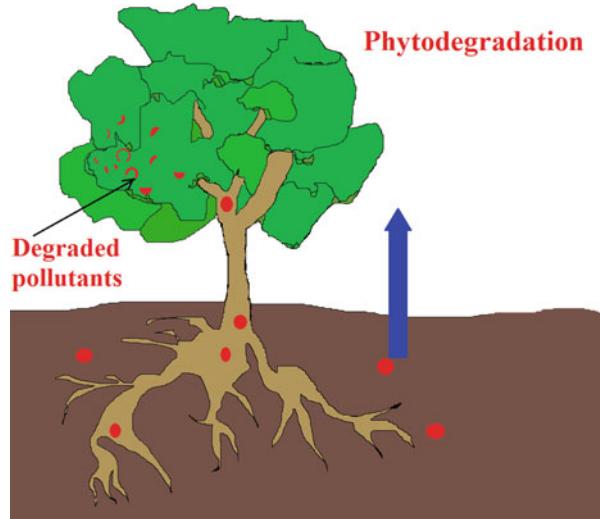
Epelde et al. [44] reported that a hyperaccumulator, *Thlaspi caerulescens*, is the most widely studied plant for phytoextraction of metals due to its ability to phytoextract Zn and Cd to a great extent from polluted soil. One of the drawbacks of employing metal hyperaccumulators for metal remediation is that they yield low biomass, the growth rates are slow, and there is scarcity of such hyperaccumulators for growth in metallic pollutant environment rich in lead, uranium, arsenic, etc. [34].

1.5.2 Phytodegradation or Phytotransformation and Phytostimulation

Phytodegradation, or phytotransformation, is the process in which the plants uptake, store, and degrade or transform complex organic pollutants to a lesser harmful substance and simpler organic compounds. Phytostimulation is also known as plant-assisted bioremediation, i.e., the stimulation which is assisted by microbial or fungal. The enzyme or exudates are released to the root zone. Soil organic contaminants can be degraded directly by plant enzyme systems or indirectly by improving living conditions for the soil microorganisms, to enhance their activity and accelerate the degradation of pollutant [45]. The indirect phytotransformation is called as phytostimulation [46]. Phytodegradation process involves the uptake of the contaminants, storing and degrading the contaminants within the tissue. The contaminants can be absorbed by the plant, and the plant enzymes break down the contaminants [47]. Figure 2 presents the schematic representation of phytodegradation process.

Plant-assisted microbial degradation or phytostimulation or rhizodegradation is also categorized as phytotransformation. The root zone of plants is the zones for accelerated biodegradation, due to presence of consortia of microorganisms in rhizosphere, the soil-root interface. Growing of the root stimulates the proliferation of the microbes which utilizes the exudates of plants. The exudates act as a source of carbon and energy [48]. Further, the proliferation of microbes facilitates in the uptake and degradation of components, e.g., hydrocarbon [49]. The rhizosphere region is the soil area of the plant, and it secretes substances that can accelerate the rate of degradation of the organic contaminants. The rhizosphere has 100 times greater quantity of microbes than the surface because of the various nutrients like amino acids, enzymes secreted by the plant, sugars, etc. present in the soil. It also has

Fig. 2 Phytodegradation



the roots which allow larger surface area for the growth of microbes and provide adequate supply of oxygen [50]. The inoculation of *Lewia* sp. which is a fungus associated with *Festuca arundinacea* has shown the removal of polycyclic aromatic hydrocarbon from spiked soil and accumulation of pyrene [51]. In this process, the seeds are inoculated with the plant growth-promoting rhizobacteria (PGPR), which target the roots to minimize the plant stress caused due to the presence of contaminants and enhance the plant biomass growth. Secondly, the exudates in the soil like organic acids or sugars promote the growth and boost the metabolic activity in rhizobacteria. The well-balanced positive interaction stimulates the degradation of hydrocarbons. However, sometimes root exudates may also result in a repressive effect on the biodegradation. For BTEX hydrocarbons, trees with deep rooting are condign; grasses are usually practical for polycyclic aromatic hydrocarbon. The higher rates of degradation of PAHs were detected at 3 millimeters from the root zone [52]. Some points to be taken into consideration for the improvement and longevity of the tree are by planting the tree before the growing season, making sufficient hole diameter, and turning over the soil or mixed with fresh soil. Plantation of mixed trees and grasses can also improve the efficacy of phytostimulation technique [53].

Chemical fertilizers, e.g., atrazine, can be detoxified by the microbial consortia in the rhizosphere leading to fewer detrimental effect on the plant. Caçador and Duarte [54] used halophytes as phytoconverters for the phytoconversion of hexavalent chromium, which is the toxic form of chromium to the less toxic trivalent form. Lytle et al. [55] reported soluble hexavalent chromium reduction by water hyacinth wherein hexavalent chromium is externally reduced by the lateral fine roots due to oxalate exudation and the plants uptake less toxic trivalent chromium. Newman et al. [56] have found that 2,4,6-trinitrotoluene (TNT) from contaminated soil can be effectively degraded by a TNT-cometabolizing *Pseudomonas* sp. along with plant species such as *Bromus erectus* Huds. The *Pseudomonas* strain cometabolized TNT through aromatic nitroreduction and sufficiently reduced the phytotoxicity of TNT and allowed plant growth. Stimulation of rhizosphere enhanced the growth of bacterial populations possessing the genes specific for degradation of 2-nitrotoluene and 4-nitrotoluene [56].

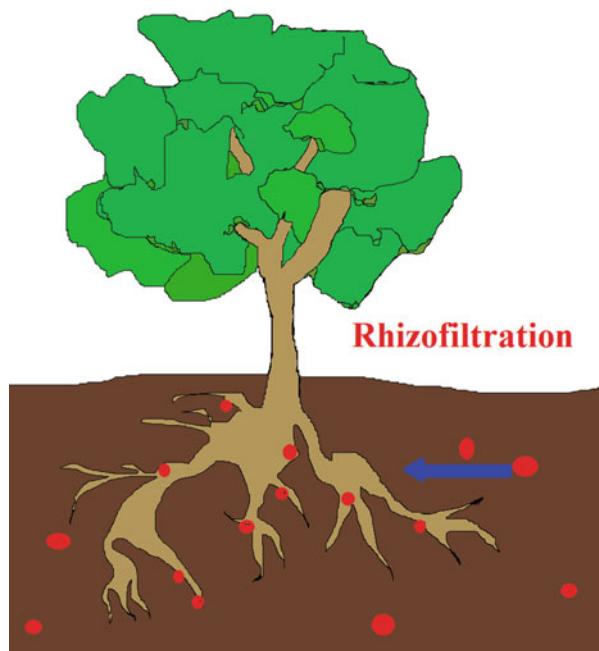
During cometabolism biotransformation, numerous reactions which include hydrolysis, reduction, oxidation, rearrangement, and conjugation [57] may occur in the rhizosphere or soil by the action of enzymes from a consortium of bacteria, which are phase I transformations. In plants, oxidative enzymes may act to form hydroxylated metabolites of aromatic rings. These metabolites further conjugate to sugars, amino acids, or glutathione, via glutathione S-transferase. These are phase II transformations. The additional reactions [58], leading to further conjugations followed by sequestration of the metabolites in organelles or incorporation into plant tissues [59], also occur, which are phase III transformations. Thus, microbial-mediated phytotransformation involves three phases [60].

1.5.3 Rhizofiltration

Rhizofiltration or phytofiltration is the process of employing plant biomass for removal of contaminants, primarily toxic metals from the surface waters or wastewater [61]. In rhizofiltration, the removal of pollutants from water sources occurs by plant roots. The heavy metals are removed by absorption, concentration, and precipitation by the root of the plant. Figure 3 presents the schematic representation of rhizofiltration.

Phytofiltration can be conducted in situ. The plants are grown in the contaminated surface water body. Rhizosphere plays an essential role, if the contaminated groundwater is in the vicinity of the root zone to carry out in situ process. In some cases, the contaminated groundwater may be pumped into troughs where larger and longer root plant species is affirmed. This will initiate the significant absorption of the metals or contaminants by the roots. In addition, metals may also be removed from the groundwater through precipitation by the liquid secreted by plant tissues, which triggers the precipitation, and precipitates are removed by filtration after it passes through the plant troughs. Depending on the plant species used, the roots can be harvested, and the shoots may be further transplanted to grow into new roots. For better operational results, the plants in the system can be replaced. Aquatic plants like *Myriophyllum brasiliensis*, *Juncus xiphiooides*, and *Typha latifolia* have showed the ability to phytoremediate Se in wetlands by accumulation and volatilization [60]. Sunflowers were used near Chernobyl to extract radioactive strontium and

Fig. 3 Rhizofiltration



cesium from the surface-contaminated ponds [30]. The terrestrial plants, like *Brassica juncea* (L.) Czern. and *Helianthus annuus* L., and various grasses grown on surface water, effectively remove toxic metals such as Cu^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} through their roots from water [62].

1.5.4 Phytostabilization

The technique in this remediation aims to reduce the amount of pollutants especially metals, percolating through the soil matrix [63] to reduce the bioavailability. Phytostabilization is the use of certain plant species for immobilizing contaminants in the soil and groundwater by means of adsorption and accumulation onto the roots, or to precipitate within the plant root zone. This mechanism prevents the mobility of the contaminant to the ground and lowers the bioavailability of metal into the food chain. To restore the vegetation at contaminated sites, metal-tolerant plant species is to be employed [28]. Thus, it reduces the contaminant exposure, without being destructive to the structure and biological activity of soils. In addition, the generation of by-products is minimized [64]. The association of the plant and the microbes helps in the immobilization mechanisms or in inactive form. Figure 4 presents phytostabilization process.

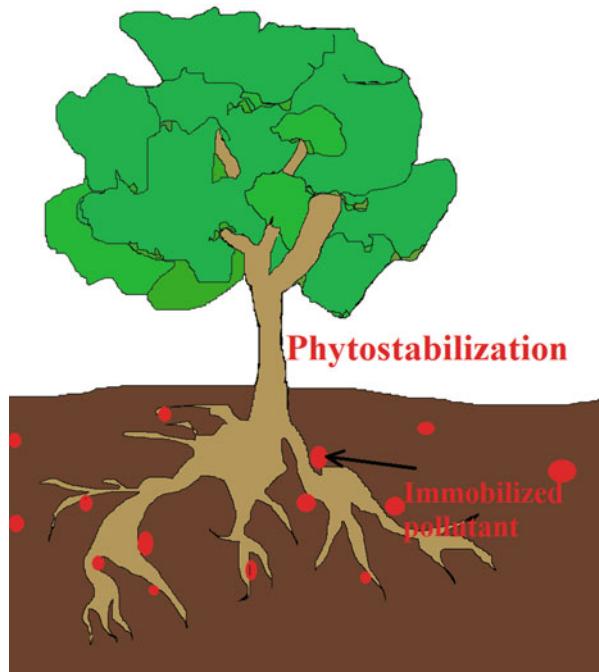
The mechanisms for metal immobilization in plants are the following:

1. The entry of the metal through permeable barrier is prevented/concentration gradient of metal outside the cell.
2. The adhesion to the extracellular polymers.
3. The transformation where the metal can be chemically modified to less simple active form. The interaction of heavy metals with amine and amide functional group, sulfonate, hydroxyl, carboxyl, and sulphydryl group leads to the immobilization and the prevention for the entry to the root system.

Metals bind to the extracellular polymers which consist of polysaccharide and proteins [33]. Dense root system stabilizes the soil and soil erosion can be prevented. It is effectual when there is a need of preserving the groundwater and surface water, and the disposal of biomass can be prevented. Plants may be identified or can be engineered. The secreted compounds by the plants could have the ability of immobilizing contaminants by redox processes or by precipitating the insoluble compounds in the rhizosphere, e.g., Pb is precipitated as phosphate, and Cd forms complexes with sulfide in the roots and the rhizosphere of *Agrostis capillaris* and *Silene vulgaris*, respectively [65]. However, the major drawback of this technique is the contaminant remains in soil and therefore requires regular monitoring [66]. The cleanup site must be properly controlled and monitored to achieve such cause [67].

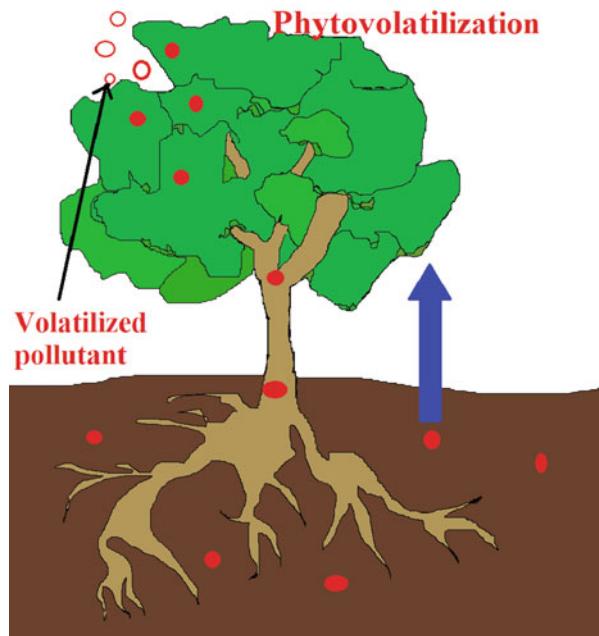
1.5.5 Phytovolatilization

In phytovolatilization [68], the pollutants are taken by the plants from the growth matrix, transformed, and released into the atmosphere. The contaminant is

Fig. 4 Phytostabilization

partitioned into the airspaces within a plant and subsequently diffuses into the ambient air, provided ambient air is less contaminated. For volatile organic compounds (VOCs), phytovolatilization is the major loss mechanism. Figure 5 presents the phytovolatilization process, substantial dilution and photochemical decay of the contaminant in the atmosphere. However, phytovolatilization may cause degradation of air quality and may lead to exposure of human beings to the contaminant released to air and poses risk in the urban areas. Phytovolatilization of both inorganic and organic contaminants have been reported. Volatile forms of several inorganic compounds such as Se [49], As [69–71], and Hg [72] can be volatilized from plants.

In direct phytovolatilization, the contaminants that the plants uptake are translocated and eventually volatilize from the stem/trunk and leaves. In indirect phytovolatilization, volatile contaminant flux from the subsurface increases due to plant root activities. Volatile contaminants like trichloroethylene (TCE) and tetrachloroethylene (PCE) are reported to undergo phytovolatilization from traditional phytoremediation plants such as willow and hybrid poplar [73]. Phytovolatilization of methyl tert-butyl ether (MTBE) in weeping willows [74] and in hybrid poplar trees [75] has been reported.

Fig. 5 Phytovolatilization

2 Factors Affecting the Uptake Mechanisms

The uptake, accumulation, and distribution of heavy metals in the plant depend on the plant used for phytoremediation, element species which is being taken up, temperature, dissolved oxygen, chemical and bioavailability, cation exchange capacity, redox potential, pH, and secretion by roots [76]. The uptake of a contaminant is greatly affected by the characteristics of plant species. Therefore, the plant species with superior remediation properties are to be selected after screening. It is important to choose a plant species that can efficiently hyperaccumulate heavy metals and which yields large amount of biomass. A plant which is able to accumulate the heavy metal more than 0.1% in its dry weight is a hyperaccumulator [77]. Meagher [78] has defined that any plant which has the ability to remediate the soil by reducing the contaminant level by 50% in 24 h is termed as a good phytoremediation agent. It is essential that along with the ability to bioaccumulate the metal, the hyperaccumulator should have a tolerance to the heavy metal. Hyperaccumulators should have the metal concentration of 1% for Mn and Zn; 0.1% for metals such as Al, Cr, Co, Cu, Pb, and Ni; 0.01% for Cd and Se; and 0.001% for Hg of the shoot dry weight [79]. The plants from family of *Brassicaceae*, *Cunoniaceae*, *Caryophyllaceae*, *Asteraceae*, *Euphorbiaceae*, *Cyperaceae*, *Fabaceae*, *Lamiaceae*, *Violaceae*, *Poaceae*, etc. [19], *Alyssum* species, *Thlaspi* species, *Brassica juncea*, *Viola calaminaria*, and *Astragalus racemosus* take up heavy metals and radionuclides in high concentrations [19, 80, 81]. Table 1 presents some of the plants used in phytoremediation.

Table 1 Some of plants species used for phytoremediation

Plant	Compound	References
Alfalfa (<i>Medicago sativa L.</i>)	Pyrene, phenanthrene	Gao et al. [82]
<i>Azolla filiculoides</i> , an aquatic plant	Sulfadimethoxine at concentrations of 50–450 mg/L	Forni et al. [83]
<i>Chrysopogon zizanioides</i> (vetiver grass)	5–15 mg/L tetracycline	Datta et al. [84]
<i>Calendula officinalis L.</i>	Cd and Pb	Mani et al. [85]
Canola plant	Cr, Co, Ni, and Pb	Adiloglu [86]
Improved <i>Nicotiana</i> spp. plants	Cu, Cd, Zn	Gardea-Torresdey et al. [87]
<i>Linum usitatissimum</i> (flax)	59–355 mg/L of diclofenac, 41–247 mg/L of ibuprofen, and 30–181 mg/L acetaminophen	Kotyza et al. [88]
<i>Populus nigra</i>	0.03–30 mg/L of ibuprofens	Iori et al. [89]
<i>Rhizobium meliloti</i>	Various PAHs	Teng et al. [90]
<i>Pteris vittata</i>	Arsenic soil	Yang et al. [91]
<i>Typha</i> spp.	0.5–2 mg/L of clofibric acid and ibuprofen	Dordio et al. [92]

The application of phytoremediation on large scale is limited by availability of the plants with the remediation potential and size of such plants. Native plants may not have the required ability to tolerate, detoxify, and accumulate contaminants [93]. Plant performance is improved by selective breeding and transgenic approach [4, 94, 95]. Biochemical and genetic mechanisms for important processes involved in phytoremediation are being understood, and the rate-limiting processes are optimized [96]. The soil properties affect the uptake. The higher clay content soils have the capacity to hold higher concentration of elements than sandy soil. The colloidal particle of clay can retain up to 1,000 mg Hg, 317 mg Cu, 560 mg Cd, 1,030 mg Pb, 326 mg Zn, and 173.3 mg Cr(III) for each kg soil. The efficacy of clay to absorb trace elements is dependent on the cation exchange charge of particular clay minerals [50]. The alkaline conditions, high organic matter content, and silty or silty loamy texture of soils may reduce the availability of heavy metals to plants [97].

The root zone is one of the highlighted zones in phytoremediation process. Rhizosphere is a soil microenvironment in which the properties of soil and the activities of the plant roots and microorganisms interact with each other in a coordinated manner [98]. Contaminants can be absorbed and stored or metabolized inside the plant tissue. Plant enzymes are secreted from the roots which facilitate in the degradation of contaminants and assist in phytoremediation mechanism [99]. These enzymes are associated with the wall and catalyze the formation of products. The plant roots or the microorganisms in rhizosphere uptake the products [100–102].

A morphological adaptation to drought stress can promote the enlargement of root diameter and decrease in the root elongation as a response to less permeability of the dried soil. The contaminants in the soil may be immobilized by certain plant species through absorption, accumulation, and adsorption onto the roots or precipitation within the root zone [103]. Phytoextraction occurs in the root zone of plants. The root zone is generally shallow, and bulk of the roots are at shallower regions, which is a limitation for phytoextraction. The remediation was limited to the top 15 cm of soil when lead-contaminated soil was remediated using *Brassica juncea* [104].

For the enhancement in the remediation process, pH plays a significant role in the soil. Lower pH value increases the mobility for cationic species, while the opposite is true for anionic species [50]. The mobilization and immobilization of metals and ligand depend on the pH [105]. To reduce the uptake of lead, the pH of the soil may be adjusted to neutral 6.5 to 7.0. Soil pH determines the solubility of heavy metals and nutrients. The increase in pH results in the formation of less soluble forms of trace elements in the soil and restricts the possibility of their accumulation by plants. Leaching of biogenic components may be prevented by an increase in pH value [106].

The addition of biodegradable chelating agents and micronutrients increases the bioavailability of the metals and the metal uptake by the plants. The heavy metal uptake capacity of the microorganisms in the soil is stimulated by the chelating agents and micronutrients. It facilitates the faster uptake of heavy metals, thus reducing the requirement of remediation time [28]. It has been reported that exposure of the soil to chelating agents such as EDTA and citric acid could improve the uptake of metals [107–109]. The presence of a ligand results in the formation of metal-ligand complexes which influences the leachability of metals from below the root zone [105].

The conditions of the environment affect the vegetative uptake. The temperature in the root and above the soil surface affects the plant growth and consequently the length of the root. Root structure is influenced by environmental conditions.

The seasonal variations in climate create gradients in temperature, light intensity, and light regime [110]. The uptake of phosphorous and arsenic was found to fluctuate during the growing season [111–114]. Plant age affects the metal uptake. Generally, growth of young roots is faster, and they uptake nutrients at higher rates than older roots [115].

Rofkar and Dwyer [110] have observed that the arsenic uptake by *S. pectinata* occurred at a greater rate in summer than in spring, while *C. stricta* showed similar uptake in both the seasons. They suggested that to maximize arsenic removal, (1) a diverse group of warm- and cool-season plant species may be employed to supplement the uptake during seasonal variations, and (2) plants may be allowed to accumulate arsenic during the growing season, and then older plants which has enough time to transfer a large portion of the accumulated arsenic to shoots may be harvested. Plant age was found to affect transfer of arsenic from roots to shoots. In addition, when metals are bound to the soil, the pH, organic matter content, and redox potential influence the metals to exist in ionic and plant-available form

[28]. Plants have the ability to lower the pH and oxygenate the sediment in the soil which affects the availability of the metals [116].

In the soil, the solubility and mobility of heavy metals are reduced naturally through sorption, precipitation, and complexation reactions [117, 118]. Addition of organic compounds to soils increases its cation exchange capacity [119] and accelerates the attenuation process [120]. This increases binding of heavy metals to soil, thus rendering them less transportable.

The effect of high soil moisture content on the growth of plant species and hyperaccumulation of Ni and Zn in *Alyssum murale*, *Berkheya coddii*, and *Thlaspi caerulescens* was studied by Angle et al. [121]. Their results showed that the growth and biomass of hyperaccumulators are higher at high soil moisture content.

3 Genetic Engineering in the Plant Species

Genetic engineering of the plant species is focused on genes whose protein products are involved in the uptake and accumulation of metals. Plant biotechnologists target on chelation and metal transport, making the two key processes for the success of phytoremediation [122]. Genetic manipulation may be applied to plants and the associated microorganisms to uptake or to volatilize the contaminants. Zhao and McGrath [123] reported Se uptake by a plant in contaminated soil and drained water from irrigation. When selenium is present as selenate, it is highly bioavailable to plant roots. Some of the reports showed that the transgenic *Brassica juncea* (Indian mustard), whose genes have overexpressed, are involved in sulfur (S)/Se metabolism and have increased in the accumulation and tolerance to Se. The transgenic plants overexpressing adenosine triphosphate sulfurylase (ATPS) catalyze sulfate/selenate activation before they are reduced to sulfite/selenite. Selenite reduction and assimilation can be enhanced by overexpression of APS and/or the APS reductase (APR) [123]. Agata et al. [122] enhanced the phytoremediation of a mercury-polluted soil by integration of *merT* gene into *ppk*-transgenic tobacco which resulted in accelerated and enhanced mercury uptake into tobacco. One of the effective methods to ameliorate the process is by introducing a xenobiotic microbe to the rhizosphere to contribute in the secretions of the exudate and promote in the decomposition of contaminants. The aim of this method is that plants need not absorb the contaminants but the secreted enzymes can decompose the contaminants [124].

4 Drawback and Limitations of Phytoremediation

Phytoremediation is a long process and it may take many years to clean up a site from the contaminant; still the site may not be fully remediated. The use of invasive, non-native species can affect biodiversity. The consumption of contaminated plants by wildlife is also a remarkable concern. After the cleanup process, the harvested

plant biomass produced may be classified as hazardous waste; thus proper handling and disposal are essential. Unfavorable climate may limit the growth of the plant and phytomass production, thus decreasing process efficiency [125].

5 Conclusion and Future Prospects

Researchers in the past few decades have developed wider and better understanding of how the mechanisms of phytoremediation, the plants, and the microorganisms contributed for the efficacy of these methods [20]. Basic research is still needed to be exploited to offer the best efficient technology. In addition to that, integration of latest molecular tools with known basic pathways is essential. The application of genetic engineering to improvise the phytoremediation potential is important. The physiology and biochemistry of the plant have to be understood in terms of the contaminant degradation. Proper screening and selection of plant species to be employed are the major key for the success of this technology [126].

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Recent Advances in Organic Acid Production from Microbial Sources by Utilizing Agricultural By-Products as Substrates for Industrial Applications



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Abstract Organic acids are considered to be the third-largest entity among the other chemical substitutes. The worldwide market rate was projected to be US\$6.55 billion, and it was expected to reach about US\$9.29 billion by 2021. These

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compounds have proven to be used in the numerous applications as additives in the food industries and due to their major demand as the feedstocks in the chemical industries. These compounds are also used as the silages in the perspective of drinking water. Organic acids could be produced through chemical and microbiological processes. But fermentation is considered as the major phenomena in the commercial large-scale production of numerous organic acids. Mostly genetically engineered strains could produce the high yield of organic acids using alternate residues from the chemical feedstocks. The choice of raw material and microbial sources is considered as the major significant factor for the enhanced productivity and yield, especially in the large-scale production. Mainly solid-state fermentation with renewable source as the feedstock was preferred because of the economic factor of low cost and easy availability. Citric acid is considerably produced in large quantities among the other acids with 1.6 million tons, whereas acetic acid and lactic acid constitute to be the second and third place in the productivity of various organic acids. These organic acids are extensively found to be used in the numerous applications of food industries, dairy products, and pharmaceuticals and also in the production of various components like inks, plastics, lacquers, etc.; they play a prominent role as a chelating agent in the removal of various metal pollutants from soil. The cost of the petrochemical derivatives tends to increase the usage and provokes the strong interest toward the agricultural by-products to be used as the major feedstock in the numerous organic acid production. These agricultural by-products are considered to be both renewable and economically cheap material as the feedstock to be easily consumed by numerous microorganisms in the commercial and large-scale production of various organic acids.

Keywords Agricultural by-products, Cost and production, Feedstock, Microbial sources, Organic acids, Petrochemical derivatives

1 Introduction

Organic acids (OA) are considered to be the primary groups in the building block of chemicals. They are synthesized from the numerous renewable materials by using microbial phenomena [1]. Mainly they are produced either as the intermediaries during microbial synthetic pathways else occur as the natural products that could be secreted by the various microbes [2]. OA, as well as their derived products, are extensively used in the chemical industries across worldwide due to their unique functional groups which pave a way to emerge in the market [3]. The production of OA and their derivatives could widely be used as the alternative source of numerous petroleum-derived commodities. Maleic anhydride could be replaced with various organic acids of fumaric, malic, and succinic acids which are considered to be more economical, and it tends to provoke the interest on the production of OA in the markets [4].

Agro-industrial wastes are prominently considered among the various industrial by-products due to their abundant carbon and oxygen contents as well as the

presence of bioactive compounds. Processing valuable by-products from waste material have been gained as the key interest that promotes these waste compounds to be considered as the valuable sources [5]. Various agricultural residues such as wheat, cereals, rice, potato, sugarcane, and beet are used as the primary substrates due to the abundant starch content. These carbohydrate-rich feedstocks are numerously used in the food industries as well as in the industrial fermentation phenomena and the synthesis of numerous chemical compounds [6]. Due to their easy availability and low cost, these sources are subjected under various processes like physical, biological, and chemical methods to produce many valuable compounds. The US department of energy has estimated that nearly 500 million tons of these agro-based raw materials are available within the price range of nearly 20–50\$/ton [7].

Various pretreatments of renewable sources for OA production are available with the major factors that should be considered for maximal production. The enhanced concentration level of saccharides and the physiochemical treatment of the multifarious substrates have been targeted for the concerned OA production are the key limiting step in the practical applications. The production of intermediaries like furfural, phenol derivatives, acetic acid, hydroxymethylfurfural, and formic acids during the breakdown of monosaccharides inhibits the OA production [7]. The factors like selection medium, pH maintained with the simultaneous OA accumulation, and production of various metabolites and inhibitors should also be concentrated for the maximum OA production. Though numerous raw materials act as the source and the different microbial communities participate directly or indirectly, this present volume of study focuses on the different agro-based substrates used in the various organic acid productions [8, 9].

2 Organic Acids

Organic acids owing to their extensive shelf life period are used as the preservatives and food additives that prevent the deterioration of nutrients present in them. Normally it could be classified based on functional derivatives like monocarboxylic and multicarboxylic acid. Based on the length of the carbon chain, they could be classified as short-chain constitutes about 1–6 carbon atoms, medium-chain represents 7–10 carbon atoms, and long-chain fatty acids have more than 11 carbon atoms [10]. The commercially important acids such as lactic, citric, itaconic acids, sugar derivative acids of gluconic and ascorbic acids, play a key vital role in various aspects of industrial applications [11], shown in Figs. 1 and 2.

2.1 *Organic Acid Production*

Organic acids are produced based on the aspects of biochemical pathways and industrial pathways. Microbial sources produce based on the metabolic sequence of the organisms which includes the glycolysis and tricarboxylic metabolic

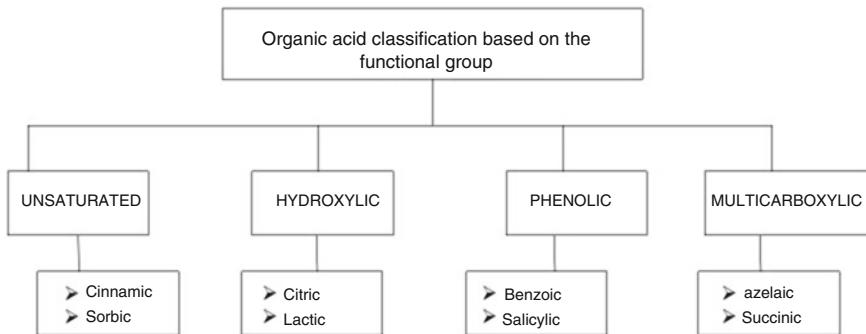


Fig. 1 Classification of organic acids based on the functional group

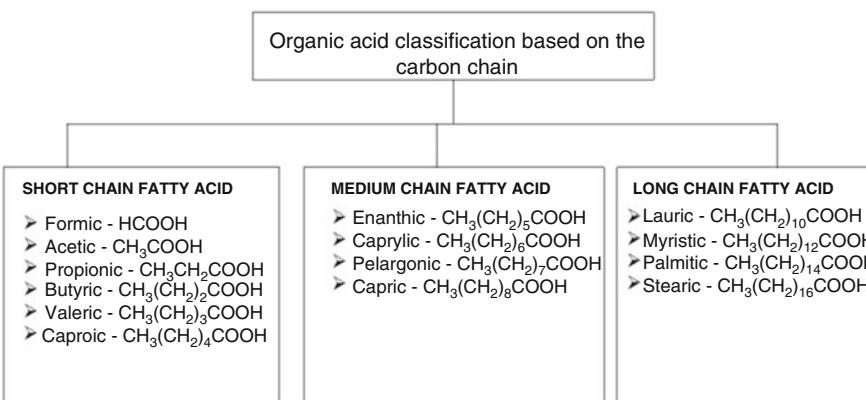
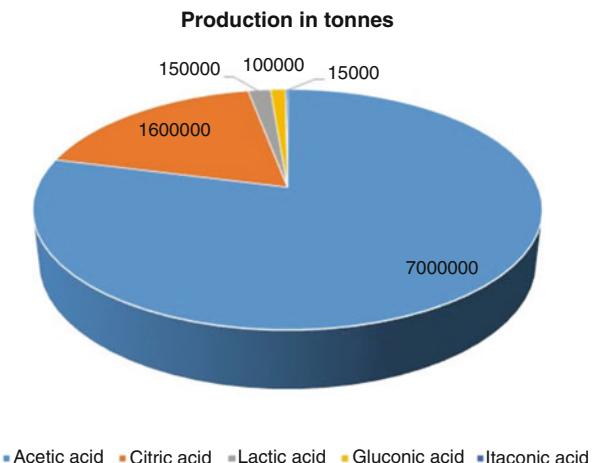


Fig. 2 Classification of organic acids based on the carbon chain

pathways. Lactic, citric, malic, and the itaconic acids are subjected to be produced by this method. The other group of acids like gluconic acids is synthesized by the direct glucose oxidation method [11]. Also, the metabolic engineered gene of the various microbial sources is concentrated in OA production. The global market is subsequently increased in the organic acid production by 4\$ billion concerning the demand of various chemicals in the market [12]. China was found to be the largest producer of organic acids and is leading in the production of engineering plastics, vinyl and polyester compounds. India is driving toward the organic acid production by the growth of small- and medium-scale enterprises and found to grow at its superior annual growth rate among the certain period. Though chemical process produces organic acids, industries give preference to the microbial production of numerous organic acids through fermentation methods, shown in Table 1. Citric acid was mostly produced in the large quantity through submerged fermentation with enhanced productivity and greater yield of about 1.6 million tons with annual production by microbial processes. Next to citric acid, acetic acid is produced with

Fig. 3 Production of various organic acids



the annual production of about 7,000,000 t, and lactic acid is produced with 150,000 t [13], depicted in Fig. 3.

3 Lactic Acid

Lactic acid or 2-hydroxypropionic acid is composed of both hydroxyl and carboxylic functional groups that are extensively used in the numerous applications of textile, food, leather, pharmaceutical, and chemical industries [21]. It could also be utilized as the feedstocks for polylactic acid production that have been used in the medical applications, and biodegradable plastics are synthesized from the petroleum resources. The optical isomers of lactic acid exist as D (−) – and L (+)-lactic acids [22], and L (+)-lactic acids are mostly considered since they could be assimilated in the human body.

3.1 Production of Lactic Acid

Though lactic acid could be synthesized either by fermentation or chemical synthesis, microbial fermentative synthesis is mostly preferred since a pure form could be obtained in this method and a racemic mixture was produced by chemical synthesis. Due to less energy utilization, suitable lower productive temperature, environmental sustainability, and greater purity yield made microbial fermentative method to be dominantly used by the industries [23]. The raw material cost for lactic acid production plays a vital role, and the study has revealed that the fermentative production cost is 34% greater than the overall production cost. So various attempts were made to use agricultural residues, rice bran, green microalga, and paper sludge as the raw materials for lactic acid production [24].

Table 1 Various substrate used in the production of numerous organic acids

Substrate used	Microbial source	Production of organic acids	Method of production	References
Wheat, rice straw, pine sawdust, aspen	<i>Rhizopus oryzae</i>	Lactic, fumaric and succinic acid	Simultaneous enzymatic saccharification and microbial fermentation	[14]
Sugarcane bagasse and orange peels	<i>Aspergillus oryzae</i>	D-Galacturonic acid	Fermentation	[15]
Sugarcane vinasse	<i>Clostridium, Lactobacillus, Bacillus, Ruminococcus</i>	Butyric acid and butanol	Fermentation	[16]
Kraft black liquor	–	Oxalic, malic, lactic, formic, acetic and propionic acid	Hydrothermal treatment	[17]
Glycerol	<i>Yarrowia lipolytica</i>	Citric or isocitric acid	Fermentation	[18]
Skimmed milk	<i>Lactobacillus casei, Lactobacillus rhamnosus, Lactobacillus plantarum, Lactobacillus paracasei, Lactobacillus curvatus</i>	Lactic, acetic, formic, citric, succinic and glutamic acids	Fermentation	[19]
Sugarcane molasses, soybean meal hydrolysate, beechwood xylan, glycerol	<i>Escherichia coli</i>	Succinic acid	Fermentation	[20]

3.2 Microbial Production of Lactic Acid

Lactobacillus, *Streptococcus*, *Weissella*, *Oenococcus*, *Lactococcus*, *Teragenococcus*, *Enterococcus*, *Leuconostoc*, *Pediococcus*, *Carnobacterium*, *Aerococcus*, and *Vagococcus* at both the low temperature (5°C) and high temperature (45°C), pH (4.0–4.5) with the nutrients of minerals, nitrogen, and vitamins show a high yield of lactic acid production [25]. Both wild-type and genetically modified strains are used to synthesize lactic acid with numerous feedstocks [26].

3.3 Lactic Acid Is the End Product from Metabolic Pathways

Lactic acids could be produced via homo- and heterofermentation from different metabolic pathways like pentose phosphate and Embden–Meyerhof pathways with different sugar substrates like pentose and hexose, respectively [26, 27] is shown in Fig. 4.

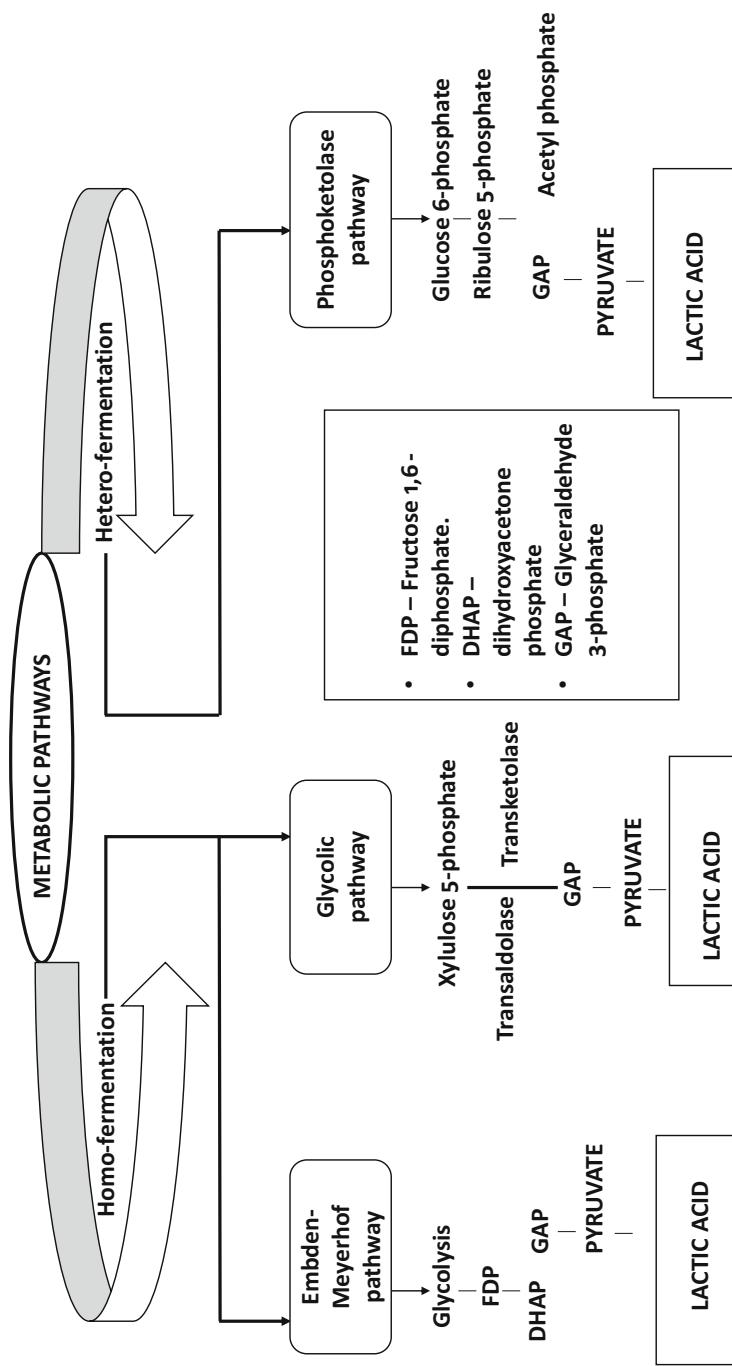


Fig. 4 Metabolic pathways – production of lactic acid

Table 2 Agricultural residues as the feedstocks in the production of lactic acid

Feedstock	Microbial source	Method of production	Yield (g g ⁻¹)	Lactic acid production (g L ⁻¹)	References
Wheat straw	<i>Bacillus coagulans</i> MA-13	Saccharification and Fermentation	1.23	1.11	[30]
Rice straw slurry	<i>Lactobacillus plantarum</i>	Simultaneous Saccharification and Fermentation	0.35	1.0	[31]
Orange peel waste hydrolysates	<i>Lactobacillus delbrueckii</i>	Fermentation	0.86	2.02	[32]
Dairy products	<i>Enterococcus hirae</i>	Fermentation	0.89	13.9	[33]
Sugarcane molasses	<i>Clostridium sensu stricto</i> , <i>Escherichia</i> , <i>Enterococcus</i>	Fermentation	0.81	112.34	[34]

The yield of lactic acid also depends on the derivative of sugar that has been used as the source of carbon in the productive metabolic pathways. Though the genetically engineered strains such as *Lactobacillus plantarum* *ΔldhL1-xpk1::tkt* and *Enterococcus mundtii* QU25 produce lactic acid from pentose sugar derivative through homolactic acid fermentation, the yield was comparatively low, and also the concentration of pentose sugar was also affected due to the metabolic flux created by the above microbial sources [28]. When xylose was selected, as the carbon source, the yield of production was high in comparison with the other sugar derivatives [29] is shown in Table 2.

4 Citric Acid

Citric acid or 2-hydroxy-1,2,3-propane tricarboxylic acid has been extensively used in the wide industrial applications of food, cosmetics, pharmaceutical, beverage, and nutraceutical products since they found to be the emulsifier, acidulant, preservative, and buffering agent [35]. Citric acid is widely found in fruits, animals, and plants such that it plays a prominent role in the biochemical pathways that were explained in the Krebs cycle [36]. Citric acid is the excellent cross-linking agent when it gets dissolved with glycerol where it shows the enhanced thermal degradable property with stable mechanical properties in starch films [37].

4.1 Production of Citric Acid

Citric acid was initially produced as the commercial source from *Aspergillus niger* and later chemicals like glycerol and 1,3 dichloroacetone act as the primary substrate

for its production [38]. Microbial communities like *Penicillium restrictum*, *Aspergillus niger*, *Aspergillus flavus*, *Aspergillus wentii*, *Aspergillus nidulans*, *Aspergillus luchensis*, *Acremonium* sp., *Trichoderma viride*, *Penicillium janthinellum*, and *Ustulina vulgaris* produce citric acid in the presence of medium that contains inorganic salts and sugars [38]. Some species of fungi like *Candida*, *Saccharomyces*, *Hansenula*, *Kloeckera*, *Torula*, *Pichia*, *Yarrowia*, and *Zygosaccharomyces* produces numerous amount of isocitric acid which reduces the final yield of the product. Among various microbial sources, *Aspergillus niger* produces a high yield of about 112 g per 100 g of sucrose [39].

Citric acid was normally produced in industries via three methods which include submerged, solid-state, and surface fermentation methods with the appropriate reaction conditions like media selection, inoculum preparation, suitable nutrients to enhance the growth of the inoculum, etc. Solid-state fermentation has been extensively carried out in incubators, conical flasks, and bioreactors that include both single and multilayered packed bed reactors [40]. Around 80% of citric acid was produced using submerged fermentation technique, and industries prefer this method due to the high productivity and low cost. Submerged fermentation could be carried out via batch, fed-batch, and continuous method [41]. Surface fermentation method is usually preferred by small and medium-scale industries because of its low cost, less energy utilization, and simple installation procedure. The phenomena occur in the fermentation chambers, and the culture is poured in the trays that got arranged in these chambers. These chambers are controlled with proper aeration and humidity. Both physical factors like pH, suitable aeration, and product recovery methods like extraction, adsorption, and solvent precipitation and chemical factors like selection of the microbial source, nutrients, and substrate selection play a major and vital role in the citric acid production [42] is shown in Table 3.

Table 3 Agricultural residues as the feedstocks in the production of citric acid

Feedstock	Microbial source	Method of production	Yield (g g ⁻¹)	Citric acid production (g L ⁻¹)	References
Sugarcane bagasse and vinasse	<i>Aspergillus niger</i> and <i>Trichoderma reesei</i>	Solid-state cultivation	1.31	7.34	[43]
Sugar beet molasses and chicken feather peptone	<i>Aspergillus niger</i>	Simultaneous saccharification and fermentation	–	68.8	[37]
Spanish style green olive processing wastewater	<i>Aspergillus niger</i> B60	Fermentation	0.56	85	[44]
Cassava peel substrate	<i>Aspergillus niger</i>	Submerged fermentation	0.8	88.73	[45]

5 Itaconic Acid

Itaconic acid or methylene succinic acid is composed of one carboxyl group conjugated with the additional methylene entities. Itaconic acids are extensively used in the numerous applications as adhesives and plastic coatings, and their sulfonated entities are widely applied to prepare various detergents and shampoos [46].

5.1 Production of Itaconic Acid

Filamentous fungi mainly *Aspergillus* is used as the microbial source to produce itaconic acid. The microbial sources like *Aspergillus terreus* could produce itaconic acid in bioreactors which are inhibited in the presence of numerous metal concentrations. *Candida* and *Rhodotorula* species in the presence of phosphate could yield about 35% itaconic acid under appropriate conditions. *Pseudozyma antarctica* NRRL Y-7808 uses glucose as the substrate in the presence of nitrogen and produces itaconic acid under appropriate conditions. *Ustilago maydis* have synthesized the highest amount of about 68.36 g/L of itaconic acids under appropriate growth conditions [47]. Though *Aspergillus terreus* could produce itaconic acids through the tricarboxylic acid cycle with cis-aconitate decarboxylation, due to the high viscous nature oxygen and the mass of filamentous fungi, the production decreases which results in the synthesis of improvised genetically modified strain [48].

5.2 Biochemical Synthesis of Itaconic Acid

Itaconic acid is synthesized from the glucose molecule via the glycolysis pathway that results in the pyruvate production. One part of carbon dioxide released is coupled with acetyl-coA which results in the formation of compounds like citrate and cis-aconitate. The other part of carbon dioxide is synchronized with oxaloacetate where itaconic acid is produced from aconitate decarboxylase. Itaconic acid is formed as the intermediary products from enzymatic fractionalizations [47]. Table 4 represents the various agricultural sources used for the production of itaconic acid.

6 Other Acids

6.1 Succinic Acid Production

Succinic acid or butanedioic acid with dicarboxylic acid entities is produced from both the microbial sources and the chemical precursors like succinate salts, N-methyl pyrrolidinone, adipic acid, 2-pyrrolidinone, gamma-butyrolactone, and 1,4-butanediol [53]. The current market production of succinic acid is found to be 30–50 kton/year produced from petrochemical precursors through maleic anhydride. So industries tried to

Table 4 Agricultural residues as the feedstocks in the production of itaconic acid

Feedstock	Microbial source	Method of production	Yield (g g ⁻¹)	Itaconic acid production (g L ⁻¹)	References
Potato starch waste	<i>Aspergillus terreus</i>	Fermentation	0.41	29.69	[49]
Wheat chaff	<i>Aspergillus terreus</i>	Fermentation	0.41	27.7	[50]
Corn stover	<i>Aspergillus terreus</i> AT-90	Fermentation	0.13	26.46	[51]
Sweet potato peel	<i>Aspergillus niger</i> and <i>Aspergillus terreus</i> ATCC 20542	Fermentation	0.75	115.67	[52]

develop this compound from the various microbial sources [54]. Microbial sources like *Actinobacillus succinogenes*, *Mannheimia succiniciproducens* MBEL55E, *Anaerobiospirillum succiniciproducens*, and recombinant strain of *Escherichia coli* produce an increased amount of succinic acid under suitable environmental conditions [53]. Succinic acid is produced as the intermediary product of tricarboxylic acid and produced as the final product as a result of fermentation when glucose or glycerol is consumed. Numerous microbial sources convert phosphoenolpyruvate to succinate which in turn could produce succinic acid. The production could be enhanced by following these methods alike enhancing substrate concentration, projecting the pathways for direct succinic acid production, to delete the gene corresponding to produce by-product inhibitors [55]. Succinic acid could be extensively used as solvents, plasticizers, lubricants, adhesives, pharmaceuticals, sealants, and coating in numerous industries [54] and its consumption is shown in Table 5.

6.2 Gluconic Acid

Gluconic acid or penta-hydroxy caproic acid is a polyhydroxy carboxylic acid and is a natural compound that is found in most of the humans and other animals. It is composed of carbonic acid entities that could be used in the textile, food, beverage, pharmaceutical, feed, and construction industries. Due to the high demand, the cost of gluconic acid and their derivatives are too high of about US\$ 1.20–8.50/kg [56]. The agricultural residues rich in carbohydrate sources like grape, banana, and sugarcane molasses produce a maximum yield of about 95.8% gluconic acid. Microbial source like *Aspergillus niger* with glucose as the substrate produces the maximum yield of 98% gluconic acid [57]. Other microbial sources include *Penicillium* fungi, *Gluconobacter oxydans*, and bacterial strains like *Acetobacter diazotrophicus* and *Zymomonas mobilis* are also identified to produce gluconic acids [58]. Fermentation industries have improvised the methodology of production to maximize the yield. Altering the microbial source with the appropriate conditions in both submerged and solid-state fermentation with high-energy utilization,

Table 5 Numerous applications in the production of succinic acid

Application	% usage of succinic acid in the market
Plasticizer	9.0
Polybutylene succinate	13.0
Solvent and lubricant	9.5
Polyols	7.0
Pharmaceutical	15.0
Other industrial usages	15.0

maintenance by adding neutralizers with glucose as the substrate, and immobilization technique with the cells or enzymes, the yield could be enhanced drastically than any other methods [59]. The disadvantage in the fermentation process is the purification and separation technique results in the development of the classical methods to reduce the cost of the downstream process [57]. Also, many studies have focused on the agro-based by-products to be used as the substrate to meet the demand and to reduce the cost since they are readily available in abundance with eco-friendlier nature [58].

6.3 Fumaric Acid

Fumaric acid is mainly the intermediary product produced in the tricarboxylic acid and are mainly used as beverages in the food industries. Fumaric acid could either be produced from the chemical synthesis and fermentative methods. Also, these could be produced as the by-products from the microbial sources as the result of oxidative metabolism [60]. *Rhizopus* is mainly used with numerous substrates like starch, molasses, sucrose, and glucose in the fermentation phenomena to produce a sufficient quantity of fumaric acid [60]. It could also be synthesized from the maleic acid isomerization and are mainly used in manufacturing the different resins which could be used in the paper industry [61].

The other acids like glucaric acid, galactonic acid, and lactobionic acid are produced in the very less quantity by the chemical methods and by the microbial sources is shown in Table 6. Glucose is the majorly used substrate used to produce these acids by fermentation phenomena. Microbial sources like *Pseudomonas*, *Gluconobacter*, *Aspergillus niger*, *E. coli*, and *Streptomyces cerevisiae* involved in the large-scale production on commercial purposes [62].

7 Production of Organic Acids by Genetically Engineered Organisms

Numerous approaches like genome shuffling and random mutagenesis have been widely used in the wild-type strain to increase the optimum yield of the various organic acid productions [69]. It is one of the evolutionary methods that limit the

Table 6 Production of other organic acids from agricultural by-products

Feedstock	Microbial source	Method of production	Yield (g g ⁻¹)	Organic acid production (g L ⁻¹)	References
Wheat straw, corn stalk and sugarcane bagasse	<i>Yarrowia lipolytica</i>	Fermentation	Succinic acid – 0.45	Succinic acid – 209.7	[63]
Sugarcane bagasse	<i>Aspergillus succinogenes</i>	Fermentation	Succinic acid – 0.81	Succinic acid – 27.7	[64]
Cassava starch	<i>Leuconostoc mesenteroids</i>	Fermentation	Succinic acid – 0.69	Succinic acid – 106.17	[65]
Apple pomace	<i>Rhizopus oryzae</i> 1526	Fermentation	Fumaric acid – 0.35	Fumaric acid – 25.2	[66]
Potato waste	<i>Gluconobacter oxydans</i> DSM 2003	Hydrolysis and fermentation	Gluconic acid – 0.82	Gluconic acid – 546.48	[67]
Whey hydrolysate	<i>Gluconobacter oxydans</i>	Fermentation	Galactonic acid – 0.90	Galactonic acid – 61.8	[68]
Sugarcane bagasse and orange peels	<i>Aspergillus oryzae</i>	Fermentation	Galacturonic acid – 0.60	Galacturonic acid – 247	[15]

improvement in normal programs in the classical strain [70]. Though the number of classical methods includes UV and chemical mutagenesis, the advantage of the genome shuffling over multi-parental incorporation of foreign DNA plays a significant role in the inducing or suppressing of the various genes to increase the organic acid production [71]. The gene shuffling depends on the various parameters like the selection of the organisms, characterization of the wild-type strain, diversity, phenotype and genotype characterization, and recombination [72]. The various organisms are genetically engineered to optimize the yield of different organic acid productions is shown in Table 7.

8 Applications of Organic Acids in the Removal of Metal Ions

Heavy metal accumulation in the soil is considered as the most prominent threat to the environment. These metals are not biodegradable, and their persistent accumulation in the soil affects animals, humans, and microorganisms of the biological system. Though various remediations like leaching, soil washing, and immobilization using chemicals methods are there, organic acids like citric acid, tartaric acid, and ethylenediamineacetic acid act as the chelating agent that has been used to remediate the soil from the metal pollutants [82]. Various metal contaminants, when

Table 7 Genetically modified organisms to produce different organic acids

Genetically modified organism	Feedstock	Organic acid production	References
<i>Yarrowia lipolytica</i> overexpression of gene GUT1 and GUT2	Crude glycerol	Citric and isocitric acid	[18]
<i>Raoultella planticola</i> CECT 843	Raw glycerol	2,3-butanediol	[73]
<i>Ustilago trichophora</i> TZ1	Glycerol	Malic acid	[74]
<i>Aspergillus niger</i> LaeA ATCC11414	Glucose	Citric acid	[75]
<i>Aspergillus niger</i> D15	Glucose	Oxalic acid, Gluconic acid.	[76]
<i>Propionibacterium acidipropionici</i> A strain	Glucose	Propionic acid	[77, 78]
<i>Escherichia coli</i> 1650-ME	Glucose and Glycerol	Succinic acid	[79]
<i>Clostridium glutamicum</i> expression of gltA gene	Glucose	Itaconic acid	[80]
<i>E. Coli</i> BW25113 expression of ldhA gene	Glucose	Pyruvic acid	[81]

allowed beyond their permissible limits, cause various ill-effects to the humans and animals present in the ecosystem is shown in Table 8.

Adsorption is the physical treatment method used to remove these heavy metal contaminants from various sources. The contaminants are bind by either electrostatic, Van Der Waals or covalent forces. This phenomenal transfer may occur due to physisorption or chemisorption [83]. Various organic acids interact with the metal and soil in the distinct ways based on their unique functional groups and types of the metal complex they formed on interaction. The different concentrations of citric, malic, acetic, and oxalic acids interact with the metal ions to form a metal complex that undergoes on the various machines in the removal of different metal pollutants from soil [84] is shown in Table 9.

9 Conclusion

Agricultural residues are considered as the major substrate in the numerous organic acid productions because of its excess and easy availability and preferable low-cost material with eco-friendlier nature to the environment. This tends to be a major shift from the dependence toward petroleum-based derivatives as the raw materials for organic acid production. Numerous microbial sources and genetically modified strains could use these agricultural residues as the major feedstock in the organic acid production via various methods like hydrolysis, simultaneous saccharification, and fermentation which are discussed above. These are preferably used by the

Table 8 The numerous metal contaminants and their effects

Metal contaminants	Permissible limit (mg/L)	Source of contamination	Ill effects
Arsenic	0.05	Production wastes from glass and electronics	Cancer, damage in the circulatory system, and skin disease
Antimony	0.006	Contaminants from petroleum refineries, electronics, ceramics waste and fire retardants	Lowers sugar level in blood and enhanced cholesterol level in the blood
Cadmium	0.005	Galvanized pipes getting corroded, waste from metal refineries, batteries and paints	Kidney problems
Chromium	0.1	Waste from steel and leather industries	Dermatitis
Copper	1.3	Waste from plumbing and wood industries	Kidney and liver disease with gastrointestinal problems
Lead	0.015	Waste from the plumbing system and natural deposits getting eroded from the ecosystem	Physical and mental disorder, kidney disease with elevated blood pressure
Mercury	0.002	Waste from factories and refineries and leaching from cropland	Kidney disease
Selenium	0.05	Waste discharge from petroleum, mines, and metal refineries	Blood circulation problems, tiredness, and hair loss

industries in the commercial large-scale production. Though genetically modified strains could be used for the organic acid production, several problems are to be considered like by-product formation that acts as the inhibitor for the key organic acid production. So in future, the complex metabolic cellular pathways have to be studied in detail as they are inherently connected with the process performance. Also, microbial stress resistance should be addressed as a vital key factor for the large-scale production process. Thus this study has provided an overview of the organic acid production with numerous microbial strains from various agricultural residues as their main feedstocks. Also, it could be inferred that the agricultural residues could act as the alternative feedstock from the petrochemical derivatives for the organic acid production in the large-scale commercial production. These feedstocks are economically viable from the petrochemical residues, and a large number of biotech products tend to be produced using these agro-based residues. These organic acids due to the presence of unique functional group and properties interact with the various metal ions and act as the chelating agents to form the metal ion complexes. Thus they remove these pollutants and help in the soil remediation.

Table 9 Removal of metal contaminants from soil using various organic acids

Removal of metal contaminants	Organic acids used to remove metal contaminants	References
Lead	Citric acid and acetic acid	[84]
Copper, cadmium, zinc, and lead	Salicylic acid	[85]
Cobalt and lithium	Citric acid	[86]
Zinc	Citric acid monohydrate, maleic, tartaric, oxalic acid dihydrate, succinic acid, and ethylenediaminetetraacetic acid	[87]
Cadmium	Fulvic acid	[88]
Copper, zinc, nickel, lead, and arsenic	Humic acid	[89]
Cadmium, lead, and zinc	Carboxyalkylthiosuccinic acid, the copolymer of maleic and acrylic acid	[90]

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Lignocellulosic Sugarcane Tops for Bioethanol Production: An Overview



Subramaniapillai Niju and Mani Swathika

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Abstract Better living standards, population growth, and expanding urbanization escalate the energy requirement tremendously. Declining stockpile of nonrenewable fossil fuels and its severe impact on environment have created huge consciousness among government, researchers, and industries to develop alternative renewable energy sources. Bioethanol has been considered as one of the most efficient alternative liquid fuels to replace the existing conventional crude oil-based petrol. Among the different lignocellulosic biomass, agricultural residues especially sugarcane tops (SCT) are becoming a promising feedstock for bioethanol production. However, the presence of high amount of lignin possesses a major hurdle in converting this promising feedstock to bioethanol. Hence, this review paper summarizes the various pretreatment methods, hydrolysis, and fermentation techniques reported in the bioethanol production from underutilized SCT. From the overall

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studies, it was evident that the SCT can be used as a potential renewable feedstock for the production of fermentable sugars and bioethanol.

Keywords Bioethanol, Fermentation, Hydrolysis, Pretreatment, Sugarcane tops

1 Introduction

High population growth, industrialization, and urbanization increase the energy requirement tremendously. Nonrenewable energy sources such as coal, crude oil, nuclear power, propane, and natural gas were utilized to meet the ever-increasing energy demand, and these sources were found to be the major contributors of environmental pollution [1]. To overcome these issues, utilization of the most sustainable renewable resources offers an attractive solution to meet the world's primary energy demand. Biofuels are fuels which are derived from renewable energy resources that provide energy security, strengthen the rural and agricultural economies, and emit no or less toxic gases. Bioethanol is one among the dominant global renewable transport biofuels since it can be produced from a wide range of agricultural residues. Bioethanol produced from sucrose-containing feedstocks (sugarcane, sugar beet, and sweet sorghum) and starch-rich feedstocks (corn, wheat, and cassava) are named as first-generation bioethanol [2]. However, it holds several limitations in producing energy from these substrates owing to its conflicts between fuel and food. Hence, the lignocellulosic biomass has been considered as a potential source for the biofuel production [3, 4].

Biomass is a lignocellulosic-based bio-residue that exists in water-based vegetation, forest or organic waste, crop production, and agro or food industries waste. There are various forms of biomass resources available for the production of biofuels and are mostly available in the form of grasses, woody plants, fruits, vegetables, manures, and aquatic plants. These sources can be majorly classified as residues of an agricultural crop, energy plantation, and municipal and industrial waste [5]. Recently, lignocellulosic biomass especially non-food crops and industrial and municipal waste acquires huge attention among researchers since it has been identified as the low-cost and sustainable feedstock for the production of biofuels and other value-added products [3, 5]. Among various types of lignocellulosic biomass, the agricultural residues or wastes such as rice husks, wheat straw, rice straw, energy grass, corn cobs, sugarcane bagasse, dry sugarcane leaves, etc. are available abundantly. Till date, most of these underutilized agricultural residues are being burnt in the open fields after cultivation of crops thereby creating a severe impact on the environment with huge loss of energy [6].

Sugarcane (*Saccharum officinarum*) is a species of tall perennial true grasses of the genus *Saccharum*, tribe Andropogoneae, which has stout jointed fibrous stalks that are rich in sugar and measure 2–6 m tall. Sucrose accumulated in the stalk

internodes of sugarcane was extracted and purified in specialized mill factories and is used as raw material in food industries or fermented to produce ethanol. Ethanol is produced on large scale by the Brazilian sugarcane industry and yet the world demand for sugar is the primary driver of sugarcane agriculture [7].

Sugarcane tops or trash (SCT) is regarded as an agricultural residue that represents the top fragment of the sugarcane plant along with its leaves [8], and the one-third portion of sugarcane plant holds SCT (dry mass basis) [9]. Currently, these unutilized residues were dumped and burnt on the fields after sugarcane cultivation. To some extent, the green SCT obtained immediately after the cultivation was used as animal fodder [4, 10]. This cellulose-rich SCT can be employed to extract the bioethanol by taking advantage of its rich cellulosic matter and the huge availability. Extraction of bioethanol from cellulosic SCT will neither affect food supply nor interfere negatively with sugar-based food or juice extracted from stalks of sugarcane plant.

2 Steps Involved in Bioethanol Production

The process of converting lignocellulosic biomass into bioethanol mainly consists of four unit operations such as pretreatment, hydrolysis or saccharification, fermentation, and product recovery [3, 11, 12]. The overall schematic representation of bioethanol production from lignocellulosic biomass is presented in Fig. 1. Prior to pretreatment step, the raw lignocellulosic biomass was subjected to size reduction as shown in Fig. 2. Pretreatment is essential to alter the biomass size and structure and its sub-microscopic chemical composition so that hydrolysis of the carbohydrate-rich solid fraction to monomeric sugars can be achieved more rapidly with greater yields. Hydrolysis involves the processing step that converts the carbohydrate polymers into monomeric sugars. Six carbon sugars (hexoses) are readily fermented to ethanol by various naturally occurring organisms. However, the five carbon sugars

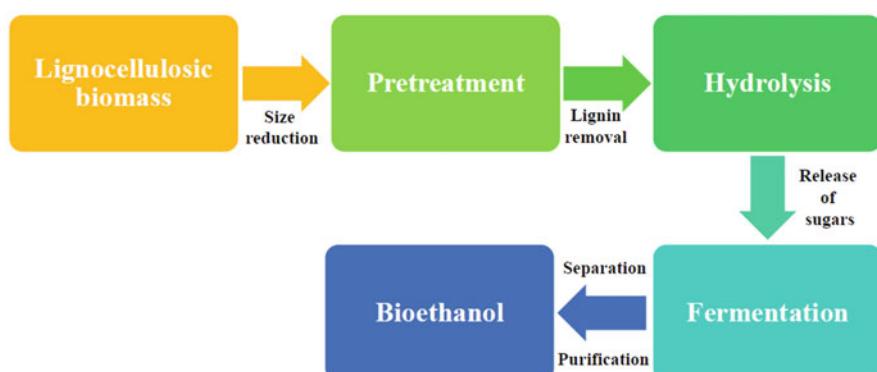


Fig. 1 Steps involved in bioethanol production



Fig. 2 Size reduction process employed prior to pretreatment step

(pentoses) were utilized by few native strains to produce ethanol at relatively low yields.

The basic five stages of this process are:

1. Pretreatment step – makes the raw material amenable to hydrolysis
2. Hydrolysis step – to break down the cellulose present in solid fraction into sugars
3. Collection of liquid hydrolyzate and detection of inhibitory compounds such as furfurals, hydroxymethylfurfural (HMF), and acetic acid
4. Fermentation of the five and six carbon containing sugar solution
5. Distillation and dehydration step to produce absolute ethanol

3 Different Pretreatment Techniques Employed on SCT

The pretreatment is the most crucial step in biomass conversion as it possesses a huge impact on the efficiency of bioethanol production. Lignocellulosic biomass mainly consists of densely packed cellulose and hemicelluloses along with lignin which serves plant for performing several functions [13]. The aim of the pretreatment is to make cellulose more accessible to the enzymes for the conversion into fermentable sugars which can be done by disrupting the recalcitrant lignin structures using different pretreatment techniques. The removal of lignin mainly depends on the type of pretreatment employed and the optimum conditions

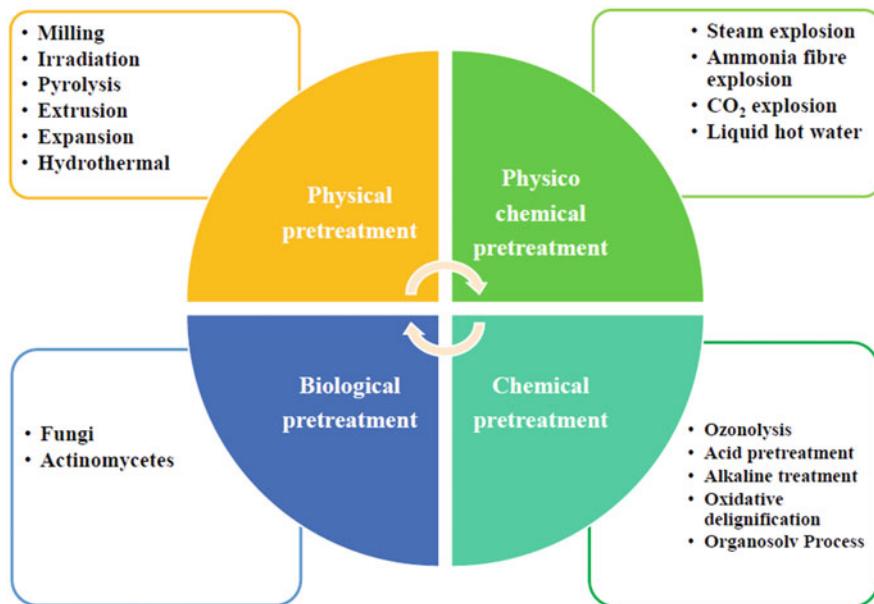


Fig. 3 Different pretreatment technologies available for biomass conversion

maintained. Various pretreatments employed for successful biomass conversion were presented in Fig. 3.

Sindhu et al. [8] performed dilute acid pretreatment on sugarcane tops and observed a decrease in hemicellulose content from 18.9% to 6.16% under the conditions of 3% w/w H_2SO_4 , incubation time of 60 min at 121°C with 15% w/w solid loading. Sindhu et al. [6] experimented surfactant-assisted acid pretreatment on sugarcane tops and perceived 50% lignin removal and 53% hemicellulose removal under 2.5% w/w Triton X-100 and 1.5% sulfuric acid concentration with 30% biomass loading for a period of 45 min at 121°C. Sindhu et al. [14] enhanced the sugar release using a novel method of surfactant-assisted ultrasound pretreatment on sugarcane tops. Authors reported 40% lignin removal and 30.2% hemicellulose removal under the conditions of 20% w/w biomass concentration and 3% w/w surfactant (Tween 40) concentration, incubated at 121°C for 60 min followed by 1 min sonication. Sindhu et al. [11] observed a maximum lignin removal of 89.80% and hemicellulose removal of 45.78% on NaOH pretreated SCT under the optimal conditions of 3% NaOH, 15% biomass loading incubated for 60 min at 121°C.

Sherpa et al. [4] carried out statistical optimization on delignification of sugarcane tops using laccase and observed 73.86% lignin removal under 20% w/v of substrate concentration, 6 h incubation time, pH 7, and 500 IU/mL enzyme titer maintained at 40°C. Maurya et al. [15] observed 67% lignin removal on microwave alkali-pretreated sugarcane tops under the conditions of 2% (w/v) NaOH and 10% biomass loading with microwave operating at 320 W for 10 min. Srinorakutara et al. [1] performed alkali and acid pretreatment on sugarcane trash for ethanol production

and reported 2% w/v NaOH concentration, 15% w/v biomass loading, autoclaved at 121°C for 15 min, followed by 2% w/v sulfuric acid concentration autoclaved at 121°C for 15 min with 15 lb./in². Raghavi et al. [16] developed a novel sequential pretreatment for the bioethanol production from sugarcane trash. Authors observed 2.3% lignin and 47.5% hemicellulose removal under the optimal conditions of 3% v/v glycerol in presence of 1% NaOH and different transition metal concentration of 1% w/w at 121°C for 60 min. Althuri and Banerjee [17] observed 70–80% lignin removal by performing enzymatic pretreatment on SCT using 500 IU/mL laccase maintained at pH 7 with substrate concentration of 30% (w/v) incubated at 35°C for 6 h.

4 Dilute Acid Pretreatment

Pretreatment of the biomass that acts as feedstock is the first step in the production of bioethanol. It helps to alter the structure of the biomass and the chemical composition so that higher yields of monomeric sugars are obtained from the hydrolysis process. The dilute acid pretreatment helps to disrupt the recalcitrant lignin structures in the feedstock such as the covalent bonds present in it which helps further in the hydrolysis process due to more accessibility of the enzymes. It solubilizes the hemicellulose present in the biomass as well as makes the cellulose more accessible [18, 19]. The xylan and glucomannan are relatively acid stable and hence will not be affected during the acid pretreatment. The hydrolyzation of cellulose and the solubilization of the glucose result in an increase in the crystallinity index (CrI) in the biomass which can be obtained from the XRD spectra [13]. The type of pretreatment employed and the process parameters plays an important role for the basis of lignin removal. Dilute acid pretreatments are widely chosen for the pretreatment by the industries due to its cost and its corrosion properties. The pretreatment efficiency depends on several process parameters such as incubation temperature, biomass loading, and the acid concentration. All these parameters in combination play an important role to give better yield, and hence the optimization of the parameters is considered to be necessary in order to produce high yield of monomeric sugars.

Pretreatment of SCT with sulfuric acid with mixed size particle and incubation time of 60 min gave higher reducing sugar and improved the hydrolysis efficiency fourfold when compared to the yield given by the native SCT. 3% w/w was found to be more suitable in maximum reducing sugar production of 0.611 g/g. The effect of biomass loading on acid pretreatment showed that 15% w/w is the optimum condition and the efficiency decreased with the further increase in the biomass loading which could be due to decrease in the accessibility of the pretreatment agent [8].

The hybrid pretreatment involving surfactant and dilute acid has improved the dissolution and hence the removal efficiency of lignin. It helps in the removal of both hemicellulose and lignin. Triton X-100 as the surfactant in the presence of dilute sulfuric acid was found to be more efficient in producing reducing sugar. The total lignin content was reduced to 50% during the pretreatment process with the increase

in cellulose content to 45.39% which is a twofold increase from the native SCT. Maximum reducing sugar of 0.448 g/g was obtained after pretreatment at optimum conditions like 2.5% (w/w) Triton X-100, 1.5% H₂SO₄ concentration, and 30% (w/w) of biomass loading [6].

5 Alkaline Pretreatment

Alkaline pretreatments are considered to be among the major chemical pretreatment technology besides the acidic pretreatments. It can either use chemicals like sodium hydroxide, calcium hydroxide, or ammonia as the reagent. Pretreatments including sodium hydroxide have enhanced cellulose digestibility. Alkaline pretreatments require lower temperatures and pressures, but the incubation time is recorded in terms of hours or days. It results in the removal of lignin in the solid fraction which can be recovered using appropriate recovery measures, and the solid fraction contains hemicelluloses and celluloses. The residual alkali obtained can be reused by the chemical recovery process. This pretreatment is based on delignification process which includes a high amount of hemicellulose being solubilized. The major aim is to remove the lignin from the biomasses and thus improve the reactivity of the polysaccharides present in it. Apart from it, this pretreatment also helps to swell the cell wall, thus improving the cell wall accessibility for subsequent enzymatic hydrolysis. The reaction mechanism supposed to take place is the solvation and saponification of the intermolecular ester bonds that cross-link with the hemicellulose and lignin leading to the cleavage of the lignin carbohydrate complex and therefore expose the cellulose microfibrils present in it [20]. Alkali helps in the removal of acetyl groups and various uronic acid substitutes, and hence steric hindrance of the enzymes in the hydrolysis process is reduced, thus increasing their accessibility towards the carbohydrates. The formation of furfural and HMF in the hydrolysates is found to be lower when compared to the dilute acid pretreatment. The degree of polymerization of the cellulose is decreased and hence causes swelling of cellulose leads to increase in its internal surface area [13].

Alkali pretreatment on SCT with 15% w/w biomass loading and 3% NaOH and incubation time of 60 min yielded 0.684 g of reducing sugar after the enzymatic hydrolysis. The compositional analysis proved that the amount of cellulose was almost intact during the pretreatment, but substantial amount of lignin (89.80%) and hemicellulose (46%) was found to be removed. SEM images revealed that the pretreated sample had distorted structure and an increase in the surface area in SCT thus improving the hydrolysis efficiency when compared to the native SCT which had a compact rigid structure. X-ray spectrum of native and pretreated SCT showed that the crystallinity index had increased in the preheated sample being 67.4% when compared to the native sample of 37.4% thereby influencing the enzymatic hydrolysis process [11].

Another study on SCT showed that alkaline followed by acid pretreatment yielded the maximum reducing sugar after enzymatic hydrolysis. It was observed

that 2% (w/v) NaOH followed by 2% (w/v) sulfuric acid with autoclaving at 121°C for 15 min produced maximum ethanol of 48.17 g/L [1].

The combination of microwave with alkaline pretreatment studies was also an efficient hybrid method in producing reducing sugars. Pretreatment of SCT using this method was able to remove 67% of the lignin from the biomass and hence increases the cellulose and hemicellulose content making it more accessible for the enzymes for the saccharification process. Furthermore, optimization of hydrolysis process parameters using Box-Behnken design resulted in higher sugar yield of 0.376 g/g which represented 90.24% of the theoretical maximum based on the contents of cellulose and hemicellulose present in the pretreated biomass [15].

6 Ultrasound Pretreatment

Ultrasound pretreatments are considered to be efficient technique due to the fractionation of the lignocelluloses present in the biomass into bioethanol. Most of the other pretreatments including acid, alkali, ionic liquids, and steam are said to form unwanted by-products which then result in the loss of carbohydrates. However ultrasonic irradiation helps in the intensification of various pretreatment methods employed in biomass, the principle behind the ultrasonication is the cavitation, which involves the spontaneous growth and collapse of microsize cavities caused due to the propagation of ultrasonic waves, further causing high temperatures and pressure gradients. This results in the enhanced surface areas and leads to higher transfer rate. It helps to accomplish the necessities for bioethanol production by the formation of reactive cellulose fraction for reducing sugar formation along with reduction in power requirements as well as permitting the usage of sources which are inexpensive. The degree of fractionation can be increased by the combination of ultrasound with conventional pretreatment techniques. The ultrasound when applied to the biomass helps in disrupting the structure of the cell wall, increases the specific surface area, and therefore decreases the degree of polymerization to higher extent thereby enhancing the utilization of lignocellulosic biomass [21].

Yuan et al. [22] showed that the extent of delignification brought about by the ultrasound pre-treatment is 96% as well as 75% removal of the hemicellulose present by the ultrasound-assisted organosolv pretreatment [22].

Studies were also done on SCT based on surfactant-assisted ultrasound pretreatment. Tween-40 being the surfactant produced reducing sugar of 0.661 g/g after enzyme saccharification with process conditions as 3% (w/w) Tween-40 for 60 min, followed by sonication for 1 min and biomass loading at 20% w/w. SEM results showed distorted structure of the pretreated sample since it helps in the removal of some of the fibers present externally which appears to be in the form of a complex [14].

7 Enzymatic Pretreatment

Lignocellulosic biomass being the key building block of plant cell wall comprises of cellulose, hemicellulose, lignin, extractives, pectin, and ash. These fractions of components may vary with the plant type, species, their age, and the particular climatic conditions. The plant cell wall is a complex structure comprising of several β -glucan chains that are bound by hydrogen bonds to form elementary fibrils which are further bundled together to form microfibrillar structures. Studies done on biomasses that are pretreated using enzymes have shown that it does not require additional washing due to the absence of inhibitors and pH neutralization steps as needed in other chemical or physicochemical pretreatment methods since it is processed at pH conditions of 11–12. Further it helps to enhance the cellulases and xylanases accessibility to the polysaccharides present in the delignified biomass. Laccase is the enzyme usually used for the enzymatic pretreatment since it is said to fit well with the feedstocks containing higher hemicellulosic content because of the maximum recovery being achieved when compared to other pretreatment techniques. Laccase pretreatment of the biomasses is non-hazardous to the environment and also non-corrosive to the bioreactors with no issues regarding the waste disposal and the recycling of the toxic chemicals, therefore reducing the operational costs to a great extent.

Laccase-mediated pretreatment studies done on SCT using central composite design (CCD) based on response surface methodology (RSM) showed that maximum delignification of 79.1% was obtained when the operational process parameters were processed at temperature of 40°C, pH at 7, biomass loading of 21% (w/v), enzyme titer of 430.3 IU/mL, and incubation time of 6 h [4].

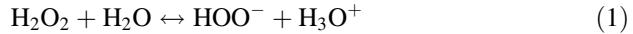
Other studies done on a combination of biomasses including *Ricinus communis* (RC), *Saccharum officinarum* (SCT) top, *Saccharum spontaneum* (KG), *Lantana camara* (LC), *Ananas comosus* (PA) leaf wastes, and *Bambusa bambos* (BB) where laccase enzyme of 500 IU/ml, with substrate concentration of 30% (w/v), 1 g of mixed substrate at 35°C, and incubation time of 6 h followed by simultaneous saccharification and fermentation proved to be efficient in the production of bioethanol of 1.396 g/L/h [17].

8 Alkaline Hydrogen Peroxide (AHP) Pretreatment

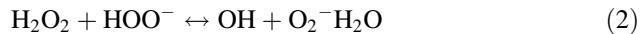
AHP pretreatment is one of the most effective pretreatment for delignification and a variety of lignocellulosic agricultural residues such as rice husks or hulls [23, 24], rapeseed straw [25], wheat straw [26, 27], sugarcane bagasse [28–30], sweet sorghum bagasse [31], cashew apple bagasse [32], bamboo [33], olive tree biomass [34], poplar [35], *Jerusalem artichoke* stalk [36], and seaweed *Ulva prolifera* [37]. AHP has oxidative action on the cell wall of biomass and breaks ester linkages with less sugar degradation and increased digestibility. No or very less secondary

product formation was reported during the AHP pretreatment [25, 38, 39]. Thus, it can be employed effectively to achieve higher lignin removal during the pretreatment.

The use of H₂O₂ for the pretreatment of lignocellulosic biomass is based on the chemical reactions that this oxidizing agent undergoes in the alkaline liquid medium [39]. Its dissociation generates the hydroperoxide anion (HOO⁻) through Eq. (1)



In the alkaline medium, the hydroperoxide anion can react with H₂O₂, leading to the formation of superoxide and hydroxyl radical, as expressed in Eq. (2).



9 Hydrolysis Employed in SCT

Bioethanol production from lignocellulosic biomasses includes processes like pretreatment, hydrolysis, and fermentation. Pretreatment helps to alter the biomass structure and chemical composition that aids in rapid and efficient hydrolysis of the carbohydrates into reducible sugars. Hydrolysis is a process that converts the polysaccharides into monomeric sugars which is further taken into fermentation. It is considered as one of the most important steps in the production of fermentable sugars. Fermentation is carried out by organisms that can utilize this monomeric sugar and produce ethanol wherein the organisms can be either naturally grown or genetically modified. Cellulose in the biomass is organized into microfibrils containing thousands of glucose residues. These celluloses can be hydrolytically broken down into glucose either by enzymes such as cellulases or by chemicals like sulfuric or other acids.

Hemicellulose also present in the biomass is composed of pentose and hexose sugars being 5-carbon and 6-carbon, respectively, and they can be hydrolyzed by enzymes such as hemicellulases or by acids to release the sugars which include xylose, arabinose, glucose, galactose, or mannose. There are certain process configurations being carried out in order to obtain better yield of bioethanol. These processes include separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), simultaneous saccharification and co-fermentation (SSCF), and consolidated bioprocessing (CBP). The processes adopted is based on the feedstock and the other process parameters which further helps in giving higher yield of bioethanol. There are two major types of hydrolysis processes being carried out which includes chemical reaction using acids and enzymatic reaction.

10 Acid Hydrolysis

Hydrolytic treatment of lignocellulosic biomasses with acid at higher temperatures will improve the efficiency in producing higher yield of fermentable sugars. Sulfuric acid is the mostly used acid, and it is operated under high temperature and low acid concentration. Higher acid concentration makes it highly corrosive and dangerous. But as a disadvantage, they produce large amounts of gypsum during the neutralization process, thereby increasing the investment and operational costs. Dilute acid hydrolysis is a commonly used method among the chemical pretreatment methods. This method can be used either as a pretreatment of lignocelluloses for the subsequent enzymatic hydrolysis or as a method of hydrolyzing into fermentable sugars. At a higher temperature (140–190°C) and lower acid concentration (0.1–1% sulfuric acid), they can result at high reaction rates and thus improve cellulose hydrolysis and along with it 100% hemicellulose removal. It can be performed in short retention time of 5 min at higher temperature of 180°C or in longer retention time of 30–90 min but at lower temperatures of 120°C. In olive tree biomass when used as the biomass, 75% of maximum total sugars were obtained when it was pretreated by dilute acid at 180°C with 1% sulfuric acid concentration and maximum hemicellulose recovery of 83% [40]. The major drawback is the formation of different types of inhibitors such as carboxylic acids, furans, and phenolic compounds which will inhibit the microbial growth during the fermentation process and results in lesser amount of yield and productivity of ethanol [41].

Dilute acid hydrolysis usually occurs in two stages. The first stage being performed at a lower temperature to maximize the hemicellulose yield, and the second stage involves higher temperature at optimized conditions for the cellulose hydrolysis. Mild process conditions (0.7% H₂SO₄, 463 K) are opted in the first stage to recover the five carbon sugars, whereas in the second stage, the remaining solids containing more resistant cellulose undergo harsher conditions (488 K, but a milder 0.4% H₂SO₄) that help to recover the six carbon sugars. In order to allow adequate acid penetration, the reduction of the size of the feedstocks is necessary where the maximum particle dimension is in the range of a few millimeters. When considering concentrated acid hydrolysis process, it involves an acid (dilute or concentrated) pretreatment to help liberate the hemicellulosic sugars present in the biomass, while the subsequent stage requires the pretreated biomass to be dried followed by the addition of concentrated sulfuric acid (70–90%). The concentration of the acid used in concentrated acid hydrolysis process ranges between 10 and 30%. Reaction times are found to be much longer than the dilute acid process. This process provides a complete and rapid conversion of cellulose to glucose sugars and hemicelluloses to five carbon sugars with degradation level being very less. The critical factors needed to be considered to make this process economically viable are the optimization of the sugar recovery and cost-effectiveness during the acid recovery taken for recycling. The concentrated acid process offers more potential for cost reductions and leads to little sugar degradation than the dilute acid process. However, environment and

corrosion problems as well as the high cost of acid consumption and recovery present major barriers to economic success [2].

11 Enzymatic Hydrolysis

Hydrolysis catalyzed by enzymes that helps in favoring 100% selective conversion of cellulose to glucose is known as enzymatic hydrolysis. This process is considered to be a very slow process due to some factors like structural parameters of the substrate, surface area, and the cellulose crystallinity. Utility cost of enzymatic hydrolysis is low when compared to chemical hydrolysis technique since they are usually conducted at mild conditions (pH 4.8) and temperature (318–323 K) and do not produce corrosion. The enzymatic hydrolysis has resulted in high yields (75–85%) with improvements being still developed. It is an environmentally friendly process that involves enzymes like cellulases and hemicellulases to hydrolyze or degrade the carbohydrates into fermentable sugars. Cellulose is typically hydrolyzed by an enzyme called cellulase which is being produced by several microorganisms, like bacteria and fungi. Cellulase is the most commercially used enzymes that synergistically hydrolyze cellulose that involves synergistic actions by endoglucanases, exoglucanases, and β -glucosidases. These enzymes together help to hydrolyze intramolecular β -1, 4-glucosidic bonds present in the cellulose to release soluble cellobiose or glucose and further hydrolyze cellobiose to glucose in order to eliminate cellobiose inhibition. The different process factors affect the enzymatic hydrolysis of cellulose, like the substrates chosen, cellulase activity, reaction conditions (temperature, pH, as well as other parameters), and product inhibition. Therefore, optimization of the hydrolysis process is necessary to improve the yield and rate of enzymatic hydrolysis [2]. Three different enzymes present in cellulase hydrolysis β -1, 4 glucosidic linkages in the cellulose chains thus converting them into simple sugars. Three steps involved in enzyme hydrolysis are shown in Fig. 4.

Sindhu et al. [8] observed a fermentable sugar yield of 0.775 g/g under enzymatic saccharification using 50 FPU cellulase enzyme with 11.25% w/w biomass loading and 0.2% (Tween-80) surfactant concentration incubated at 50°C for 42 h. Sherpa et al. [3] performed enzymatic hydrolysis under the conditions of 14% w/v biomass loading and 19.33 IU/ml enzyme titer with pH maintained at 5 having an incubation time of 7 h with temperature ranging from 45° to 55°C.

Maurya et al. [15] observed 0.376 g/g sugar yield under enzymatic hydrolysis using cellulase enzyme with 10% w/w biomass loading, 0.04% surfactant concentration, and 100 FPU/g enzyme concentration incubating for 72 h. Srinorakutara et al. [1] reported 0.509 g/g sugar yield with 15% w/w biomass loading and 50 FPU/g enzyme titer with pH 5 incubated for 48 h. Raghavi et al. [16] observed 0.796 g/g sugar yield under enzymatic hydrolysis using cellulase having 80 FPU/g activity with 5% w/w biomass loading and 0.05% surfactant concentration incubated for 24 h.

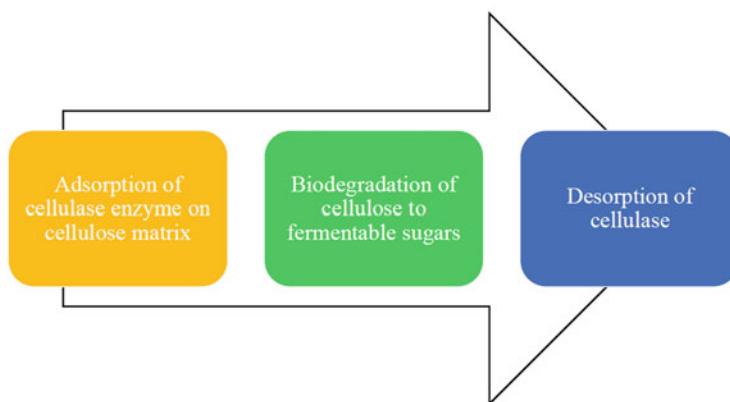


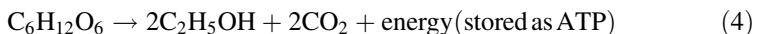
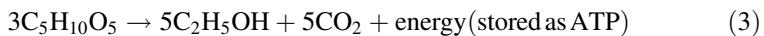
Fig. 4 Steps involved in enzymatic hydrolysis

Sugarcane tops pretreated with different methods such as dilute acid, surfactant-assisted acid, and surfactant-assisted ultrasound were subjected to enzymatic hydrolysis, and the optimum conditions of 11.25% (w/w) biomass concentration, 50 FPU enzyme concentration, 0.2% of surfactant concentration, and 60 h incubation time yielded the maximum reducing sugars such as 0.665 g/g [8], 0.711 g/g [6], and 0.649 g/g [14], respectively. Alkaline-pretreated sugarcane tops were subjected to enzymatic hydrolysis with optimum conditions of 11.25% (w/w) biomass concentration, enzyme concentration of 50 FPU, 0.2% of surfactant concentration, and incubation time of 42 h; the yield of fermentable sugars was about 0.779 g/g [11]. Enzymatic hydrolysis of microwave-pretreated SCT with optimum conditions such as biomass concentration of 10% (w/w), cellulase loading of 100 FPU/g, surfactant concentration of 0.04% (w/w), and incubation time of 72 h yielded 0.376 g/g glucose [15].

Enzymatic-pretreated SCT was hydrolyzed with 15% w/v substrate loading; 50 FPU/g enzyme loading maintained at pH 5 for 48 h yielded 117.16 g/L of reducing sugar [1]. Enzymatic hydrolysis on the sequential pretreated SCT showed a maximum reducing sugar yield of 0.796 g/g with 5% (w/w) biomass loading, 80 FPU cellulase loading, 0.25% (w/w) surfactant concentration, and 48 h incubation time [16]. Enzymatic saccharification of laccase enzyme-pretreated SCT yielded 508 mg/g of reducing sugar with the optimal conditions of 14% (w/v) solid loading, 50°C temperature, 7 h incubation time, and 19.33 IU/ml enzyme titer at pH 5 [3]. Enzymatic (laccase)-pretreated SCT showed 3.3-fold increase in fermentable sugars after delignification [4].

12 Fermentation Process

Fermentation is the final step in the ethanol production. A variety of microorganisms like bacteria, fungi, and yeast can ferment the monomeric sugars to ethanol. In general, fermentation is carried out under anaerobic conditions leading to the glycosylation of one molecule of glucose into two moles of ethanol and two moles of carbon dioxide as shown in Eqs. (3) and (4).



Saccharomyces cerevisiae is the most commonly used yeast for fermentation, and it is substrate specific. The efficiency of the fermentation depends on the concentration and nature of the substrate, the methods followed for the pretreatment and hydrolysis, and the nature of the organism. It is necessary to maintain proper process conditions such as temperature and pH for the optimal yeast growth. Yeast shows tolerance to high sugar concentrations, is resistant to adverse conditions generated by the presence of ethanol, and is stable at higher temperature [41].

S. cerevisiae can ferment only hexose; co-culturing with other microorganism having the capability to ferment pentose can increase the yield of ethanol. Fermentation of SCT-derived fermentable sugars obtained after dilute acid pretreatment and enzymatic saccharification, with 18 h-old culture of *S. cerevisiae* incubated at $28 \pm 2^\circ\text{C}$ for 72 h, yielded high amount of ethanol of 11.365 g/L [8].

Alkali (NaOH) followed by dilute acid (H_2SO_4)-pretreated SCT yielded 48.17 g/L of ethanol by using 10^7 cells/mL of *S. cerevisiae* TISTR 5596 strain [1]. Fermentation of the non-detoxified hydrolyzate obtained from the sequential pretreated SCT using *S. cerevisiae* produced 31.928 g of bioethanol/g of dry biomass [16]. Fermentation of liquid hydrolyzate obtained after enzymatic-saccharified SCT using *S. cerevisiae* yielded 27.2 g/L of ethanol [3]. Fermentation of liquid hydrolyzate obtained from separate hydrolysis (SHF) and simultaneous saccharification (SSF) of pretreated lignocellulosic mixture revealed higher ethanol productivity of about 1.396 g/L/h in SSF [17].

13 Conclusion

From the reported studies, it is evident that different pretreatment technologies have been applied to SCT for efficient delignification and hemicellulose solubilization. The application of combined pretreatment technologies needs attention in order to convert the SCT into bioethanol. Also, the developed pretreatment should be effective in delignification with low consumption of energy. From various reports, it was proved that hydrolysis using enzyme efficiently converts the delignified SCT into fermentable sugars. However, most of the SCT-based reports utilized the yeast

S. cerevisiae to ferment the sugars to ethanol. Application of co-culturing techniques involving different microorganisms should be encouraged for further enhancement of bioethanol yield. Furthermore, limited reports are available regarding the acid hydrolysis, commercial scale production, and economic analysis on bioethanol production from SCT.

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Recent Developments in Food-Based Bioplastics Production



Babuskin Srinivasan and Garima Kulshreshtha

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Abstract The problem of pollution has been rising all over the world right now, and plastics are the one that plays major role in it, which has been in daily use like packaging materials, carry bags, manufacturing of different types of materials, etc. Among them around, 40% are particularly used for the production of food packaging materials. A feasible way to solve this issue is to gradually decrease the consumption of plastics prepared of petrochemical origin and subsequently substitute it with plastics made up of biodegradable materials. The transformation process of bioplastics materials (starch, polyhydroxyalkanoates, cellulose, and polylactide) for food packaging applications by employing traditional plastic manufacturing techniques such as injection molding, extrusion, and compression molding has

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been discussed in this chapter. Active packaging is one of the latest packaging techniques which contain active ingredients in them utilized to scavenge free radicals or eradicate undesirable organisms, thereby extending the shelf life of the product. The application of bioplastics materials in the production of active packaging has also been reviewed and discussed in this chapter.

Keywords Active packaging, Barrier, Bioplastics, Food packaging, Polyhydroxyalkanoates

Abbreviations

HDPE	High-density polyethylene
HPMC	Hydroxypropyl methylcellulose
HSAC	α -Hydroxysulfonic acid cellulose
LDPE	Low-density polyethylene
MOI	2-Methacryloyloxyethyl isocyanate
PBAT	Poly(butylene adipate-co-terphthalate)
PBS	Poly(butylene succinate)
PCL	Poly(ϵ -caprolactone)
PE	Polyethylene
PEG	Polyethylene glycol
PET	Poly(ethylene terephthalate)
PHA	Polyhydroxy alkanoate
PHB	Polyhydroxy butyrate
PHBV	Polyhydroxybutyrate-valerate
PLA	Polylactic acid
PP	Polypropylene
PS	Polystyrene
PTT	Poly(trimethylene terephthalate)
PUR	Polyurethane
PVC	Polyvinyl chloride
TFA	Trifluoroacetic acid
TPS	Thermoplastic starch

1 Introduction

Plastics produced from petrochemical sources are in use for a long time in different kinds of applications like packaging, automotive, healthcare, and electronic devices. They are non-avoidable owing to the economic advantage it offers and its versatility, robustness, and aesthetic qualities. In the current scenario, some of the frequently utilized polymers in packaging applications are polyethylene (PE, 29%), polypropylene (PP, 19%), polyvinyl chloride (PVC, 13%), polystyrene (PS, 7%), poly(ethylene terephthalate) (PET, 7%), polyurethane (PUR, 6%), and others. However

usages of such polymers have created immense negative impact in the atmosphere, because of their toxic nature after incineration, non-biodegradability and pollution of water bodies [1].

1.1 Global Production and Impact

The demand for polymers in food packaging applications has been constantly on the rise owing to the increase in consumption of convenience foods. Global trades in processed foods have reached more than two trillion US dollars, and packaged foods contribute for half the quantity of that. When compared with other packaging materials like metal, paper, and board, plastic packaging occupies a major share of it (40%) [2]. The packaging materials employed in food industries have very short lifetime, cannot always be recycled, and after their utilization, majority of them accumulate in the landfills and water bodies, causing serious ecological concerns. It has been identified that only less than 3% of the plastic bags (500 billion) that are distributed in the market every year are recycled [3]. The plastic packaging materials used are frequently contaminated by biological substances and by foodstuff, thereby making it complicated for recycling process.

A feasible way to solve this issue is to replace non-natural polymers with eco-friendly materials particularly for packaging applications. However there are stiff challenges faced in using biodegradable polymers owing to their processability, cost, and functional properties when compared with synthetic polymers. The biodegradable polymers can be produced by utilizing natural resources like plants, animals, and microorganisms or from other renewable resources and are degraded by the enzymatic action of fungi, yeast, and bacteria; and they are compostable by acting as fertilizers and soil conditioner. Some of the important examples are polylactic acid, cellulose, starch, chitosan, lignin, and proteins [4].

2 Classification of Bioplastics

The bioplastics are categorized into four sections depending on their method of synthesis, source, and chemical composition.

Based on their chemical composition, source, and synthesis method, bioplastics can be classified into four categories (shown in Fig. 1): (1) polymers derived straightly from biomass (e.g., protein, starch, cellulose); (2) polymers produced through chemical synthesis by utilizing bioderived monomers (e.g., bio PE, PHB, PLA); (3) polymers produced from microbial fermentation (e.g., polyhydroxyalkanoates); and (4) polymers produced through chemical synthesis by utilization of both petroleum-based and bio-derived monomers (e.g., PTT, PBS) [6].

Bioplastics made out of starch, cellulose, PLA, and PHAs have gained commercial importance in recent times, due to their ease in processing using existing

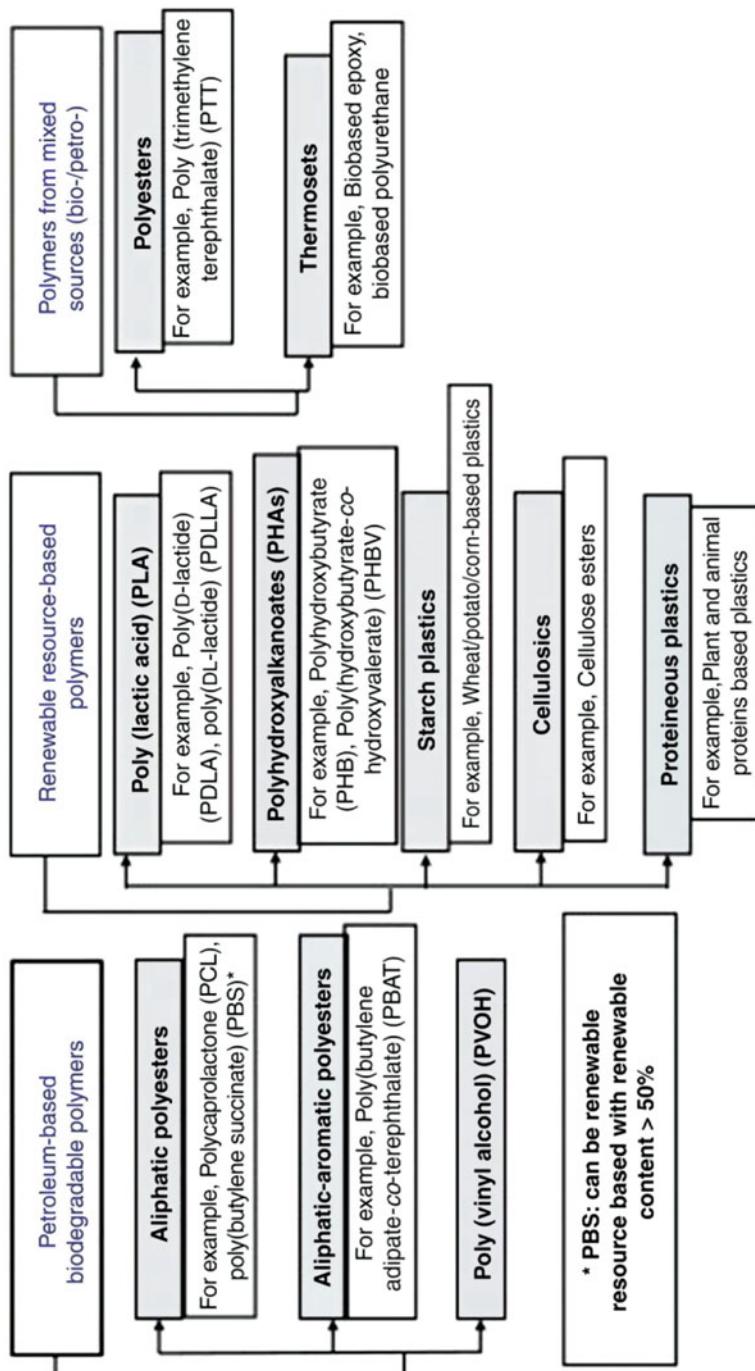


Fig. 1 Resources of biodegradable polymers (with permission from [5])

processing equipment, good functional properties, and they can be manufactured in bulk at competitive costs [6].

2.1 Starch

Starch is a polysaccharide containing vast numbers of glucose units linked together by glycosidic bonds which are made up usually of amylopectin (75–80%) and amylose (20–25%). Starch is produced as reserve material in plants such as corn, rice, cassava, oat, wheat, barley, soybean, and potatoes in granule form, varying in size (0.5–175 µm) and in composition. They are hydrophilic, and the water content of starch varies with relative humidity. In starch, the amylopectin contributes for crystalline areas and the amylose for amorphous areas. Due to the hydrophilic nature and processability, there are limitations regarding application of starch as a packaging material. This problem can be solved by adding plasticizers like carboxylic acid, sorbitol, or glycerol or by blending with polymers like polyols, epoxides, or poly(*ε*-caprolactone) (PCL).

The polymers have distinct chemical structures and it causes immiscibility issues when blended with starch; this can be solved by an alternative approach of grafting vinyl and acrylic monomers on the starch polymer chain, thereby enhancing its hydrophilicity or hydrophobicity; this may depend on the processing condition. A number of essential characteristics such as flexibility or elongation and hardness can be adjusted by modifying the concentrations of plasticizers added.

Flexibility of a blended polymer can be easily enhanced by increasing the plasticizer content. When compared to pure starch or chemically modified starch, thermoplastic starch provides finer phase dispersion in the blend system [7, 8]. Thermoplastic starch can be produced by blending glycerol with starch subsequent to the gelatinization process. Though TPS has excellent oxygen barrier properties, due to their hydroscopic nature, they can't be used for packaging liquid food and high moisture-containing products. Thermal and mechanical properties of thermoplastic starch can be increased by adding aliphatic polyesters like PHBV, PLA, PCL, etc., and the strength of the plastics may vary depending on the polymer blend [9]. Thermoplastic materials from starch can be utilized for manufacturing plates, food wrappings, and food containers and cups [10].

Thermoplastic starch was blended with talc nanoparticles, and by thermo-compressing, the films' packaging bags were made. The maximum strength was obtained for films added with 3 wt% of talc; however, the films displayed poor water vapor barrier and mechanical properties when compared to plain starch films. Corn starch can be used to produce 100% biodegradable polymers when blended with plasticizers, and the resin manufactured can be transformed into injection-molded pieces, loose-fill packaging material, and films [11].

The films made up of starch are odorless, colorless, and tasteless, and they have showed low humidity and less permeability to oxygen [12]. When compared with plain starch film, films made by blending PCL (up to 10% wt) with citric acid and

glycerol being added as compatibilizers displayed good water vapor barrier property and also lowered the glass transition temperature [13].

Biodegradable films can be also manufactured by utilizing oxidized or acetylated arracacha starch. Due to the high transparency displayed by films produced from acetylated starch, also because of their good physicochemical properties, these can be used for food packaging applications [14].

The biodegradable packaging film was produced by blending sugar palm starch with plasticizers like sorbitol, glycerol, etc. Water vapor permeability values were observed in the increased range of 4.855×10^{-10} to $8.70 \times 10^{-10} \text{ g}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ irrespective of the plasticizer types in films [15]. Starch can be transformed into foamed material through water steam, thereby substituting polystyrene foam for packaging purposes. The processed material can be transformed into trays and disposable dishes by pressing. The products produced were nontoxic and easily biodegradable in the microbial environment within short period of time leaving CO_2 and water as by-products [16]. Novament produces its own starch blends, and it is one of leading company in manufacturing starch-based products [4].

2.1.1 Starch Composites

Starch-based polymers have displayed deprived mechanical properties and high water vapor permeability when compared with synthetic plastics. Microcrystalline cellulose (MC), carbon nanotubes, carboxymethylcellulose (CMC), nanoclays, fibers, etc. were added to starch-based polymers to improve their properties [8, 17]. The polymer blends produced by blending PLA, PCL, and starch have shown better biodegradation in natural environment when compared to pure PLA [18].

2.2 Cellulose

Cellulose is formed from linear chain of glucose molecules linked by highly polar and hydrophilic glycosidic $\beta(1\rightarrow 4)$ bonds, and it is the most commonly found biopolymer in nature. Cellulose acts as structural component in plant materials, fungi, sea animals, and some amoeba [19]. As cellulose-based films are cost-effective and completely biodegradable, they offer immense scope in replacing petrochemical based plastics [20].

As cellulose are hydrophilic in nature, it encompasses a high crystalline structure and poor solubility, and it is difficult to use them as such for food packaging. But this can be solved by manufacturing cellulose derivatives through esterification reactions where cellulose are derivatized in the solvated state, thereby making it fit for packaging applications. The additives of cellulose esters like cellulose (tri)acetate and cellulose (di)acetate were previously added to convert them into thermoplastic materials. Cellulose ethers like ethyl cellulose when added with plasticizers could be

utilized for molding and extrusion applications. A cellophane film was produced by dissolving cellulose in carbon-disulfide and sodium hydroxide mixture to make cellulose xanthate and then recasting them in sulfuric acid solution to produce cellophane film, suitable for food packaging applications [21].

Cellulose acetate-based nanocomposites comprising modified montmorillonite, triethyl citrate (plasticizer), and thymol (antimicrobial) have shown real promise to use it them for food packaging applications [22]. Modified form of cellulose like hydroxypropyl methylcellulose with silver nanoparticle matrix has also shown good ability to use it for food packaging [23]. The modification of cellulose fibers with other polymers or plasticizers increases their tensile strength and mechanical properties, e.g., PVA reinforced cellulose fiber showed increased tensile strength, thereby making composite films more suitable for packaging [24]. Dicarboxylic cellulose and α -hydroxysulfonic acid cellulose (HSAC) both modified cellulose fibers can be transformed into nature-friendly film materials. They have exhibited good mechanical properties like 9.6 GPa modulus and 47.0 MPa tensile strength [25].

Trifluoroacetic acids (TFA), which are naturally organic and completely biodegradable, have the ability to transform agro-wastes abundant in cellulose to bioplastics material through aging them in TFA solution [26]. The mechanical property of biopolymers (brittle and rigid, soft and stretchable) varies according to the type of plant species and their chemical composition. Cellulose in TFA solutions can be blended with vegetable waste solutions to attain plasticization, and these plasticized materials are having the ability to replace petrochemical-based plastics [27]. Cellulose acetate, a cellulose derivative produced commercially worldwide, has the great capability to be used for food packaging applications (baked food, fresh food). So far many studies were carried out by adding cellulose fibers to starch-based films [28, 29], PLA (Sanchez-Garcia and Lagaron [30], and PHBV films [31]; it has been proved that they can be potentially be utilized for food packaging applications.

Cellulose fibers can be blended with PLA to produce biopolymer matrix material, but there exists the challenge of uniformly distributing the cellulose fibers in PLA matrix [32]. The hydroxyl groups present on the surface of cellulose fibers sometimes will join together and form agglomerate that results in crack formation and composite breakdown. The addition of surfactants [33], silylation [34], grafting [35], and acetylation [36] were followed to improve the dispersion mechanism, and significant progress has been achieved.

2.3 *Polylactic Acid (PLA)*

PLA is a completely biodegradable polymer manufactured from both fossil and renewable resources, and it's proven to have potential to replace commercial polymers like HDPE, LDPE, PS, and PET [37]. Bacterial fermentation of corn or cane sugar is performed to manufacture lactic acid (LA), which is then converted to PLA through ring opening polymerization of LA with the use of a catalyst (shown in Fig. 2). This mechanism has been followed because normal method of

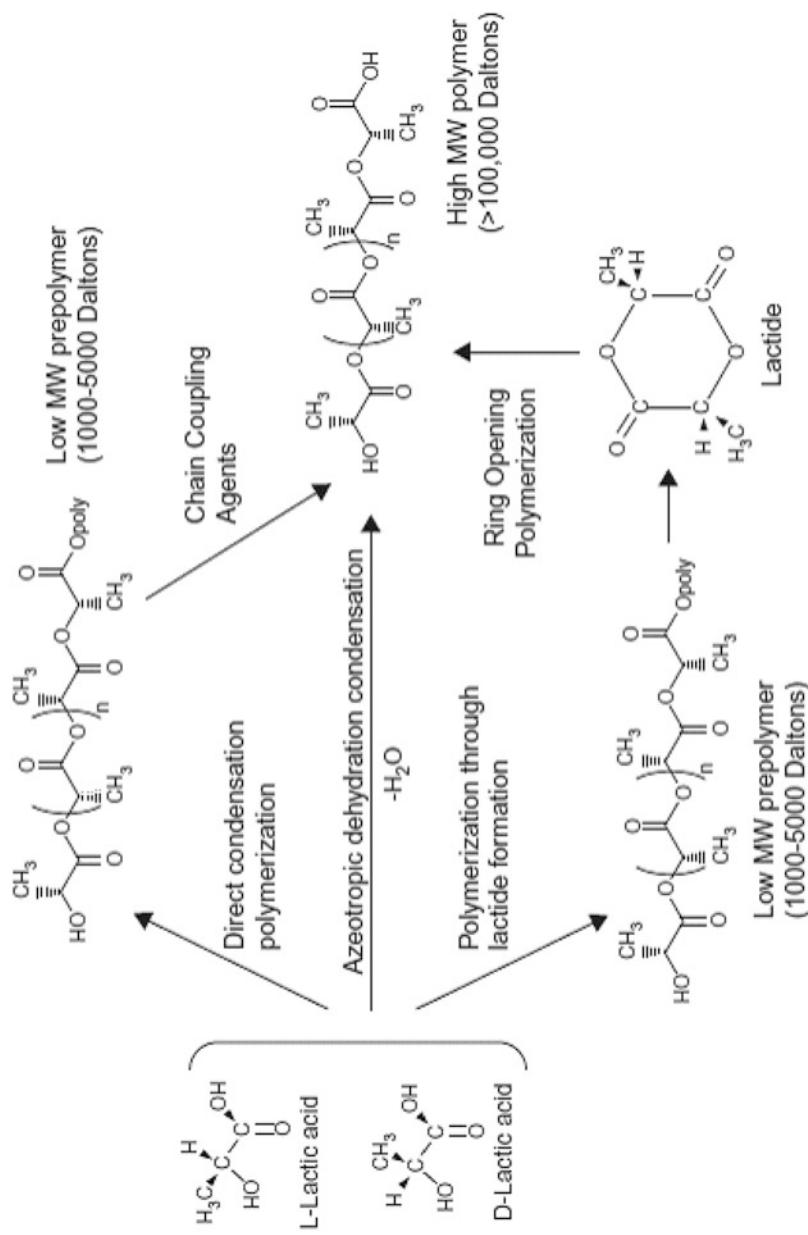


Fig. 2 Synthesis of Polylactic acid (PLA) from D and L-lactic acids (with permission from [38])

polymerization generates more water, where its presence may degrade the formed polymer chain. By adding hydroxylic compounds, it is possible to control the molecular weight of PLA, and PLAs with high molecular weight are certified as GRAS (generally regarded as safe) by US FDA. It is an odorless, colorless, glossy, stiff, low-toxicity polymer, suitable for direct food contact, and this biodegradable polyester has highest melting temperatures, around 160–190°C [39].

The PLAs can structurally be classified into three types, namely, poly(D,L-lactide) (PDLLA), poly(D-lactide) (PDLA), and poly(L-lactide) (PLLA) [40]. Among these, PDLLA is fully amorphous, where the others PDLA and PLLA are semicrystalline. Poly(D,L-lactide) with 90% L-lactide has been widely used for producing packaging materials [41].

PLA is having performance similar to that of PET, so it is feasible to use PLA as a potential substituent for PET in products like pouches, films and bottles, etc. Because of its brittle nature, less elongation (<10%) at break, deprived gas barrier properties, and high modulus and hydrophilic character, primarily its application has been limited to thermoformed packaging [42]. As PLAs have low melt strength, to process them into extruded sheets, foam and films' higher melt strength is required [43].

The PLA has better thermal properties when compared with other biopolymers like poly(ϵ -caprolactone) (PCL), PHA, and polyethylene glycol (PEG). The PLA has long crystallization rate, as it takes more period of time to form helical packing structure. The PLA needs to be modified and blended with further biodegradable polymers to use it for a wide variety of packaging applications. Conventional techniques such as blow molding, injection molding, film extrusion, fiber spinning, and thermoforming can be used for processing the blended PLAs [44]. The PLA majorly can be used for producing disposable tableware and especially for packaging foods having short shelf life like juices, yogurt, vegetables and fruits, etc.

For enhancing the properties like ductility and to accelerate crystallization, the PLAs are needed to be blended with fillers or other additives to form PLA composite films. So far many materials like nanoclays [45], plasticizers [46], starch [47], and carbon nanotubes [48] were blended in making PLA matrix. The significant improvements in thermal and mechanical properties were achieved when 2-methacryloyloxyethyl isocyanate (MOI) was blended with PLA [49]. The produced PLA-MOI, when compared with pure PLA, had 20 times higher percentage of elongation. Jiang and Zhang [50] blended PLA with other bioplastics like PBS, PHA, PCL, thermoplastic starch, and PBAT and achieved improved toughness and ductility.

In a recent study carried out by Bandera et al. [51], a latex-coated paper which is suitable for food packaging has been prepared by blending PLA with montmorillonite, surfactants, plasticizers, water, and chloroform via emulsion/solvent evaporation method. Improved water vapor transmission rate (up to 85%) was achieved in coated papers and the latex material is nontoxic, so it can securely be used for food packaging applications.

The properties of PLA may differ considerably from amorphous to semicrystalline based on D-lactide/L-lactide enantiomers ratio. In PLA the amorphous one,

having 12% D-lactide enantiomer has the properties similar to polystyrene and can easily be processed via thermoforming. It has been effectively employed in food packaging sector under the name Natureworks-PLA manufactured by Natureworks-LLC (Blair, NB). Currently this has been in use for packaging of short shelf life products [52].

The water vapor and oxygen barrier properties of PLA were enhanced by coating PLA with PEO-Si/SiO_x (polyethylene oxide), PCL-Si/SiO_x (polycaprolactone), and MAP; these PLA films can potentially be employed for packaging medium shelf life products (vegetables, cheeses, fresh meat, processed meat) [53]. Also significant improvement in oxygen barrier and water vapor properties were achieved for number of polymers (nano-fibrillated cellulose film, PLA film, PHB, PLA-coated board) quoted with thin layer of AlO_x (25 nm) Hirvikorpi et al. [54].

2.4 *Genetically Modified or Naturally Occurring Organism-Based Bioplastics*

Bacteria synthesize polymers like PHB and PHA via fermentation of starch or glucose, and further they are extracted by using solvents like methylene chloride and chloroform [55]. The properties of PHA like tensile strength, chain length, and brittleness depends upon the type of microorganism, carbon source used, and the monomer unit composition [56].

The melting point of PHAs ranges from 40 to 180°C based upon monomers involved in synthesis. PHAs when combined with starch or other bioplastics can effectively be used for packaging applications [57]. Poly(D-3-hydroxybutyrate) (PHB) is one of the monomers of PHA; apart from its brittleness, it has almost similar mechanical properties of PP [58, 59]. The huge crystalline domain is responsible for the brittle nature of PHB, as it has high *T_g* and crystallinity [60].

As the melting temperature (175–180°C) of PHB is similar to isotactic polypropylene (iPP), it can be used for intermediate bulk containers and shrink packaging [55]. Though the cost is high, it degrades in microbial environment in the shorter period (5–6 weeks) of time giving out CO₂ and water as by-products under aerobic condition and, under anaerobic condition, it produces methane [61].

2.5 *Multilayer Film Systems*

In recent times, an alternative strategy of developing multilayer film systems based on PLA and PLA has emerged as the latest trend in improving the technological properties of biopolymers [62].

3 Active Packaging

The emergences in innovative packaging techniques are due to demand from consumer for palatable, mildly processed, and ready-to-eat foods with good quality and long shelf life. The ultimate goal of food packaging technology is to avoid food spoilage during farm to fork and also to eradicate hazards leading to foodborne illness. Recent changes in lifestyle where the consumer has less time to prepare meals have propelled the food packaging sector to develop new and inventive food packaging methods.

Latest techniques in the area of food packaging are intelligent packaging, active packaging, and bioactive packaging, which have shown significant promise in maintaining the freshness and extending the shelf life, thereby improving the quality and safety of food products [63].

Active packaging is an inventive concept which refers to the utilization of active materials including moisture absorbent, scavengers, and antimicrobial- and antioxidant-releasing systems that are used in food-enveloping environment to enhance the performance of packaging systems [64].

The major aims of active packaging are to prevent moisture infusion and microbial attack, reduce oxidation, regulate respiratory process, etc. It can be achieved with the help of CO₂ scavengers/emitters, time-temperature sensors, biosensors, aroma emitters, ripeness indicators, ethylene scavengers, and prolonged release of antioxidants into the package during storage period.

A range of compounds such as organic acids including propionate, benzoate, sorbate and bacteriocins (pediocin and nisin), enzymes like lysozyme, fungicides, and metals were tested previously in food packaging for their antimicrobial activity [65–67]. For example, in Japan they have incorporated Ag-substituted zeolite as antimicrobial agent in packaging films. The Ag-ions have wide antimicrobial spectrum, and in active packaging films they inhibit variety of metabolic enzymes. However, there are some limitations that exist such as Ag-zeolite is costly and so far there are few descriptions reported regarding their application as packaging material. LDPE films comprising potassium sorbate have shown very good inhibitory effect against yeast cells. Currently, there are two commercial biocidal films available in the market; one is chlorine dioxide and the other one is a chlorinated phenoxy compound. The biocidal agent in both films resides in the polymer spaces and is released upon food contact or in response to changes in the environment.

3.1 Antimicrobial Packaging Concept

The antimicrobial agent may be coated onto films, or it can be directly incorporated into polymer material or packaging films to produce antimicrobial packaging films. The utilization of active antimicrobial compounds included in packaging material could be one approach for controlling bacterial pathogens in the food packaging

system. This would ensure microbial food safety for consumer and also helps in extension of food's shelf life.

The mechanism of action in antimicrobial film may be migrating or non-migrating, it depends on the interaction between food matrix and the packaging. The antimicrobial agents can be infused in vapor or gradually diffused through food surface for migrating film applications, whereas it can be applied over the surface for non-migrating film applications. The release of active antimicrobial compounds in the food packaging should be tightly regulated and controlled; otherwise it might pose a safety risk to consumers.

3.1.1 Bacteriocins

Bacteriocins are peptidic antimicrobials which are synthesized mostly by lactic acid-producing bacteria and show bactericidal activity against major food pathogens. Bacteriocins can be used in antimicrobial packaging to improve product quality, safety, and shelf life as their use in food has been well recognized by the US FDA, WHO, and FAO. For example, the population of lactic acid bacteria has been reduced many folds in ham and sliced cheese stored at refrigerated temperatures, when they were applied with antimicrobial agent like immobilized bacteriocins lacticin 3,147 and nisin, thereby extending the shelf life. In a different study, low-density polyethylene film coated with sonorensin, a subfamily of bacteriocins, effectively reduced growth of Gram-positive food spoilage bacterial pathogens like *Listeria monocytogenes* and *S. aureus* in chicken meat and tomato samples [68]. Recently, Emiliano et al. demonstrated that triticale flour films with bacteriocin-like substance effectively controlled the growth of *Listeria innocua* in food packaging containers [69]. Natamycin-based anti-fungal coating is commercially available under the brand name SANICO® to be used in cheese and sausages [70].

3.1.2 Enzymes

Enzyme immobilization can be employed as an effective system for antimicrobial-based food packaging. Lysozyme has been permitted to be used as antimicrobial agent by the US FDA, and its use as a food additives falls under Directive 94/2/EC. Lysozyme is a single peptide protein which targets and destroys the glycosidic linkages in the peptidoglycans of Gram-positive bacteria. Cellulose triacetate (CTA) films immobilized with lysozyme have reduced *M. lysodeikticus* cell numbers by 7 log cycles (equivalent mass) within 24 h, suggesting its potential for food packaging applications [71]. In a different study, lysozyme-chitosan composite films incorporated with 60% lysozyme have reduced *Streptococcus faecalis* and *E. coli* by 3.8 and 2.7 log cycles (equivalent mass), respectively [72]. The covalent immobilization of lysozyme over the surface of ethanol vinyl alcohol copolymers have reduced the growth of Gram-positive *Listeria monocytogenes* (1.08 log reduction

for an equivalent mass of covalently immobilized lysozyme) with no migration of lysozyme from the films, suggesting utilization of these films for food packaging applications [73]. The antimicrobial membranes attained from polyamide 11(PA11) and nano-hybrid composed of halloysite nanotubes (HNTs) filled with lysozyme were effective as antimicrobial pads for chicken meat storage. The membrane filled with 5.0 wt% of HNTs-lysozyme reduced the growth of *Pseudomonas aeruginosa* for up to 13 days of storage at 4°C [74]. Antilisterial films of lysozyme based on zein were developed with a consumer-controlled and pH-triggered release mechanism. During transportation the antimicrobial stress is increased over pathogens in consumer-controlled release mechanisms [75].

3.1.3 Plants Extracts and Phytochemicals

A great interest has been shown in the utilization of plant extracts for edible polymer-based food packaging applications. Incorporation of phytochemicals into polymer-based packaging material has shown to improve its physiochemical properties. For example, incorporation of clove, star anise, and cinnamon extracts into hydrolyzed gelatin film has reduced their water vapor permeability and improved tensile strength. In a different study, incorporation of grape seed extract (GSE) into soybean protein isolate films resulted in bactericidal effects against food safety pathogens including *Listeria monocytogenes*, *Escherichia coli* 0157:H7, and *Salmonella typhimurium* [76–78]. Antimicrobial activity of plant-based antimicrobial films may be attributed due to the high phenolic content containing components like carvacrol, thymol, and eugenol. For example, thymol and carvacrol (8 wt%) have shown promising application as active additives in polypropylene (PP) films with dual response of controlled antioxidant and antimicrobial release into food material. Thus, they can be able to replace synthetic antioxidants employed in PP film formulations [79]. Nanocomposite antimicrobial films prepared using LDPE and carvacrol have displayed remarkable oxygen barrier property and thermal stability with significant antimicrobial activity against *Pseudomonas* stains [79]. In another study, five chitosan-based films containing carvacrol showed antimicrobial activity against *Bacillus subtilis*, *Escherichia coli*, *Listeria innocua*, and *Salmonella enteritidis*. The minimal vapor inhibitory concentration obtained for *S. enteritidis* was 1.08×10^{-7} g mL⁻¹ ($K_{\text{mass}} = 1.01 \times 10^{-4}$), and for *B. subtilis*, *E. coli*, and *L. innocua*, it was 4.62×10^{-8} g mL⁻¹ ($K_{\text{mass}} = 1.13 \times 10^{-6}$), respectively. Carvacrol-activated active films have displayed antimicrobial effect at their vapor phase against bacterial pathogens [80].

3.1.4 Essential Oils

Essential oil incorporation into packaging system reduces transparency and improves the antimicrobial and water barrier properties. Essential oils extracted from plants and spices such as cumin, fennel, laurel, mint, sage, savory, garlic,

clove, and cinnamon are rich source of antimicrobial compounds. Major antimicrobial action mechanisms include disruption of phospholipid bilayer of cell membrane, disruption of enzyme activity, effect on protein synthesis, and production of hydrogen peroxide [81, 82]. Antimicrobial properties of garlic, rosemary, and oregano essential oils dispersed in whey protein isolate (WPI) films were tested against *Salmonella enteritidis*, *Lactobacillus plantarum*, *Staphylococcus aureus*, *Escherichia coli*, and *Listeria monocytogenes* by means of assay of zone of inhibition. Results indicated that the films incorporated with oregano oil (2%) were observed to be effective against bacteria when compared with other spices [83]. In a different study, essential oil of rosemary has been incorporated in chitosan films, and it showed effective antibacterial activity against bacteria like *Streptococcus agalactiae* and *Listeria monocytogenes* [84]. Biodegradable trays (polyvinyl alcohol and cassava bagasse) containing oregano and clove essential oils were manufactured by two methods: direct incorporation (6.5–10.0%) and surface coating (2.5–7.5%); high antimicrobial activities were observed for surface-coated trays against spoilage yeasts, molds, and Gram-negative and Gram-positive bacteria [85]. Electrospun polyvinyl alcohol/β-cyclodextrin(PVA/CEO/β-CD)/cinnamon essential oil nanofibrous antimicrobial film has shown effective antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus* with MBC of approximate 7–8 mg/mL and MIC of 0.9^{-1} mg/mL [86]. Dextrin-based nanosplices incorporated with coriander essential oil (CEO) have shown significant bactericidal effect against food safety pathogens. Authors reported that whole essential oils incorporated in nanosplices (CD-NS) displayed efficient ability in controlling the oil release, while restraining bacterial growth, hence providing a promising strategy in overcoming the inefficiency of present antimicrobial food packages [87].

3.2 Antioxidant Release

Antioxidants are utilized into active packaging films to maintain oxidation stability of lipids and to prolong shelf life of dried products and O₂-sensitive foods. Natural, synthetic, and nanoparticle-based antioxidants have been successfully developed into multiple layer films. The synthetic antioxidants like thioester, butylated hydroxytoluene, and organophosphates sometimes migrate into food products, thereby creating potential toxicity issues, and due to this, the usage of such antioxidants are restricted in active packaging [88]. Hence, such artificial additives are currently replaced with natural alternatives like essential oils and plant extracts which exhibit antioxidant properties. The oxidative damage caused to foods can be reduced by employing edible-coated films which does it by reducing the oxygen transmission rate. The selection of bioactive compound depends on its compatibility with the packaging. For example, food packaging material ethylene vinyl alcohol copolymer (EVOH) matrix incorporated with antioxidants like quercetin, ferulic acid, green tea extract, and ascorbic acid had significantly decreased water permeability. Moreover, green tea extract incorporated films has shown great protection

against lipid oxidation [89]. In a different study, cassava starch films comprising rosemary extracts have shown better barrier properties against UV light and good antioxidant activity [90]. Solvent casting method was used to incorporate oregano, rosemary, and thyme essential oils (EOs) into polylactic acid resin (PLA, concentration 10% w/w) to produce antioxidant packaging films. Addition of EOs significantly reduced lipid oxidation and improved the shelf life of the product [91]. An active packaging material of κ -carrageenan incorporated with different amounts of mulberry polyphenolic extract (MPE) has improved water vapor, UV light barrier, antioxidant, and pH-sensitive activity of the films [92].

One of the major advantages of using antioxidant incorporated packaging films rather than antioxidants directly added to food is that the active antioxidant materials incorporated in packaging could be able to provide a controlled release of them into food, when compared to constant usage of antioxidants during storage [93]. Taken together, sometimes direct coating of antioxidants over the surface of packaging material and/or food may result in sensory disapproval. Hence, when packaging materials are produced by incorporating antioxidants in the packaging matrix, it may aid in improving food safety and quality by reducing direct accumulation of chemicals.

4 Conclusion

Nowadays due to recent advancements in technologies and awareness among people to conserve our planet, there is a great potential for using bioplastics as food packaging materials. Most of bioplastics are currently employed in the production of loose film which is having potential to be used for service packaging such as cutlery, cups, carry bags, and plates and for recent packaging like active packaging (antimicrobial, antioxidant), intelligent packaging, modified atmospheric packaging, etc. Over the last few years, there were much efforts undertaken to enhance the functional properties like flexibility, functionality, biodegradability, stability, and processability of bioplastics through physical, biological, and chemical treatment such as blending, compounding, copolymerization, and fermentation. The bioplastics developed by improving the functional properties may have almost same properties like petroleum-based plastics, but due the high developmental costs involved, the cost of production of biopolymers are still high. More investigations are needed in the future toward the development of cost effective intelligent and smart packaging systems, which can be able to provide information related to properties of the food within the package (microbiological safety, quality, shelf life, nutritional value). The smart packaging systems not only provide information regarding food to customers; they also act as potential barrier in safeguarding the food and ensuring the integrity of food properties. On the other note, it is also expected that more support is needed from the governments, particularly in the developed countries to cut down the large price difference between biodegradable packaging and conventional plastic packaging.

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Valorization of Waste Algal Boom for Value-Added Products



A. Annam Renita and P. Senthil Kumar

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Abstract Undesirable algal boom causes serious disposal problems which can be cost inductive and can cause secondary pollution problems. There is a need for valorization of such waste algal biomass which is otherwise disposed of as solid waste in land filling or incinerated. The algal blooms which are problematic can be processed technically to value-added products, and this in turn will also provide a sustainable solution to eutrophication hassles. Valorization techniques involve industrial processing of algal waste which can be converted or recycled into useful products or serve as a source of energy thereby increasing the value of the original material. This technology is the most promising solution to achieve low carbon economy. This review outlines the valorization techniques which can be adopted to convert the waste algal biomass which can be used in industries like energy, agriculture, and wastewater treatment plants.

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1 Introduction

Eutrophication of water bodies has been a long-term problem for which a permanent solution has not yet been found. The factors for eutrophication are the nutrient enrichment of water bodies and favorable growth factors like temperature, poor circulation, and physical dimensions [1, 2]. Eutrophication disturbs the aquatic ecosystem being superfluous in growth. The direct damage from eutrophication are (1) reduced biodiversity, such as the loss of dominant species, (2) damage to the water environment due to increased toxicity, and (3) changes in the physical properties of water like increased turbidity [3]. Moreover, algal blooms affect the ecosystem locally and indirectly the economy of the nation [4]. Economic losses of approximately \$2.2 billion for freshwater algal blooms and \$100 million for coastal algal blooms are being incurred every year in the USA [5]. The disposal cost of *Ulva* species from Brittany's coasts amounted up to US\$ 10–150 per ton in 2011 [6]. Severe *Microcystis* and *Aphanizomenon flos-aquae* algal blooms in freshwater Dianchi Lake, China pose health threats to animals and human, and their cell density could be as high as 10^9 units/L [7]. Ten thousand wet tons of *Ulva lactuca* are being produced approximately in shallow coastal estuaries in West Cork [2]. One million tons of *Ulva rigida*, *Valonia aegagropila*, *Chaetomorpha aerea*, and *Gracilaria confervoides* are being produced annually in Venice lagoon, Italy [8, 9]. Brown macroalgae *Fucus vesiculosus* predominates the algal bloom along the German/Danish coastline of the Baltic Sea [10]. Green tide, a rapid reproduction of toxic marine green plankton, is often encountered in countries like Denmark, France, Japan, China, Italy, Ireland, Australia, and Argentina [2, 8, 11–17]. Red tides have been reported in countries like USA, Norway, Sweden, Spain, Chile, Japan, and China due to proliferation of the toxic red algae. [18–22].

Algal bloom has now become a universal problem which is progressing in frequency and size throughout the world. Problematic algal blooms are also found in industrial effluents like effluent treatment plants where nitrogen and phosphorus content and photic zones enhance their growth. Microalgal consortium of *Leptolyngbya foveolaurum* and *Chlorococcum infusionum* was collected from coke-oven effluent treatment plant in Durgapur, India [23]. Algal blooms not only contaminate the water bodies but also release toxins which prove to be harmful to humans and animals. The third largest lake in China, Taihu Lake which provides drinking water for more than two million people, was contaminated by the foul blue-green algal bloom during the summer of 2007. Algal bloom releases toxins in the water bodies which find way to humans and animals through food chain or through water pipeline systems. *Microcystis aeruginosa*, a cyanobacteria, produces toxins that can damage the liver, intestines, and nervous system leading to liver failure and diarrhea [24]. Hence it becomes imperative to find a solution to the disposal of such nuisance causing algae since their growth is very difficult for prediction. The methods usually adopted is skimming the algae by mechanical or manual means

and then dumping in landfill, composting, or incineration. But these algal blooms which are disposed off as waste can be valorized industrially to increase their original value.

Algae has been identified as an untapped source of value-added products like biofuel, food supplement, pigments, adsorbent, fertilizer, biogas, cosmetics, etc. Usually these algae are cultivated in-house in monitored culturing conditions because of the safety of the end use, especially in cosmetic, pharmaceutical, and food industries. Nevertheless, the algal bloom which grows in mixed cultures of wild condition cannot be used for such purposes, but it can be processed to products like biochar, biooil, and biogas and as an adsorbent which have market value and are subtly outlined in this review.

2 Algal Bloom Valorization

Algae both microalgae and macroalgae have vast potential application in industries like food, pharmaceutical, water treatment, nutraceutical, textile, and energy [25–29]. New applications are surfacing in recent years in industries like agriculture, polymer, construction, solar cells, and printing inks [30–32]. Nevertheless, researchers all over the world will accept algae to have enormous market potential in terms of its application. Algae are usually cultured by providing the required nutrient medium and light energy to produce value-added products which have huge market base. But very less attention which is evident from the few research papers showcases the possibility of converting the annoying algal bloom to value-added products like their cultured counterparts. Algal bloom can be valorized by technical processing like pyrolysis, composting, fermentation, solvent extraction, and gasification to products of higher value than the original algal bloom since the algal composition like lipids, carbohydrates, proteins, etc. remains more or less the same.

2.1 Biogas

Biogas having a composition of methane, carbon dioxide, and traces of nitrogen, hydrogen, oxygen, and hydrogen sulfide is a renewable energy source for electricity, thermal, and transport fuel which can also be stored and utilized [33, 34]. The algal biomass is subjected to anaerobic digestion where the end products are obtained after hydrolysis, acidogenesis, acetogenesis, and methanogenesis of the raw materials. Microbial consortium is added to facilitate faster breakdown of substrates. Algal biomass can be used as such or can be codigested with other organic substrates for the production of biogas. Biogas was produced by anaerobic digestion of blue algae which was skimmed from Taihu Lake, China, which reported a yield of $189.89 \text{ mL g}^{-1} \text{ VS}^{-1}$ with a methane concentration in the biogas as 36.72% [35]. Biogas was produced by codigestion of corn straw and Taihu Lake blue

algae which gave a biogas yield of $1,184 \text{ mL g}^{-1} \text{ VS}^{-1}$ with 54.9% methane content for a cumulative 30 days period [36]. Fresh *Ulva* gave a biomethane yield of 183 L CH₄/kg VS, and dried, washed, and macerated *Ulva* gave a biomethane yield of 250 L CH₄/kg VS. Codigestion with diary slurry gave a biomethane yield of 220 L CH₄/kg VS [2]. It should be noted that due to seasonal variations, the methane yield will be different for various species of algae [37]. Generally macroalgae commonly known as seaweeds yield a considerably lower amount of methane [38]. Mixed samples of *Pilayella* sp., *Ectocarpus* sp., *Polysiphonia* sp., *Cladophora* sp., and *Enteromorpha* sp. with small amount of seagrass *Z. marina* which were collected from Sopot beach, Poland, and Skåre beach in Sweden were found to have good C/N ratio and could be an alternative solution for codigestion with other biomass [39]. Methane production from anaerobic digestion of whole seaweeds or their residues after alginate extraction is more viable from an environmental point of view than the exploitation of natural gas [40].

2.2 Biochar

Biochar can be produced from algal blooms by pyrolysis which is a high temperature thermal decomposition in an inert atmosphere. *Lyngbya* species and *Cladophora* species, algal blooms, from Maumee bay of Lake Erie, USA, were collected and pyrolyzed at 510–600°C to yield a biochar (48 wt% of algal mass) having a calorific value of 25.6 (MJ/kg). Algal biochar made by this thermochemical method also had a significantly higher nitrogen content [41]. Biochar can be used as a soil amendment which increases quality of soil by increasing nutrient retention capability of soil. Biochar has good tensile strength and hence can be used in the production of carbon nanotubes, activated carbon, and carbon fibers [42]. Synthesis gas can also be produced by steam reformation of biochar [43].

2.3 Biooil

Biooil or more specifically algal oil can be produced by subjecting the algal bloom to thermal degradation in the absence of air at temperatures usually ranging from 300 to 900°C. *Microcystis* species, a blue-green alga which was harvested from Dianchi Lake in China, was subjected to pyrolysis in a fixed bed reactor from 300 to 700°C, and a maximum of 54.97% biooil was obtained with a heating value of 31.9 MJ/kg which was much higher than pyrolysis of cellulose materials [44]. Algal bloom from Meiliang Bay of Taihu Lake, China, was pyrolyzed from 300 to 700°C in a fixed bed reactor to yield 59% biooil with a higher heating value of 21 MJ/kg [45]. It is the most promising product which has high heating value and can be used for production of electricity or heat or for cogeneration or as feed stock for industrial operations.

2.4 Bioethanol

Ethanol can be produced from algal bloom by fermenting the algae with microorganisms which is capable of metabolizing sugars. Algae have various carbohydrates such as starch, cellulose, laminarin, mannitol, and agar which can be fermented with suitable microorganisms to give a good yield of bio ethanol [27]. The kelp *Laminaria digitata* which is highly prevalent along the coast of the UK especially in the month of July was fermented with yeast *Pichia angophorae* owing to its high laminarin and mannitol content. A maximum yield of 167 mL ethanol at approximately 69 h incubation was obtained at 5% dry weight kelp, pH 4, and at 24°C [37]. Laminarales especially *L. hyperborean* collected from the Norwegian coast was fermented with *Zymobacter palmae* under anaerobic conditions and gave a maximum ethanol yield of $0.38 \text{ g ethanol (g mannitol)}^{-1}$. This yield was attributed to the carbohydrates present in the *Laminarales* fronds [46]. *Saccharomyces cerevisiae* was used to ferment *L. japonica* collected from the floating residue of *L. japonica* industry, China, at 30°C for 36 h, and 0.143 L ethanol from 1 kg floating residue could be achieved on acid pretreatment followed by enzymatic hydrolysis [47].

2.5 Adsorbent

Algae has the ability to store fluorides and heavy metals than any other land or aquatic species [48–54]. Algal biomass is collected, dried, and used such as an adsorbent or can be subjected to chemical treatment to enhance its adsorption capacity. Algal bloom in a wastewater treatment plant in coke-oven industry was valorized into a potential biosorbent. A consortia of *Leptolyngbya foveolaurum* and *Chlorococcum infusionum* was found in the storage tank of wastewater effluent treatment plant. The algal bloom hindered the reuse of the water after tertiary treatment by increasing the pH and biological oxygen demand of the treated water. The dry biomass was subjected to adsorption of fluoride, and the adsorption capacity of the mixed consortia was found to be 34.36 mg/g at temperature 30°C for an adsorbent dosage of 3.5 g/L. The adsorption characteristics were best explained by Freundlich isotherm model and first-order kinetic model [23]. A similar case was reported for the algal biomass collected from ponds in Osmania University campus, Hyderabad, India. The algal biomass was dried, and the dried algal biomass was used for fluoride removal which gave a fluoride removal of 64% for 300 min and followed a pseudofirst-order kinetic model [55].

2.6 Biofertilizer

Algae can be dried, powdered, and applied as such to plants or can be composted with other biomass before application as fertilizer. Eutrophied algal bloom compost can be both mature and highly stable which has high potential as a soil amendment

[56]. The high fiber content of seaweed acts as a soil conditioner and assists moisture retention, while the mineral content is a useful fertilizer and source of trace elements [57]. Algal bloom collected from Sopot beach along the Baltic Sea was dried and ground to a powder. Stages of algal degradation were studied, and growth tests were carried out with the algal powder and were successful as a biofertilizer [58]. Inoculation studies of *Undaria pinnatifida* (wakame) seaweed collected from Amagasaki Port of Japan with alginate-degrading bacteria *Gracilibacillus* sp. not only shortened the length of composting but also created seaweed compost with good fertilizer qualities [59]. The kelp *Laminaria digitata* obtained from the intertidal zone of the beach at East Haven Scotland was chopped and applied to the soil. The study of 90 days proved that on the addition of the algal biomass to the soil increased the aggregate stability and the pore volume of the soil [60]. *Posidonia oceanica* collected from Apulia Region, Italy, when mixed with residues of olive pruning and green wastes provided high-quality composts showing high organic content, low heavy metals content, and no phytotoxicity which suggest safe utilization of eutrophied algae as soil fertilizer in agriculture [61]. Seaweeds *Melanothamnus afaqhusainii*, *Spatoglossum variabile*, and *Halimeda tuna* from Buleji Beach, India, when applied as a pesticide showed suppressive effect on root pathogens of tomato and sunflower by reducing fungal root infection and nematode's galls on roots and nematode's penetration in roots [62].

3 Summary

Eutrophied algal blooms cause secondary pollution problems and incur huge amount of money in their removal from their aquatic ecosystem and in proper waste disposal. Algae are valuable resources which have many useful applications apart from it being the best carbon sequester, and it is being wasted off in algal blooms. Moreover they do not have the disadvantages of other biomass counterparts of utilizing land or water which makes it an attractive alternative. This review highlights the possibility of algal bloom valorization to produce biochar, biooil, biogas, biofertilizer, and bioethanol and as an adsorbent which have huge market value. Biogas and biochar processes are the simplest valorization techniques compared to others because of its relatively low number of processing steps. Energy industries especially biofuels need to consider such options which can make their process viable, sustainable, and economical.

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Algal Biomass for Biofuels and Bioproducts



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Abstract In recent times, due to rapid consumption of fossil fuels and increased pollution levels, the demand for biofuels has been on raise. Currently the resources utilized for biofuel production are derived through conventional agriculture; it may pose a significant danger to food security. Switching over in the direction of third

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generation biofuels (from algae) is one among the best possible solutions for this problem. Moreover algae contain substantial quantity of carbohydrates, lipids, and proteins, thereby making them as a potential candidate for the manufacture of biofuels like bioethanol, biohydrogen, biodiesel, biobutanol, etc. Apart from biofuel production, algae can also be able to produce valuable products like omega-3 fatty acids, carotenoids, protein-rich supplements, etc. This chapter offers an insight into the modern practices being followed in the manufacture of biofuel like screening of potential strains, avoiding contamination risks, optimization of mass cultivation conditions, easy harvesting, and extraction methods. The key concerns of these process and opportunities on the employment of algal biomass in multiple applications like fuel, food, and environment will also be discussed.

Keywords Algal biomass, Biofuels, Bioproducts, Extraction techniques, Optimization

Abbreviations

BOD	Biological oxygen demand
COD	Chemical oxygen demand
DAB	Dry algal biomass
FAME	Fatty acid methyl esters
HTL	Hydrothermal liquefaction
PBR	Photobioreactor
PUFA	Polyunsaturated fatty acids

1 Introduction

In the current era due to fast population growth and exhausting exploitation of non-renewable fossil fuel resources, there is an increasing demand for energy and resources. Therefore the requirement for alternative resources and processes is becoming impellent. A sustainable development approach should be able to reduce greenhouse effect and produce energy from non-fossil sources, along with the need of securing food to all people. These resources should be renewable to match with the sustainability principles. A renewable feedstock is a resource that have unlimited supply or be restocked over time by natural processes. Biofuel is a renewable, non-hazardous, natural fuel manufactured from diverse feed stocks [1]. Among them, biofuel from algae (third-generation biofuel feedstock) has garnered profound attraction in current times owing to their low water consumption, fast growth and usage of non-arable land for growth, etc. Moreover it does not involve the “food-versus-fuel” controversy, associated with application of various dedicated bioenergy crops like *Jatropha curcas* or food crops such as soybeans. Apart from these algae are having great potential to absorb carbon dioxide (1.8 times the biomass), ability to

make use of organic wastes, and also can be able to produce important products like omega-3 fatty acids, carotenoids, protein-rich supplements, etc. [2].

Algae by acting as green cell factories are having the ability to transform light, nutrients, and CO₂ into numerous compounds of high monetary value [3]. Due to their high CO₂ sequestering ability and good solar conversion, algae can produce more amounts of biomass and metabolites when compared with terrestrial plants [4].

Microalgae are wide set of aquatic organisms flourishing in different environments like sea water, fresh water, and saline conditions. Many algal strains that are viable industrially are extremophiles; i.e., they can able to adapt and grow in intense ecological conditions like salt pans (high salinity, e.g., *Dunaliella* sp. [5]), polar regions (psychrotolerant, e.g., *Koliella antarctica* [6]), alkaline waters (*Spirulina* sp.), high-nutrient wastewaters (*Chlorella* sp., *Scenedesmus* sp., *Monoraphidium* sp. [7]), etc. The ability of algae to survive in polluted environments having rich nutrients (nitrogen, phosphorus, potassium), the high tolerance of them to some greenhouse gases like CO₂, SO_x, NO_x, etc., makes them appealing, and they can able to potentially transform organic wastes to biofuel and other value-added bioproducts. The way of simultaneous waste treatment and production of biomass is called “integrated cultivation process” [7].

Majority of the algae are phototrophic performing solar to chemical conversion via photosynthesis. The key advantage of microalgae is that they have shown ability to synthesize high lipid content, which then can be transformed into biodiesel. However, the key bottleneck is high costs when microalgae are employed as energy source.

For long microalgae are known to produce macromolecules like proteins, carbohydrates, and lipids; hence it has been utilized as a potential stock in the manufacture of industrially valuable co-products. Different products used in cosmetics, food, and feed industries like polysaccharides, pigments, and hydrocarbons/lipids can be produced from microalgal biomass by altering the processing techniques (Fig. 1).

Microalgal lipids can potentially be converted into biofuels, polyols, polymers, and specialty lipids like polyunsaturated fatty acids (PUFAs). Pigments like phycobiliproteins, carotenoids can be utilized as natural colorants and sterols for the production of steroids, nutraceuticals. The starch, glucans, and other complex polysaccharides can be utilized for production of bioethanol, biofuel additives, and bioplastics [8]. The defatted algal biomass produced after extraction of metabolites might find its applications in biogas generation, animal feed, or can be used as absorbent in removing synthetic dyes [9]. Thus total algal biomass can be converted to worthy co-products.

The key steps involved in biofuels production and other value-added products from microalgae are screening (identification of potential strain), cultivation (algal growth in media by providing required nutrients), harvesting (separation of biomass), and post-harvest processing (extraction of products from biomass) (Fig. 2).

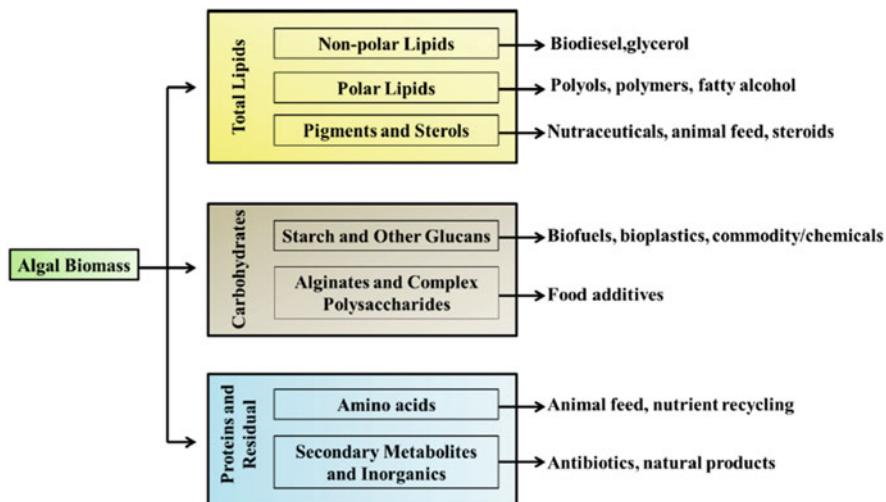


Fig. 1 Overview of products from microalgal biomass (with permission from [8])

2 Identification of Potential Strain

Microalgae are microscopic organisms that are found in extensive range of fresh and marine water environments. Some algal species can be able to accumulate up to 48% of lipid on dry weight basis, whereas other species are known for their ability to produce protein [10]. The lipid and carbohydrate contents are transformed into different kinds of biofuels, whereas the protein content could be converted into nutritional supplements, animal feed, and biofertilizer. Therefore, the selection of suitable strain is of high importance as it plays major role in deciding the overall cost and kind of end products. There are four different groups of classification in microalgae: (a) Cyanobacteria (blue and green algae), (b) Chlorophytes (green algae), (c) Rhodophytes (red algae), and (d) Chromophytes (all other algae). There are around more than thousand varieties of strains under every group of algae [11]. However so far only few numbers of cultures are exploited, and the more extensively used microalgae are Chrysophyceae, Chlorophytes, Bacillariophyceae, and Cyanobacteria. Strains like *Phaeodactylum*, *Chlorella*, and *Nannochloropsis* have exhibited good biomass productivity, and they display immense potential for industrial-level productions [12].

The strains should be screened depending on their physiological properties, such as tolerance to higher levels of CO₂, NOx, and other pollutants, environmental adaptability, and accumulation of high valuable products.

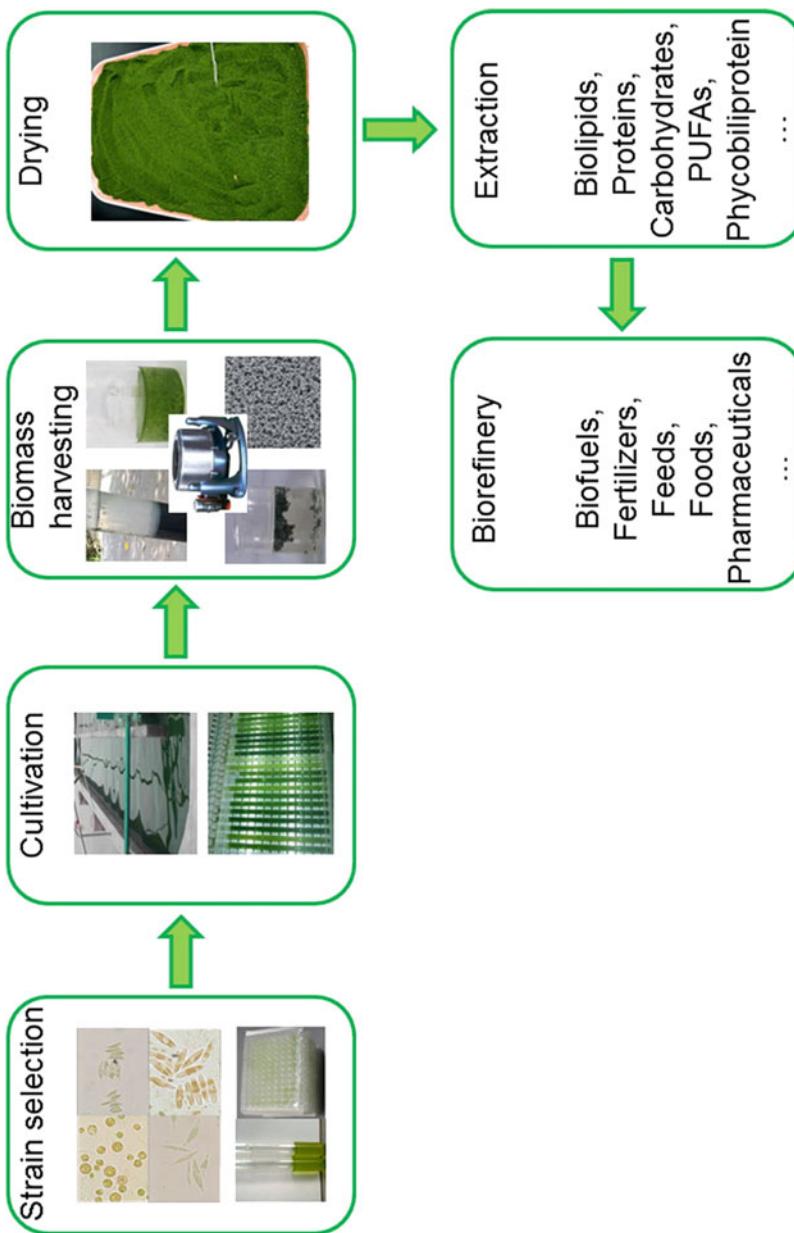


Fig. 2 Flowchart of microalgal cultivation toward biodiesel and bioproducts (with permission from [9])

3 Cultivation of Microalgae

Microalgae can be nurtured by familiar practices like open-pond raceway system and closed photobioreactor system.

3.1 Open Ponds

These systems are accepted for being simple, easy to manage, and inexpensive (low capital and control costs). They can be effortlessly clean up subsequent to cultivation [13], and less process control is required. They are effective systems for lower value products with large markets. Raceway ponds (Fig. 3a), spherical ponds tanks, shallow large length ponds, and closed ponds are presently used in industrial research.

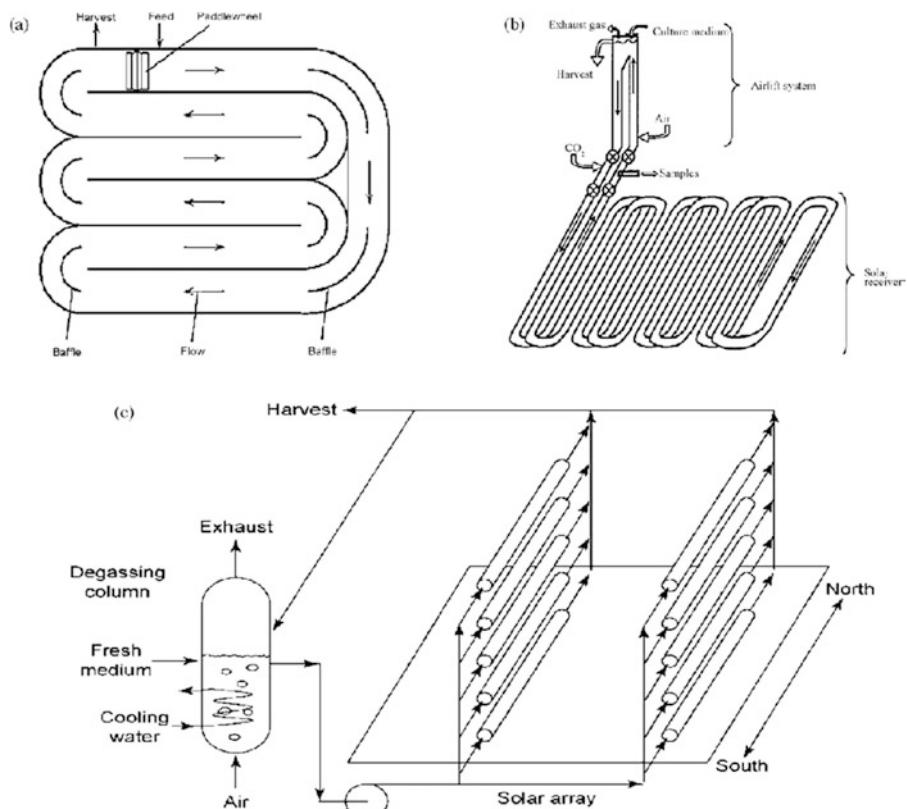


Fig. 3 Reactor configurations for microalgae cultivation (a) raceway pond, (b) external loop tubular reactor, (c) horizontal tubular reactor (with permission from [14])

In open ponds, it's almost impossible to control essential growth parameters like temperature, pH, concentration of dissolved oxygen, and light intensity. Predator contamination is another issue associated with open ponds. So far many studies have evaluated the potential of cultivating microalgae in open pond. In a study, it was reported that barely few microalgae (*Chlorella*, *Spirulina*, *Dunaliella*) can withstand the strict culture environment (high salinity, high alkalinity) [15]. *Chlorella* and *Spirulina* are cultivated for their protein content, whereas *Dunaliella* is well known for carotenoid production. In a study, *Chlorophyta* sp. and *Chlorella* sp. was effectively cultivated in raceway ponds with steady photosynthetic efficiency [16]. In another study, *Murielopsis* sp. was grown in open paddle wheel ponds for the production of lutein [17]. Open ponds are very difficult to operate because there are high chances of it getting contaminated by photosynthetic microorganisms which may appear via rain or air. Recently Sapphire Energy Inc. tried mass cultivation of algae (100 acres) in open ponds, but they couldn't able to accomplish owing to problems like invasion of species and broth evaporation [18]. Therefore there has been great challenge still exists in successful cultivation of microalgae in open ponds.

3.2 *Closed Cultivation System*

Closed system provides more options than open systems in control and optimization of microalgal growth, thus enabling them to produce high yield of biomass. Product standardization can be attained since each factor associated with production like light exposure, pH, CO₂, temperature, water supply, mixing regime, and culture density can be controlled. Photobioreactors, which are usually used for cultivation in closed systems, provides fine control of CO₂ transfer and also minimizes the evaporation loss of culture medium.

3.2.1 Photobioreactors

Photobioreactors are closed systems in which almost all factors correlated with microalgal growth can be controlled to achieve high productivity [3]. Plate type and tubular photobioreactors are normally used. The tubular reactor comprises tubes arranged in coils and straight line configurations. In tubular vertical, helical, external loop (Fig. 3b), and horizontal (Fig. 3c) arrangements are stated to be used in numerous studies [19]. However, there exist some limitations associated with the utilization of photobioreactors due to their very high specificity to microalgae strain, high start-up and operating cost, and difficulty in scale-up [14, 20]. Some authors have carried out detailed investigations to build cost-effective, simple, and effortlessly scalable PBR [21–23]. Some very good practices like intensive mixing, use of genetically improved strain, and light dilution by employing different methods were performed earlier to maximize yield and productivity [24–26].

In photobioreactor systems, high costs are involved in providing continuous intense illumination, system sterilization, to scale-up and operate the reactors [27]. To make microalgae production in photobioreactors more competitive, more innovative system configurations along with optimization of already available technology are much needed and important.

4 Modes of Cultivation

Conventional microalgal growth techniques depend on cultivation of phototrophic algae in open ponds or indoor in photobioreactors. These techniques are normally not cost-effective because of high operating costs, culture inefficiency, light insufficiency, and low biomass production. Several studies have stated that microalgal growth via heterotrophic and mixotrophic methods is cost-effective [28–30]. A lot of microalgal strains are having the ability to utilize organic carbon sources in mixotrophy (light) or heterotrophy (dark) and grow. These modes of microalgal cultivation also play a major role in boosting the production of essential fatty acids.

4.1 *Heterotrophic Cultivation*

Some microalgae species can be grown in dark conditions, utilizing an organic carbon substrate rather than CO₂ and light to supply energy to the cells growth. The advantages associated with the heterotrophic microalgae cultivation are exclusion of light requirements, easier bioreactor operation, increased growth rates, and improved lipid and protein production.

The organic carbon resources that these algae could metabolize are lactate, ethanol, acetate, pyruvate, C6 sugars, amino acids, C5 monosaccharides, disaccharides, and glycerol [31]. However the high cost of these carbon sources represents the main downside of this operation mode. Previous studies have demonstrated that glucose occupies major of the total medium cost (80%) [32]. Therefore it is imperative to find other low-cost carbon sources. Indeed, recent studies have focused on the utilization of cheap carbon sources like food waste hydrolyzate or whey permeate for microalgal cultivation [33, 34].

Heterotrophic growth mode has produced elevated lipid content owing to their high rate of algal growth and cell concentrations [35]. When compared with photoautotrophic conditions, the oils produced under heterotrophic were more saturated, making them apt for biodiesel manufacture. The class and quantity of biodiesel produced depends on the ability of strain to effectively uptake the given carbon source, grow, and accumulate oil [36]. However, new researches on cheap carbon sources are desired for the improvement of cost-efficient processes for food, feed, and biofuel production.

4.2 *Mixotrophic Cultivation*

In mixotrophic mode, microalgal growth happens majorly through photosynthesis apart from the utilization of CO₂ and organic compounds [37]. As mixotrophic mode accumulates lipid via photosynthesis and also involved in sequestering CO₂, it was considered good and much sustainable than heterotrophic mode [38]. Higher growth rates were attained for some microalgae in mixotrophic than phototrophic conditions, and they produce compounds that are synthesized during both phototrophic and heterotrophic conditions [39]. It can be considered as a potential approach for producing wide array of economically viable microalgal products in a short span of time. Mixotrophic cultivation can effectively be used for producing seed cells; subsequently it can then be used as inoculums for phototrophic microalgal biomass and lipid production.

Different culture conditions may influence the algal productivity and final composition of a microalga. Therefore a detailed investigation on all parameters relevant to microalgal composition is crucial. Light intensity in particular represents one such vital parameter. Most microalgae metabolites are obligate photoautotrophs; therefore they require light (natural or artificial) to grow [15]. However some species have the ability in consuming the carbon resources in the medium to gain energy for their metabolism, according to a heterotrophic configuration.

Although various strategies like closed PBRs, open ponds, fermentation tanks, and hybrid systems (mixotrophic and heterotrophic) are available for algae cultivation, as a piece of information, there is not a standard single approach in culturing algae at an industrial scale. To economically produce microalgal biomass, it's very important to consider set of factors like algal species type and expected end products, geographical location, and availability of resources on site for mass production. Aside from culture management, temperature and light radiation can play important role for algae-based biotechnology.

5 Site Selection and Resources Requirement

Microalgae can adapt their metabolism to changing environments, and it is feasible to culture them in diverse aquatic environments like sea and fresh water, metropolitan wastewaters, and industrial wastewaters, providing that there are sufficient measures of carbon (C) (natural or inorganic), nitrogen (N) (urea, ammonium, or nitrate), and phosphate (P), and additionally other essential components available in the growing medium [40]. When compared to sea and fresh waters, wastewaters have more nutrients appropriate for microalgae cultivation [40, 41]. The choice of cultivation site is also an important requirement for the algal growth and biomass production. The production costs may be decreased notably by positioning the plant close to the easy availability of other resources such as CO₂, nutrients, water,

sunlight, and other requirements such as electricity supply. Significant cost reduction is attainable (up to 50%) with good co-location facilities and CO₂ sources [42].

6 Factors Affecting Microalgae Growth Rate

To obtain maximum yield of biodiesel and bioproducts, the microalgae culture conditions should be optimized to provide excellent growth conditions. The following are the key factors that determine rate of microalgal growth:

- Properties of growing medium: water is one of the vital growth medium for algae production. Therefore, the water composition along with key parameters like temperature, salinity, and pH value are main factors. The temperature of the growth medium must be maintained in the optimum range, and for most algal species, the most favorable temperature range usually remains within 16–27°C.
- Properties of light: light is one important factor required for the photosynthesis process. The proposition of lipids and other microalgal products differs with the light intensity used and light exposure duration. The cells shading and equal exposure of all cells to light can be accomplished by doing proper mixing. To cut down the biofuel production costs, algal growth should depend on sunlight available throughout the day, though there are seasonal changes in intensity of natural light [3, 43].
- CO₂: CO₂ is one of the crucial necessities for algal growth. Therefore, an adequate supply of CO₂ must be ensured for its proper growth. Proper aeration should be given to boost the rate of algal growth and for proper mixing.
- Nutrients: essential nutrients like phosphorus (P), iron (Fe), nitrogen (N), and in some cases silicon (Si) are essential for the nourishment of algal cells to grow and mature. To make cells absorb maximum nutrients, ample supply of nutrient should be dispersed in the growth medium.

7 Harvesting Techniques

The microalgae are very small in cell size and are submerged into water. The harvest of fully matured microalgae happens by filtering and drying them toward the production of microalgal biomass which act as a feedstock for future applications.

The different techniques like biological, chemical, electrical, and mechanical-based systems can be utilized for harvesting the algal biomass. Some of the broadly used methods are centrifugation, filtration, sedimentation, flocculation, etc. Some method might be used as preliminary technique to enhance coagulation, aggregation, and easy removal, and chemical flocculation is one such technique normally used to boost the molecular dimension of microalgae before utilizing another technique. In centrifugation method (mechanical system), most of solid biomass can be recovered

rapidly with high reliability. In another mode, the algal cells passes via electric field and gets collected as result of adding negative charge to biomass particles [44].

The decrease in harvesting cost can be attained with proper design of dewatering system and via nutrients and water recycling. The technique employed for microalgae harvest must be able to process huge volumes of grown culture by utilizing less energy and cost. Initially very less concentration of algal biomass (0.5 g L^{-1}) is present in culture broth, but during the harvesting period, the broth thickens leading to rise in concentration of biomass (up to 200 g L^{-1}). To make harvesting more simple and effective, it is imperative to use combined technologies instead of using single technology [45, 46]. The harvesting methods employed must not disturb or intervene the culture medium recycling (e.g., if intervene it may cause contamination).

7.1 Flocculation

In flocculation process when flocculating agents (bioflocculants, chemicals, metals) are added to broth, many microalgal cells combine together to form large particles known as flocs.

The flocs added during process should be effortlessly removed from microalgal biomass and recoverable; otherwise these chemicals might end up as contaminants in biomass further hindering the post-harvest operations. Another interesting approach is reducing the pH may leads in microalgae flocculation. The flocculation happened in microalgal cells when the pH of the medium was tuned near 4; it leads to protonation and neutralization of carboxylic acids on cell surface of microalgae to form flocculates [47].

7.2 Gravity-Based Technologies

7.2.1 Sedimentation

Gravity sedimentation involves the usage of cheap infrastructure and low energy for sedimentation process as it is done in simple settling tanks.

Gravity sedimentation done in simple settling tanks is a very attractive option because it requires very little energy and relatively low-cost infrastructure. As it is a very slow process, this may sometimes result in degradation of biomass quality during harvesting. Due to production of dilute slurry, the gravity sedimentation could chiefly be used as pre-concentration mechanism before employing other methods like filtration, flocculation, and centrifugation [48, 49]. In Israel, Algatech has initially used gravity sedimentation for harvesting *Haematococcus* cysts rich in astaxanthin (oral communication, Algatech). As the sluggish process of

sedimentation had affected quality of biomass produced, they switched on shortly to other harvesting methods like centrifugation.

Due to sluggish process that resulted in deterioration of biomass quality, they later switched to centrifugation as a harvesting method. For the quick harvesting technique and to evade biomass deterioration, it is important to have high settling rate.

7.2.2 Centrifugation

Centrifugation is extensively used for microalgae that produce high-value products, as it involves more energy and cost. There are various types of industrial centrifuges exist. Some of the key benefits of harvesting via centrifugal methods are it is rapid, it involves no added harmful chemicals, and also it won't degrade the biomass quality. On the other hand, use of this technique has some drawbacks like elevated investment cost and high demand of energy. Some of the following approaches to a certain extent can able to reduce the energy demand of the centrifugation method.

In a study, Evodos (the Netherlands) have developed a spiral plate centrifuge which increased the surface area by means of decreasing the distance travelled by settling microalga. Even though the harvesting efficiency is low, this technique has significantly consumed very little energy for harvesting per unit of biomass [50]. Another approach relies in pre-concentration of biomass, which significantly reduces volume of culture and thus resulting in reducing energy demand for centrifugation. This can be achieved through flocculation, which increases the particle size, thereby enhancing easy separation.

7.3 *Filtration-Based Separation Technologies*

Filtration, a physical process performed by using semipermeable membrane like filter cloth, screens for the separation of solids. The pressure drop across the membrane formed due to vacuum, gravity, or pressure acts as the driving force of filtration method. High recovery efficiency, reuse of filter permeate, separation with no added chemicals, and capability to separate shear-sensitive species all these factors make filtration an attractive option for harvesting microalgal biomass. However few drawbacks like clogging and fouling of membranes and high investment costs of pumps and membranes make filtration a costly process [51–53]. For effective microalgal biomass filtration, clogging and fouling must be avoided, and membrane cost should also be reduced. The harvesting process can be made cost-effective by performing combined harvesting techniques. A novel solution is to combine flocculation with a lamella settler and then use a filter press to dewater the sludge. Another method is filtration of the membrane for pre-concentration of biomass shared with centrifugation to produce an algal paste. Because of their heterogeneous existence, every form of microalgae needs different harvesting

approaches. The harvesting approach must be performed with at most care that it should not damage (e.g., due to shear forces) or contaminate (e.g., due to application of chemical flocculent) the biomass. The acceptable level of contamination depends on the final use of the biomass, and therefore the selection of method of harvesting may depend on the application of biomass. As microalgae cells (5–20 µm) are small in size, the application of both filtration and gravity-based methods are tricky, and the other key limitation is high harvesting cost of microalgae biomass [21, 46, 49, 54].

The efficiency of extraction and harvesting methods is based on physical characteristics of the microalgae strain (e.g., cell wall property and cell size) and the end product's application.

By properly designing the dewatering or harvesting method and via recycling of nutrients and water, the processing costs can be reduced. The algal biomass harvesting can be made easy by selective cultivation of colonial species [55]. The water requirement can be decreased to a greatest extent (up to 90%) by proper recycling of water after the harvest of biomass or use of sea or wastewater. The choice of harvesting method varies from species to species, and also it is based on the cost criteria of energy extraction process.

8 Post-Harvest Processing: Conversion of Microalgal Biomass to Biofuels and Bioproducts

Once harvest is complete, the algal biomass obtained should be dried for further processing and manufacture of bioproducts and biofuels. This can be done by performing different techniques of drying such as sun drying, freeze drying, lyophilization, heat-/oven-based drying, and spray drying. Each approach however has its own advantages and disadvantages. For instance, heat or oven drying consumes more energy, whereas sun and drum drying are not effective and economical as quoted by [56]. Other procedures, such as freezing and lyophilization, are seen as efficient but expensive methods. The drying techniques are based on a number of factors like species type, time, maintenance of culture, reuse of media, and suitability for industrial scale [51, 57]. The present techniques used for drying and harvesting are not efficient, and more innovations are the need of the hour.

After drying, cell disruption of microalgae to release cellular components and oil bodies can be performed by various methods, which include ultrasonic-assisted extraction, high press machine, chemical method, supercritical fluid extraction, enzymatic method, microwave, autoclaving, bead beating, osmotic pressure method, Soxhlet method, and homogenizer. Sometimes the extraction of lipids could not be effective due to poor cell disruption and improper lipid extraction process. This can be overcome by careful cell disruption selection and lipid extraction techniques. Sometimes renowned lipid extraction techniques such as Folch et al. [58] and Bligh and Dyer [59] using solvents such as chloroform, hexane, and dichloromethane

might not extract incomplete, essentially free fatty acids from lipids. This method sometimes may also remove large amounts of non-saponifiable and non-nutritious material such as pigments. To address this problem, a range of modern and advanced methods were implemented by improving existing methods for extracting microalgae oil bodies. Ramluckana et al. [60], for example, used single, binary, and more than two organic solvents at a time to extract oil bodies, while Boutekedjiret et al. [61] proposed the use of green bio-solvents (terpenes) extracted from aromatic plants. The oil bodies should undergo transesterification for biodiesel production, and the process comprises of methanolysis or ethanolysis in the fatty acid methyl esters (FAME) forms. The process of transesterification requires catalysts, which may be acidic or alkaline in nature. Such catalysts have their own pros and cons. The transesterification of complex lipids and free fatty can be performed by using acid catalysts, whereas basic catalysts could not be able to esterify free fatty acids.

Acid catalysts can transesterify both complex lipids and free fatty acids, while basic catalyst cannot esterify free fatty acids.

The difficulty associated with the usage of acid catalyst is it needs extended reaction time than a basic catalyst with the additional heating requirement [62]. To prevail over these hurdles, some complementary approaches are reported. Heaton et al. [63], for example, utilized both base and acid catalyst along with alcohol. Carrapiso and Garcia [62] later used a blend of a base and acid catalyst in methanol. Initially, algal biomass is wrecked down into its key contents: lipid, carbohydrate, protein, and remaining mass through extraction/fractionation technology to make them apt for conversion to bioproducts and biofuels.

The extraction method varies based on the type of product extracted from the biomass and also on the particular composition of the biomass feedstock. Chemical conversion techniques like pyrolysis, gasification, anaerobic digestion, liquefaction, fermentation, and transesterification are normally used to transform algal biomass into fuels such as ethanol, biodiesel, methane, hydrogen, acetone, charcoal, and butanol. The transformation of harvested biomass to biofuels and other bioproducts is one of the main technical challenges, and it is also not cost-effective.

9 Utilization of Wastewater for Microalgae Cultivation

Algae can effectively be grown even on harsh environment (not appropriate for other purposes) and with wastewater or water not suitable for food production [64, 65]. The algae are having the ability to grow on non-cultivable land, by using wastewater; algae could be able to produce large amounts of biofuels (per acre) when compared to oil-producing plant.

Microalgae have shown great promise in removal of phosphorus and nitrogen (as these nutrients are recycled), and it can effectively be transformed into algal biomass at cheap cost through solar energy. Biofuels produced from algae have 50% less greenhouse emissions than petroleum fuel. By overcoming the economic

hurdles through innovative research, it is feasible to produce high energy oil feedstocks which act as transportation fuels from algal biomass. We need to build biomass production systems which can produce the highest yields with the lowest inputs in future to gain more energy return on investment and to improve carbon capture efficiency [66].

The synergistic model based on production of algae biofuel combined with urban and agricultural wastewater bioremediation addresses many economic hurdles in earlier algal systems and encourages value-added products [67, 68]. The strains of dominant algae usually found in wastewater ponds include *Chlorella*, *Actinastrum*, *Scenedesmus*, *Selenastrum* and *Euglena*. They are capable of extracting organic matter and nutrients from wastewater, grow quickly, and generate biomass.

Municipal sewage water, agricultural wastewater, and livestock waste slurries contain elevated amounts of P and N, which can potentially be utilized by microalgae for biodiesel production. In a study, *Botryococcus braunii* have effectively removed nitrate (up to 80%) and displayed higher growth rates in piggery wastewater consisting of 800 mg L⁻¹ nitrates [69]. Microalgae are having the ability to grow in effluents of industries such as tanneries, textile industries, agro-industries, distilleries, and pulp and paper industries which may contain high concentrations of organic material (carbohydrate, starch, cellulose, hemicelluloses), harmful microorganisms, toxic heavy metals, etc. [70]. Normally effluents from industries may contain high COD and BOD, and there are variations in chemical compositions from one industry to another. Waters produced from meat processing industry consists of antibiotics, hormones, body fluids, and other organic waste while simple sugars are present in confectionary wastewaters. Waters from pulp and paper industries are polluted with high concentrations of suspended solids, which are rich in inorganic acid and alkali salts.

10 Bioenergy Options from Microalgal Biomass

Algal biomass presents four modes of energy production such as (a) biomass anaerobic digestion to produce methane (biogas); (b) thermo-chemical liquefaction of biomass to produce bio-oil; (c) biomass lipid extraction and transesterification to produce biodiesel; and (d) fermentation of carbohydrate and bioethanol production via distillation [71–73]. The complete transformation steps of biomass to various energy resources are represented in Fig. 4.

The lipid biomass extraction and transesterification is one of the most widely followed bioenergy production routes. This mode of biofuel production demands relatively higher lipid content in the alga biomass. Many times transesterification is a costlier process due to parameters like catalyst ratio, solvent requirement, and high process temperatures leading to negative energy balance, that is, higher input energy over output energy, nearly 2 [71].

By adopting a biorefinery approach, the sustainability and economic viability of the production of biodiesel from microalgal biomass can be greatly improved. This

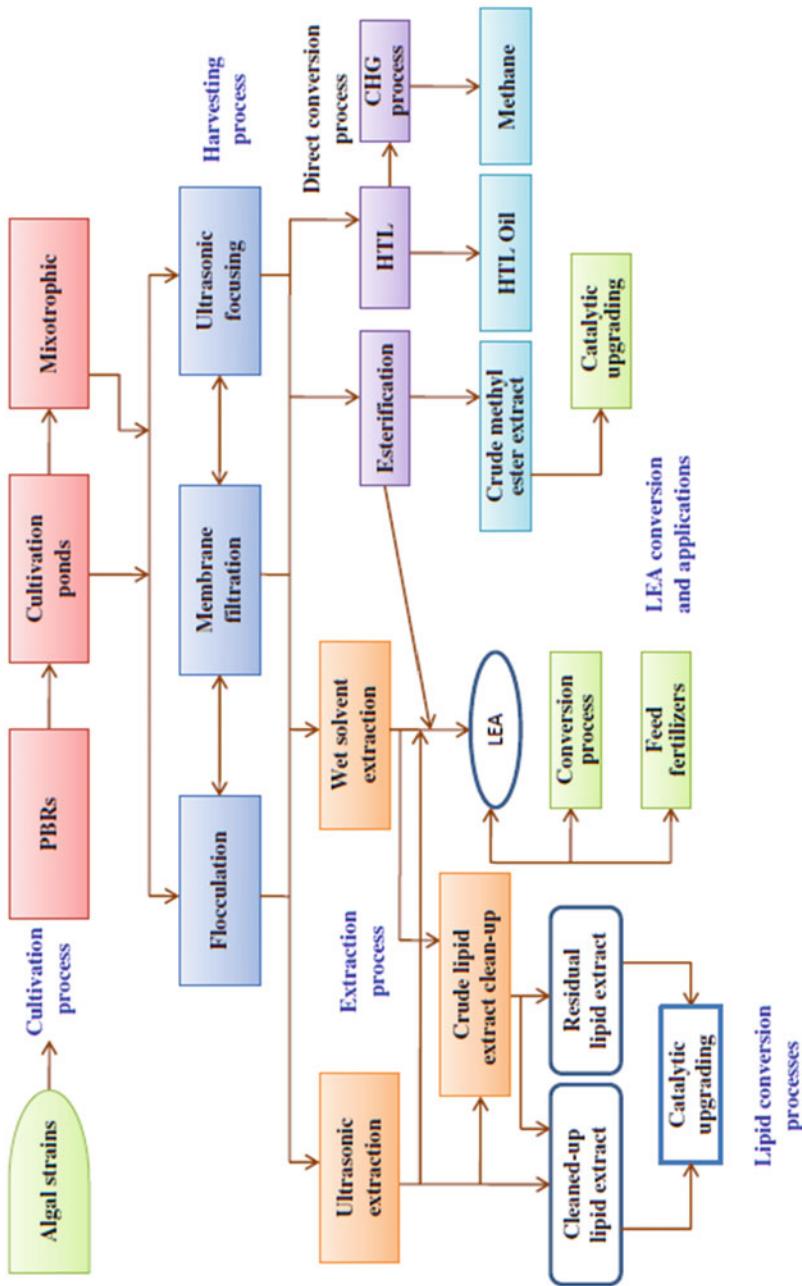


Fig. 4 Overall process matrix of algal biofuel conversion (with permission from [71])

approach aims in efficient utilization of residues or co-products for further applications.

34 kg of co-products (glycerol, lipids, defatted biomass) are produced for every 24 kg of algal biodiesel generated [74]. Glycerol and lipids (unsaponifiable) can act as precursors in the manufacturing of industrial chemicals like 1,3-propanediol which are used normally in paint and polymer factories [75]. The DAB could be utilized for production of biogas via anaerobic digestion [76] or as an animal feed (carbon-neutral) [9].

Dry algal biomass could potentially be cracked at very high temperatures of nearly 500°C under anaerobic environment for a period of 30–120 min through process called pyrolysis [77]. It contains three major steps such as dehydration (intracellular components vaporized at 80–190°C), volatilization and condensation (volatile components are produced in the temperature ranges of 190–500°C and condensed to form stable liquid or gases), and decomposition at temperatures equal to or above 500°C to generate solid biochar [77, 78]. The bio-oil yield of 20–45% having an approximate energy value of 35 kJ g⁻¹ was attained via pyrolysis.

Pyrolysis results in yield 20–45% of bio-oil with an average energy content of 35 kJ g⁻¹. However, the major issue involved with the usage of pyrolysis biocrude is due to their acidic nature (2.5 and 3.7); it causes storage concerns [79].

Hydrothermal liquefaction (HTL) is another alternative technique for transformation of wet algae biomass to energy dense heavy oil. One of the key benefits of this technique is that it can potentially transform high-moisture wet biomass (moisture content above 75%) by heating at subcritical temperatures (200–350°C) and by employing high pressure (5–20 MPa) to oil. HTL can be able to produce biocrude oil comprising of energy-dense hydrocarbons of chain length C17-C18 and PAHs. The resultant biocrude oil has heating value of about 30–40 kJ g⁻¹ with an approximate yield of 30–50% of initial wet biomass. It also generates various by-products like mixture of gases like CO₂, H₂, CH₄, C₂H₄, C₂H₆, and N₂ which may be recycled for production of energy [77]. The residual solids generated through HTL have C content >20%, which shows promise to be used for energy conversion either by anaerobic digestion or by biomass gasification. The yield of biocrude oil is significantly affected by the biomass composition in both HTL and pyrolysis process, where higher lipid content results in higher yield of biocrude.

In addition to HTL and pyrolysis, direct biomass gasification offers a third route for generating bioenergy based on thermal decomposition strategy from dry algal biomass. In gasification technique, the biomass is partially oxidized at high temperatures varying between 800 and 1,000°C. Gasification produces a mixture of flammable gases like C₂H₄, CH₄, CO₂, and H₂ [77]. Gasification is a highly energy-intensive process with low product calorific value (only 4–6 MJ kg⁻¹). The mixture of gases can be directly used for burning, in engines, or as syngas, and as feedstock for chemical production like methanol [80]. However, this method is very much energy-consuming with low economic profitability.

11 Conclusions

Biofuels can supplement the existing conventional energy sources to a great extent. Microalgae are capable of producing bio-sustainable goods that do not seem to threaten the human right to food, water, and safety and do not damage the environment as they can be produced in non-agricultural land and do not need fresh water for their growth. Moreover as the system is carbon-neutral, it is the best possible choice and sustainable substitute to nonrenewable energy sources. Nevertheless, microalgae feedstocks are not yet become cost-effective in bioproducts and biofuel production, given their exceptional potential and the well-known cultivation options. Even after many years of hard work and huge sum of dollars (billions) in investments, its unacceptably high cost remains the ultimate drawback in the industrialization of algal biofuel.

New species discovery and usage of genetically modified microalgal strains via synthetic biology approaches which can produce higher yields and could potentially reduce the cost of production on a commercial scale. To capitalize on the research benefits, both socially and economically, synergistic combination of production of microalgae biofuel and biotechnological applications, such as bioremediation of environmental pollutants and manufacture of high economic value bio-byproducts, could be an effective way of achieving economically feasible biofuel production. In addition, more research and development is required to make harvesting techniques more reliable and cost-effective to reduce future production costs. Furthermore, the techniques for biomass production (i.e., PBR and open-pond systems) often need much focus to produce algae at cheaper costs and to make it environmentally sustainable. Apart from biofuel production, several other valuable co-products like food supplements with nutritional values, animal feed, and various pharmaceutical ingredients for producing medicines, cosmetics, toiletries, and other goods including bioplastics and biofertilizer may be produced from algal biomass feedstock. The production cost can be reduced by adapting a strategy of co-production of both biofuel and valuable by-products from microalgae. It can therefore be inferred that algal biofuels can be an ideal substitute for fossil fuel in the future if the cost of production of biofuels is minimized.

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Applications and Efficacy of Exceptional Bioactive Compounds from Microalgae



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Abstract Microalgae are microscopic photosynthetic organisms that are found in both freshwater and marine environment. These are successfully used as food and feed supplements and are efficient producers of fine chemicals and biofuels. Microalgae are also an excellent source of bioactive compounds like vitamins, proteins, polyphenols, polyunsaturated fatty acids, or polysterols with antiviral, antibacterial, antifungal, and anticancer activities. Currently, the demand of these natural bioactive compounds is increasing as they impart health benefits when included and consumed in a functional food or in nutraceuticals. Thus, the utility of microalgae for the production of natural bioactive compounds should be explored

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at the commercial and industrial sector to harness the growing demands. The chapter gives the overview of different bioactive compounds produced by microalgae which have a wide range of application in different kinds of industries.

Keywords Anticancerous, Anti-inflammatory, Antimicrobial, Antioxidants, Bioactive compounds, Microalgae

1 Introduction

All around the world, research has been initiated to develop greener technologies for the production of substances that are not only beneficial to the environment but also to the human health. Thus, a substantial amount of study has been focused on utilizing natural resources for producing bioactive compounds as compared to the traditional synthetic approach [1]. Utilizing greener technologies or natural sources for production of value added compounds makes the entire process cost-effective, sustainable, and recyclable and eco-friendly [2]. Recently, microalgae have attracted a lot of attention as a potential candidate for the continuous and sustainable production of several different bioactive compounds [3]. Microalgae are a group of prokaryotic and eukaryotic photosynthetic organism found both in freshwater and marine environment. For more than hundred years, these microalgae have been used as food, fodder, fertilizer, and a source of variety of chemicals [4]. Additionally, they can be a very intriguing source of natural compounds with very high biological activity that could be successfully used in different industrial sectors. As a matter of fact, when these microalgae are exposed to adverse environmental conditions like changes in temperature, salinity, nutrient, etc., they secrete a wide variety of functional, biologically active secondary metabolites, and other substances like proteins, pigments, polyphenol, antioxidants, polyunsaturated fatty acids, vitamins, polysaccharides, and natural plant growth hormones such as cytokinin, gibberellins, and auxin to survive which most of the organisms are not capable of [5]. Table 1 summarizes some of the important bioactive compounds produced from different types of algae. These natural bioactive compounds produced from microalgae are fascinating researchers as they have immense potentiality for commercialization in the coming future because of their prospective therapeutic activities such as antiviral, antifungal, antibacterial, anti-malarial, anti-inflammatory effects, and other applications in food, pharmaceutical, and cosmetic industries [6]. Table 2 lists the biological activity of some of the compounds secreted by microalgae. Apart from these benefits, microalgae also have the advantage of simple and effortless cultivation, rapid growth, and feasibility of regulating the production of bioactive compounds by exploiting the culture conditions. Although microalgae have a lot of advantages, still a large number of bioactive compounds from them remain unexplored. Among the thousands of microalgal species that are present universally, very few have been studied and utilized for the production of bioactive compounds. According to a

Table 1 Different bioactive compounds extracted in algae

[A] Polysaccharide	[B] Pigments
Cellulose	Phycocyanin
Laminarin	Phycoerythrin
Fucoidan	Chlorophyll a, b, c
Agar	β-Carotene
Alginate	α-Carotene
Carrageenan	Fucoxanthin
Porphyran	Astaxanthin
Xylan	Lutein
Amylose	
Amylopectin	
[C] Growth-promoting compounds	[D] Other compounds
Fucosterol	Vitamins
Ergosterol	Carotenoids
Cholesterol	Polyphenols
Ethylene	Polyunsaturated fatty acids
Cytokine	Minerals
Auxin	Diterpenes
Gibberellin	Proteins
Abscisic acid	
Polyamines	

Table 2 Biological activity of different bioactive compounds extracted from algae

Biological activity/property	Bioactive compounds
Antibacterial	Polyphenols Polyunsaturated fatty acids Proteins Pigments
Antitumors	Polysaccharide Polyphenols Carotenoids
Antifungal	Polyunsaturated fatty acids Diterpenes Proteins and pigments
Anti-inflammatory	Polysaccharides Proteins Sterols Carotenoids
Antioxidative	Polyunsaturated fatty acids Polysaccharide Proteins Polyphenols Carotenoid Glutathione Tocopherol

report, microalgae produce a variety of compounds which are approximately ten times higher than any well-studied organism. Thus, more microalgae should be explored for the extraction of natural bioactive compounds as these can prove to

be of significant importance in human welfare. The first part of the present chapter primarily focuses on the different bioactive compounds isolated from algal biomass to progress in the field of biomedical and biotechnology. The second part of the chapter outlines the properties of the bioactive compounds along with their potential application.

2 Microalgae-Derived Bioactive Compounds

At present, the interest in microalgae for industrial use is growing swiftly owing to the presence of diverse and novel bioactive compounds, viz., antioxidants, fatty acids, polysaccharides, proteins, vitamins, etc. Some of the important bioactive compounds produced from microalgae are outlined below.

2.1 Polysaccharides

Polysaccharides are considered the most important product obtained from algae, as per their economic value [7] with numerous reports on their structure and function [7–9]. Algal polysaccharides can be extracted by several green techniques such as microwave-assisted extraction (MAE) and enzyme-assisted extraction (EAE) [10–12]. In recent years, these algal polysaccharides have been extensively studied due to their biological activities like antiadhesive, antitumor, antitoxin, antioxidant, anticoagulant, anti-infection, and immunomodulatory effects. Certain polysaccharides extracted from microalgae exhibits exceptional biomedical properties and thus can have promising application in food, medicine, nutraceuticals, and cosmeceuticals. For example, carrageenan, agar, and alginate are some of the commonly used algal polysaccharides in food and pharmaceutical industries [13]. Some other polysaccharides like ulvans from Chlorophyta, carrageenans, porphyran from Rhodophyta and fucans, and laminarin from Phaeophyta activate and enhance the defense response against pathogens in plants [14]. Moreover, these algal polysaccharides can directly or indirectly induce several signaling pathways, leading to the activation of the immune system. For example, enhanced phagocytosis was observed by a polysaccharide extracted from *Porphyra haitanensis* in RAW264.7 [15]. Algal polysaccharides also have remarkable antitumor activity both in vitro and in vivo which is ascribed to the activation of cell-mediated immune responses [16]. For example, polysaccharides isolated from *Sargassum fusiforme* were found to notably arrest the growth of human HepG2 cell-transplanted tumor in nude mice [17]. Polysaccharide galactan sulfate isolated from *Agardhiella tenera* was found effective against HIV-1 and HIV -2 [18]. Sulfated polysaccharides and xylogalacto fucan extracted from *Sphaerelaria indica* showed antiviral activity against herpes simplex viruses [19]. Polysaccharides from algae possess antioxidative potential and, hence, can be utilized in protecting the body from oxidative damage like a polysaccharide from

Saccharina latissima, which showed scavenging activity towards the radical 2,2'-azinobis-(3-ethylbenzothiazolin-6-sulphonate) [20].

2.2 Carotenoids

Carotenoids are a large family of yellow to orange colored pigments containing eight isoprene units [21]. These carotenoids are composed of C-40 hydrocarbon chains, providing a backbone that imparts unique molecular structure and chemical properties like light absorption which is a requisite for photosynthesis process [22]. The demand for new, unique natural compounds and colorants in food, cosmetic, and pharmaceutical industry has evoked interest in carotenoids derived from microalgae as these are a potential source of variety of high value carotenoids. Astaxanthin, β -carotene, lutein, violaxanthin, and fucoxanthin are some of the algal carotenoids that are successfully utilized for biomedical applications. Microalgae are preferred over other biological materials for the production of carotenoids because of their abundant biomass, high yield, cost-effective, simple, and eco-friendly process of production [23, 24]. Algal carotenoids showcase antioxidant, antitumor, antifungal, antiviral, antibacterial, and anti-inflammatory properties [25, 26] and are usually extracted by green technologies like microwave-assisted extraction, supercritical fluid extraction, pressurized liquid extraction, etc. [23, 24]. Astaxanthin from *Haematococcus pluvialis* and *Chlorella vulgaris*, violaxanthin from *Chlorella pyrenoidosa*, lutein from *Chlorella pyrenoidosa*, *Haematococcus pluvialis*, and *Scenedesmus obliquus* have antioxidant properties. Astaxanthin from *Haematococcus pluvialis* and violaxanthin from *Chlorella ellipoidea* are known to have anti-inflammatory property. Fucoxanthin from *Odontella aurita*, *Chaetoseros* sp., and *Isochrysis galbana* displayed anticancer activities [27].

2.3 Antioxidants

Presently, large numbers of antioxidants are utilized by different food and pharmaceutical industries to reduce the oxidative adulteration of food products and medicines. However, the utilization of synthetic antioxidants like butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and t-butyl hydroquinone for the production of food and medicines has been cramped owing to its toxic effects [28]. Consequently, there is a requirement to explore novel, natural, and cheap antioxidants from natural sources. Microalgal extracts are a potential source of natural antioxidants like vitamin C, vitamin E, astaxanthin, tocopherols, catechins, tannins, flavonoids, etc. that can be successfully used as supplement in human nutrition, in meat to prevent oxidation process, as animal feed and in aquaculture [29–32]. Some of the microalgal species that are utilized for the production of

antioxidants are *Chlamydomonas nivalis* [33], *Chlorella* spp. [34, 35], *Botryococcus braunii* [36], and *Scenedesmus* spp. [34].

2.4 Lipids

Algae are a valuable source of a variety of lipids. The lipid fraction of microalgae primarily consists of polyunsaturated fatty acids (PUFA) like omega 3 fatty acids, omega 6 fatty acids, arachidonic acids, eicosapentaenoic acid, etc. Due to their antibacterial, antifungal, and antioxidative properties, PUFAs are considered of immense importance for proper functioning of the human body [8, 37]. Essential polyunsaturated fatty acids especially omega-3 and omega-6 are well-known to have several positive effects on human health such as in the prevention of hypertension, type 2 diabetes, coronary heart disease, pulmonary disease, etc. [38]. Microalgal polyunsaturated fatty acids are extracted through novel extraction techniques such as supercritical fluid extraction, microwave-assisted extraction, pressurized liquid extraction, ultrasound assisted extraction, and enzyme assisted extraction [23, 24]. Out of these, carbon dioxide lipid extraction method offers high rate, is non-toxic, produces solvent-free lipids, and has high selectivity towards acylglycerols, and therefore, it is a promising technique for large-scale extraction of lipid from microalgae. It is disadvantageous in the fact that it requires high cost and energy for supercritical fluid compression [23, 24]. Sterols are also a type of lipids extracted from micro- and macroalgae, having applications in pharmaceuticals production by steroid therapeutics, nutrition as anticholesterol additives in food, nutraceuticals, and cosmetics [39]. Another promising use of lipids from algae is in biodiesel production since it promises reduction in dependence on petro fuels, thereby lowering greenhouse gas emission. Extraction of lipid from algae has a great potential for an impressive future market accompanied with simultaneous production of value-added co-products [40]. The current obstruction in large-scale biodiesel production from algae is cultivation and efficient lipid extraction methods. However, methods such as UAE, MAE, and SFE are being utilized for the extraction of lipids, but none of these methods have been exploited at a large scale [41, 42].

2.5 Proteins

Microalgae are contemplated as a potential source of proteins and essential amino acids. Comprehensive and nutritional analysis has revealed that the proteins derived from algae are of high standards and very much similar to the regular vegetable proteins [43]. Due to their high digestibility, nutritional value, and protein content, microalgae like *Spirulina*, *Arthrospira*, *Chlorella*, and many more are considered currently as green food. Recently, algal proteins are receiving a lot of attention on grounds of bioactive and functional properties like anti-inflammatory, anticancerous,

antioxidant, neuroprotective, and immunomodulatory activities [44, 45]. Microalgae are familiarly consumed as a dietary supplement in the form of pills, tablets, or powder. Howbeit, they have also been included into a variety of functional foods, such as bread, noodles, drinks, biscuits, beer, and sweets. Several companies sell algal products, such as AlgaVia® which produces protein- and lipid-rich algal flour from *Chlorella protothecoides* [46]. Large amount of microalgal proteins being produced by recombinant DNA technology are used as drugs and referred as biopharmaceuticals and biologics.

2.6 Diterpenes

Diterpenes are a large class of structurally distinct natural compounds which are extensively present in marine brown algae belonging to the family Dictyotaceae. These algal diterpenes are propitious drug candidate attributable to their incredible pharmacological activity. Diterpenes like dictyodial, dicytol H, dicytol C from *Dictyota ciliolata* exhibit potent cytotoxic and antiviral activities [47]. Diterpenes extracted from *D. menstrualis* were found to be effective against HIV-1 [48].

3 Applications

3.1 As Antimicrobial Agents

In spite of the fact that microalgae can produce significant amount of bioactive compounds, their use as antimicrobials is still in its early stages. Until now, very small number of compounds have been extracted and utilized commercially. Some of the compounds extracted from microalgae have potential applications in market as antibacterial, antifungal, and antiviral drugs. Table 3 lists some of the antimicrobial compounds extracted from different types of algae.

3.2 As Anticancerous Agents

The conventional techniques available for the treatment of cancer kill randomly the normal cells and multiply cancer cells consequently damaging the DNA. However, the microalgal compounds shield the normal cells from damage and cause cytotoxic effects on the cancerous cells. Some of the anticancerous compounds extracted from microalgae are represented in Table 4.

Table 3 Antimicrobial properties of compounds extracted from microalgae

S. No	Property	Compound/ fraction	Chemical nature	Source	Reference
1.	Antiviral	Naviculan	Polysaccharide	<i>Navicula directa</i>	Lee et al. [49]
		Marenmine	Pigment	<i>Haslea ostrearia</i>	Gastineau et al. [50]
		p-KG03	Exopolysaccharide	<i>Gyrodinium impudicum</i>	Yim et al. [51]
2.	Antibacterial	Ethanol extract	–	<i>Chlorella marina</i>	Elkomy et al. [52]
		Water extract	–	<i>Phormidium formosum</i>	Elkomy et al. [52]
		Acetone extract	–	<i>Navicula f. delicatula</i>	Elkomy et al. [52]
		Chlorellin	–	<i>Chlorella vulgaris</i>	Pratt et al. [53]
		α-Linolenic acid	–	<i>Chlorococcum HS-101</i>	Ohta et al. [54]
		Methanolic extracts	–	<i>Pseudokirchneriella subcapitata</i>	Pane et al. [55]
		Organic extract	–	<i>Chlorella pyrenoidosa</i>	Ali and Doumandji [56]
3.	Antibiofilm	Hexane extract	Fatty acids	<i>Coccomyxa onubensis</i>	Navarro et al. [57]
		Acetone extract	–	<i>L. danicus (FE322)</i> <i>L. aporus (FE332)</i>	Lauritano et al. [58]
4.	Antifungal	–	Polysaccharides	<i>Chaetoceros lauderi</i>	Viso et al. [59]
		Microalgal supernatant	–	<i>Chlorella vulgaris</i>	Ghasemi et al. [60]
		Organic solvent extracts and beta carotene, chlorophyll a and chlorophyll b	Pigments	<i>Chlorococcum humicola</i>	Bhagavathy et al. [61]
		Microalgal supernatant	–	<i>Heterochlorella luteoviridis</i>	Mudimu et al. [62]
			Short-chain fatty acids	<i>Haematococcus pluvialis</i>	Santoyo et al. [63]
		Organic solvent extracts	–	<i>Scenedesmus quadricauda</i>	Abedin and Taha [64]
		–	Phycobiliproteins	<i>Porphyridium aerugineum</i>	Najdenski et al. [65]

Table 4 Anticancerous properties of compound extracted from microalgae

Compound	Chemistry	Source	Reference
Nonyl 8-acetoxy-6-methyloctanoate (NAMO)	Fatty alcohol ester	<i>P. tricornutum</i>	Samarakoon et al. [66]
Decadienal, octadienal, and heptadienal	Unsaturated aldehydes	<i>Skeletonema marinoi</i>	Sansone et al. [67]
Fucoxanthin	Carotenoid	<i>Phaeodactylum tricornutum</i>	Liu et al. [68]
Astaxanthin	Carotenoid	<i>Chlorococcum</i> sp.	Kim et al. [69]
β-Carotene	Carotenoid	<i>Haematococcus</i> sp.	Davidi et al. [70]
Monogalactosyldiacylglycerol (MGDG)	Glycolipid	<i>Gymnodinium mikimotoi</i>	Maeda et al. [71]
Digalactosyldiacylglycerol (DGDG)	Glycolipid	<i>Stephanodiscus</i> sp.	Hossain et al. [72]
Sulfo-quinovosyl-acyl-glycerol (SQAG)	Glycolipid	<i>Stephanodiscus</i> sp.	Hossain et al. [72]
Sulfated polysaccharide β-(1,3)-glucan	Polysaccharide	<i>Chlorella vulgaris</i>	Guzman et al. [73], Nomoto et al. [74]
Sulfated polysaccharide	Polysaccharide	<i>Isochrysis galbana</i> <i>Porphyridium</i> sp. <i>Gyrodinium Impudicum</i>	Sadovskaya et al. [75], Matsui et al. [76], Bae et al. [77]
Extracellular polysaccharide <i>s-Spirulina</i>	Polysaccharide	<i>Arthrosira platensis</i>	Challouf et al. [78]
Phycobiliproteins	Proteins	<i>Porphyridium</i> sp.	Romay et al. [79], Zheng et al. [80]
Acetone extract		<i>S. marinoi</i> FE60/2	Lauritano et al. [58]
Fucoidan	Fucose-rich sulfated hetero polysaccharide	<i>S. polycystum</i>	Palanisamy et al. [81]

3.3 As Anti-inflammatory Agents

Inflammation occurs in the living body after some kind of physical abrasion or by intrusion of tumor cells, viruses, and bacteria. Thus, it is a complex process that demands stimulation of the immune system [82]. The application of synthetic agents to impede inflammation has revealed some very promising results in the treatment of type II diabetes [83]; howbeit, the chronic application of these agents has also led to detrimental gastrointestinal effects [84], lung disease [85], and atherosclerosis [86]. The employment of anti-inflammatory agents synthesized by microalgae completely reduces the chronic infection caused by inflammation. Table 5

Table 5 Anti-inflammatory properties of compounds extracted from microalgae

Compound/extract	Chemistry	Source	Reference
Fucoxanthin	Carotenoids	Diatoms	Peng et al. [87]
Digalactosyldiacylglycerols		<i>Nannochloropsis granulata</i>	Blunt et al. [88]
β-Carotene	Carotenoid	<i>Dunaliella salina</i>	Ramos et al. [89]
Violaxanthin	Carotenoid	<i>Dunaliella tertiolecta</i>	Pasquet et al. [90]
Zeaxanthin	Carotenoid	<i>Chlorella saccharophila</i>	Singh et al. [91]
Eicosapentaenoic acid (EPA)	Fatty acid	<i>Tetraselmis</i> sp.	Mobraten et al. [92]
Sulfated extracellular Polysaccharide	Polysaccharide	<i>Phaeodactylum tricornutum</i>	Guzman et al. [73]
Phycobiliproteins	Proteins	<i>Spirulina platensis</i> and <i>Porphyridium</i> sp.	Romay et al. [79]
Acetone extract	–	<i>C. closterium</i> FE2/I, <i>O. mobilis</i> FE326/I, and <i>P. pseudodelicatissima</i> FE1098_I	Lauritano et al. [58]

summarizes some of the common anti-inflammatory compounds biosynthesized by microalgae.

3.4 As Antioxidant Agents

Presently, the global interest is growing towards discovering novel, safe, potent, and robust antioxidants from microalgae to reduce the oxidative vandalism on the living cells and the commercialized products like pharmaceuticals, food, and nutraceuticals. Antioxidants extracted from microalgae are not that non-toxic as compared the synthetic antioxidants whose carcinogenic effect has already been reported [93]. Table 6 lists some of the common antioxidants synthesized by microalgae.

4 Future Prospects

Currently, the use of microalgae for the extraction of bioactive compounds is encouraged due to healthy food and health care and to maintain a clean environment, but still there are concerns that can be looked into in the coming future for efficient production and application of bioactive compounds. Firstly, large-scale industries

Table 6 Antioxidant properties of compounds extracted from microalgae

Compound/ fractional extract	Chemistry	Source	Reference
Fucoidan	Fucose-rich sulfated hetero polysaccharide	<i>S. polycystum</i>	Palanisamy et al. [81]
Ethanol extract	Carotenoids, polyphenols, and PUFA	<i>Dunaliella</i> sp., <i>Tetraselmis</i> sp., and <i>Nannochloropsis gaditana</i>	Maadane et al. [94]
Fucoidan	Sulfated polysaccharide	<i>Chnoospora minima</i>	Fernando et al. [95]
Water/ethanol extract	Phenols	<i>Bifurcaria bifurcata</i>	Agregán et al. [96]
Methanol extracts	Phenols	<i>Desmodesmus</i> sp.	Safafar et al. [97]

still use the same classic solvent extraction technique despite having limitations like denaturation of the extracted compound and use of large amount of solvent for extraction. Gradually, some economical green extraction techniques should be developed for use at industrial scale to overcome the aforementioned problems. Secondly, very less algal products are being commercialized, and thus, attention should be given to the development of newer products associated with other industries as well. And lastly, new regulations should be established by the countries to regulate the use of algal extracts as pharmaceuticals, food, or biostimulants.

5 Conclusion

In the present chapter, the importance of algae as a multiple source of bioactive compounds has been reported. Microalgae have the capacity to produce unusual natural bioactive compounds with remarkable biological properties. The compounds like fucoxanthin, astaxanthin, polyunsaturated fatty acids, proteins, glycolipid, and polysaccharides have been successfully used to treat diseases like cancer, malaria, Alzheimer's, TB, and many others. Despite having many advantages, very limited species of microalgae have been studied till date. Thus, newer species of microalgae can be explored for novel compounds with enhanced activity exhibiting a prolific approach in the area of biotechnology and biomedical applications.

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Supercritical Water Gasification (SCWG) Technology for Municipal Solid Waste (MSW) Treatment



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Abstract This chapter highlighted conventional and advanced waste treatment technologies in details, for sustainable wastes management. The chapter also reviewed Supercritical Water Biomass Gasification (SCWBG) from Municipal Solid Waste (MSW) at the temperature and pressure of 700°C and 350 bar, respectively. The findings show that gasification of organics from MSW using Supercritical Water Gasification (SCWG) technology can be a potential solution to the increasing biodegradables in the municipal solid wastes. However, with the ability of the system to allow the complete gasification of biomass below the working temperatures, this makes it even more attractive technology for sustainable wastes to wealth. With the wide varieties of sustainable fuels and chemicals that can be generated in the process, Supercritical Water Gasification (SCWG) technology can be a candid sustainable and economical energy solution for power generation and transport renewable fuel for automobiles (methane and hydrogen gas).

Keywords Biomass, Municipal solid wastes, Supercritical water gasification, Waste treatment technologies, Waste to energy

1 Introduction

The global energy sector is making efforts in turning waste to wealth especially in consideration of the global energy security and its allusion to global warming and climate change. In recent years, the municipal solid waste disposed of in most the developed, developing and underdeveloped countries has become a major challenge to the environment [1–3]. The global environmental problems related to municipal solid wastes (MSW) make it necessary for the discovery of the methods that can be used in converting waste to wealth. The traditional method of MSW disposal (Landfill) if not controlled properly is not only harmful and misappropriating the land for human but also contributes to the deteriorating of the climate, human health and great agent in the emission of greenhouse gases [4].

The composition of MSW varies from one country to another and from time to time. However, the most important aspect is that the per capita MSW generation depends on the economy of a giving country. The global composition of municipal solid waste (MSW) is mainly organic matters comprising about 51%, recyclables 17.5% and the rest including inert waste having 31% of the proportion. This heterogeneous nature of MSW makes it a very good alternative source of fuel for the global energy sector. The energy derived from MSW is already classified as a renewable source of energy because, if the waste is not treated, it will be dangerous to the fauna and flora, as well as a considerable source of greenhouse gases.

At present, much has not been done in developing and underdeveloped countries on waste management and disposal. Even waste to energy (WtE), which is among the most common technologies that are well developed and established across the

globe, is facing many issues ranging from policy uncertainties, economic barriers, technical difficulties and logistical challenges in the developing and underdeveloped countries. The benefit of WtE in developing countries cannot be overemphasised, despite all the challenges highlighted that are all not clearly defined or understood in the country. Given that the average heating value of municipal solid waste (MSW) is approximately 10 MJ/kg, the prospects of utilising MSW as a source of energy cannot be overemphasised. Recent studies highlighted that, in the United States, incineration with energy recovery (WtE) from MSW alone reduces the percentage MSW to about 75% of its annual increase, leaving only the ash as an issue. However, huge progress has been reported in utilising this form of ash for different applications ranging from use as constituent in building and in road constructions [5, 6].

Although several MSW treatment technologies are employed in waste management and disposal across the globe, there is no single treatment technology that can be used to solve all the problems associated with the MSW. This chapter gives a comprehensive and detailed highlight of the conventional and advanced waste treatment technologies for sustainable wastes management giving more emphasis on hydrothermal waste treatment technology, using supercritical water biomass gasification (SCWBG) for the treatment of organics, from municipal solid waste (MSW) at the temperature and pressure of 700°C and 350 bar, respectively.

Supercritical water gasification (SCWG) seems to be the most promising solution to the increasing percentage of MSW in India. The hydrothermal treatment processes using supercritical water biomass gasification (SCWG) technology can convert the organics from MSW which are mainly biomass (food waste, woods, paper and paperboard, yard trimmings, textiles, etc.) to syngas and other refuse-derived fuels (RDF).

1.1 *Background and Context*

Effective MSW is the major challenge of most cities with high population across the globe because of the heterogeneous nature of the waste and dependence on the economy of a given population [7, 8]. However, despite the dependence of waste generation on the economy of the country, one of the greatest advantages is that the per capita waste generation in low and middle-income countries generally constitutes a large proportion of organic wastes as indicated in Fig. 1.

It is clear from the figure that, regardless of the economy of a country, biomass or biodegradable wastes constitute a significant percentage of the generated waste. Unfortunately, even with the waste management hierarchy, in Fig. 2, which is designed to curtail landfilling of biodegradable wastes and other fragments of the MSW, in most countries of the globe including developed countries, a larger percentage of biodegradable wastes in the MSW directly end up in the landfills. It is worth remarking that this is a very alarming issue because the decomposition processes of biodegradable wastes in the landfills always produce methane which is a greenhouse gas. Starting from this viewpoint, one can notice that municipal solid

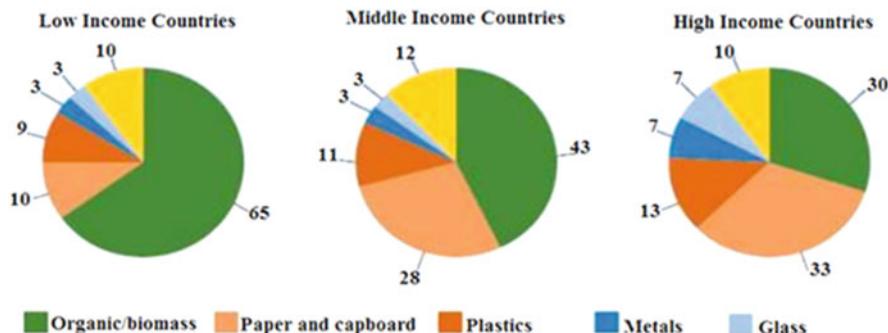


Fig. 1 Municipal solid wastes composition by the income of countries [9]

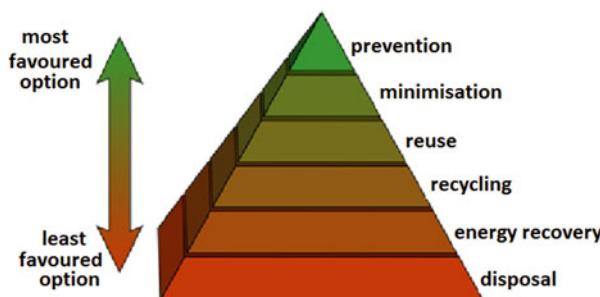


Fig. 2 Wastes management triangle (Adapted with permission from: [10])

waste management is a complex field which goes beyond prevention, collection, treatment and disposal of waste; it is about preserving, protecting and improving the quality of the environment and human health, promoting a circular economy and ensuring the efficiency of resources by turning waste to wealth [7].

Figure 2 presents the waste management hierarchy with waste prevention as the most preferable option, to disposal or landfilling as the least favoured option. However, with rapid urbanisation, many countries are facing considerable challenges in the management and treatment of waste. The recent waste generation data in India, the second populous country in the globe, indicates that about 62 million tonnes of municipal solid wastes are generated per annum across the towns and cities of India. Reports also show that only 43 million tonnes of the generated wastes are collected, out of which only 38% is treated. This means, 31 million tonnes of the collected waste is dumped in the landfills, in addition to the 19 million tonnes of the uncollected wastes. Although virtually all Indian municipal authorities provide basic solid waste management (SWM) services, in keeping the major cities clean, however, most of the collected waste by the municipalities unsystematically goes to landfill sites located within or outside the cities [11, 12]. The story is not different in China, the most populous country in the globe.

Wang et al. [13] reported in a recent study that even in rural China the daily per capita waste generation is in the range of 1.07 kg which is comparable to many developed countries such as Japan, 1.08 kg; Czech Republic, 0.72 kg; Romania, 0.9 kg; and Bulgaria, 1.2 kg. Furthermore, not only in rural China, even the urban regions of China are lacking waste management facilities and effective high-quality measures for MSW management and disposal. Although the Chinese government has developed quite a number of initiatives and laws on the prevention and control of environmental pollution by solid wastes, studies revealed that kitchen waste in urban solid waste makes up the highest proportion (at approximately 60%) of the waste stream, but about 91.4% of the generated wastes in China goes to landfills [14].

Even in the European countries, it has been expressed by the European Commission that the EU's economy is currently losing a significant amount of potential secondary raw materials which are found in the waste streams. According to the recent studies, only 43% of the generated municipal waste in the European Union is being recycled, the rest of the generated municipal solid wastes 31% are being landfilled, and 26% of the percentage is incinerated without energy recovery [7]. The problem of MSW in Africa is not different from what has been discussed in other continents of the world. In Nigeria, the most populous country in the African continent, the per capita waste generation in the country is estimated at 0.65–0.95 kg per day which is equivalent to an average of 42 million tonnes of wastes generated annually. This is very alarming because it is more than half of 62 million tonnes of waste generated in sub-Saharan Africa annually. Unfortunately, only 20–30% of the 42 million tonnes of wastes generated annually in Nigeria is collected although 52% of wastes generated are organic wastes which can be used as sources of fuel [15]. Globally, about 71% of MSW is ending up in landfills although it contains, mostly, hazardous substances including some batteries, paints, mercury-containing waste, pharmaceuticals, vehicle maintenance products and many other products. This is so unfortunate and alarming because more than 53% of the landfilled wastes consist of hardboard paper, yard waste, papers and food that are biodegradable by the anaerobic bacteria for the generation important by-products that can be used in diverse applications [16].

Based on the background study presented in this section, it is clear that with the annual municipal solid waste increase in the globe of which biodegradables constituting reasonable percentage, research reconstitution across the globe is required to speed up the development in the municipal solid waste management across all levels. This will help immensely in saving the globe from the dangerous two-degree scenario and tackling the GHG's emissions related to improper waste management. In this chapter, most of the different techniques and technologies involved in the treatment of wastes are highlighted. This can be a key to efficient waste management in many developed, developing and underdeveloped countries across the globe as a way forward towards long-term visions in municipal solid waste management.

2 Conventional Municipal Solid Waste (MSW) Treatment Technologies

Conventionally, several methods are used in the treatment and management of waste across the globe, and the widely adopted conventional municipal solid wastes management techniques are highlighted in Fig. 3.

The conventional MSW management technologies include biological treatment (which constitute aerobic and anaerobic digestions), thermal treatments of waste (incineration with energy recovery, pyrolysis, gasification, combined pyrolysis and gasification), mechanical treatment (sorting and separation, mechanical thermal treatment using autoclaving) and landfills (aerobic and anaerobic digestions that can also generate gases which can be used to generate energy in the form of recovery). The heterogeneous nature of MSW is the major driving factor for having several MSW treatments technologies since there is no single treatment technology that can be used to solve the heterogeneous challenges of MSW.

Characterising heterogeneous wastes presents a number of special problems which made it very difficult in achieving maximum waste to wealth implementation in compliance to waste management triangle across the globe. Due to the

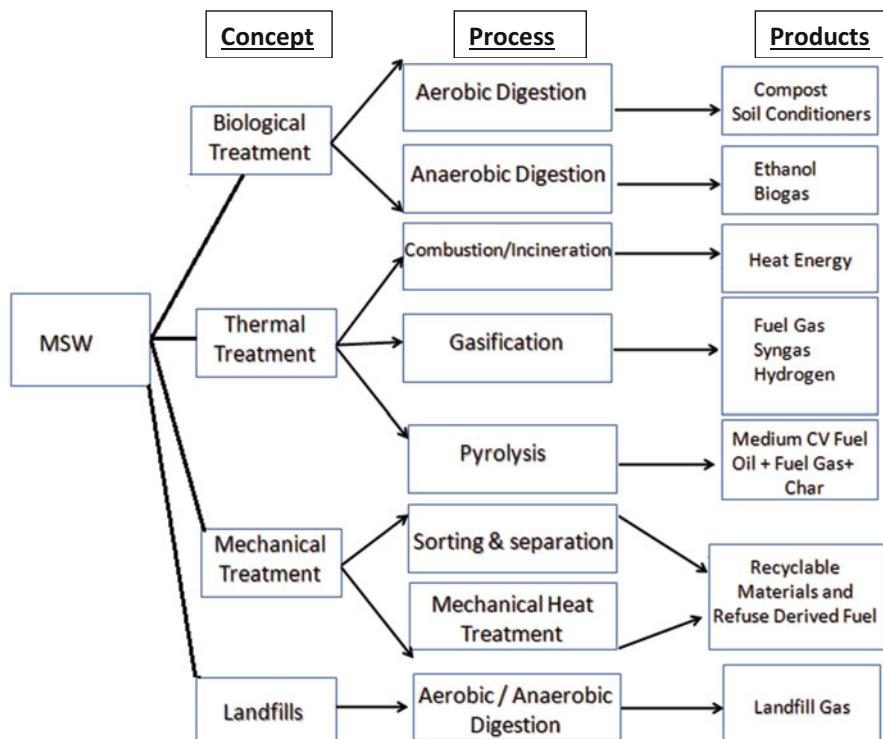


Fig. 3 Various conventional MSW treatment processing technologies (Original)

heterogeneous nature of MSW, generation of electricity in the form of incineration with energy recovery turns to be the most promising options that can reduce the challenging issue of the heterogeneous nature of the MSW. Waste to energy (WtE) technology can help immensely in the generation of green energy (heat and electricity). The technology in the form of Energy Recovery Facility (ERF) generates heat by burning MSW in a specially controlled environment; the heat is turned into steam for generation of electricity and heat for large-, medium- and small-scale applications. This technology is widely utilised in different countries, and it is proven to be economical and safer to the environment, though the most challenging issue with this system is the emission control [17, 18].

Although MSW incineration with energy recovery allows maximum treatment of different types of wastes in MSW stream including the plastics wastes which are essentially hydrocarbons with calorific values in the range between 30 and 40 MJ/kg, and food solid wastes which are sustainable and important source for certain industrial chemicals, it worth noting that the impact of incinerating the plastics and other non-biodegradable materials is hazardous to the environment due to the release of more greenhouse gases than landfill. To address this challenging issue, it is, therefore, necessary to develop some advanced waste treatment technologies for sustainable development in the process of turning wastes to wealth.

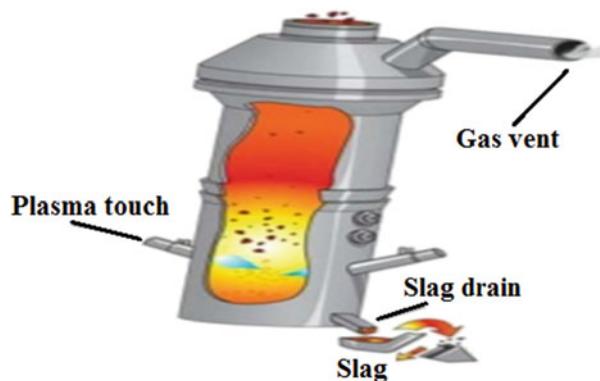
3 Advanced Municipal Solid Waste (MSW) Treatment Technologies

All the MSW management techniques have advantages as well as some disadvantages when applied in practical cases. This is the reason why a variety of waste treatment technologies are available, but there is no technology that is optimal solution to the increased MSW all over the globe. This shows that there is a need for integrated development in MSW treatment technologies for achieving a maximum level of waste to wealth conversion from MSW [19]. The quest of achieving maximum reduction of the increased MSW across the globe resulted in the development of advanced MSW treatment technologies. These advanced technologies are developed with the aim of using different treatment methods for achieving maximum reduction of the different types of waste in the municipal solid wastes stream prior to disposal. In this section, the various advanced MSW treatment technologies are highlighted.

3.1 Plasma Arc

The plasma arc is formed when quasineutral gas particles are ionised between two medium of positive and negative particles [20, 21]. The plasma arc operates on

Fig. 4 Plasma touch furnace (Adapted with permission from: [22])



principles similar to an arc welding machine, where an electrical arc is struck between two electrodes. The high-energy arc creates high temperatures as higher as 13,000°C. In the process of MSW treatment using plasma arc technology, the waste materials are fed into the chamber, and the intense heat of the plasma breaks down organic molecules (such as oil, solvents and paint) into their elemental atoms. Since the treatment process is in a carefully controlled environment, these atoms will recombine into harmless gases such as carbon dioxide.

With plasma arc technology, there is no burning or incineration and no formation of ash; the solids components such as glass and metals are melted to form materials, similar to hardened lava, in which toxic metals are encapsulated. Plasma arc technology is generally divided into two major technology types which are plasma torch and plasma arc (or DC) melter.

Plasma torch systems in the plasma touch systems (Fig. 4), an arc is struck between a copper electrode and another electrode of different polarity. This process has high destructive efficiency and is very robust in the treatment of any form of wastes without pretreatment. When using the plasma torch systems for treatment of wastes with organic contents, the organic portion of the waste is usually retained in the stable, leach-resistant slag. However, it is worth noting that the air pollution control in the plasma touch systems is usually larger than the plasma arc systems due to the need for stabilising the touch gas in the system.

Plasma arc systems the plasma arc system depicted in Fig. 5 has a very high destruction efficiency which makes them very robust in the treatment of any type of wastes in the MSW stream with or without pretreatment. The plasma arc system uses carbon electrodes to strike an arc in the bath of molten slag. The high temperature produced by the arc converts the organic contents of the feed wastes into lights organics and other primary elements. In the plasma arc systems, the consumable carbon electrodes are continuously inserted into the chamber, thereby eliminating the needs for shutting down the system for maintenance or electrode replacement. It is worth noting that, the potential of air pollution in the plasma arc systems is low because of the electrical heating in the chamber in the absence of free oxygen.

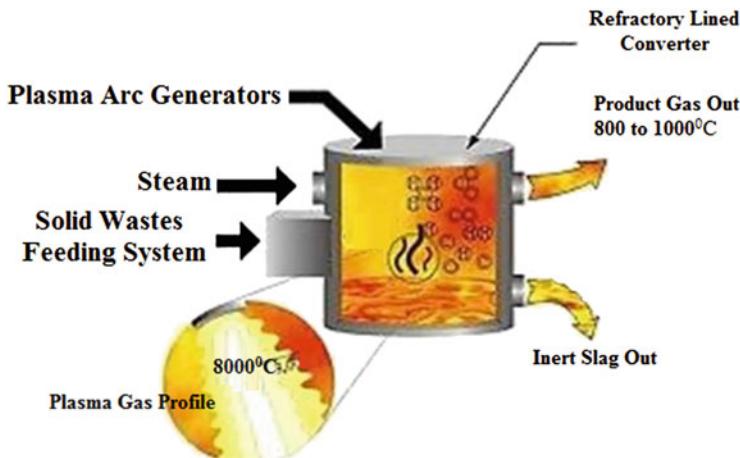


Fig. 5 Plasma arc system (Adapted with permission from: [23])

Furthermore, the combustible gas is cleaned in the off-gas system and is oxidised to CO₂ and H₂O in the bed oxidisers.

The plasma arc technology is receiving attention in the global waste treatment studies as a result of its reduced emission to the atmosphere in comparison to other treatment technologies. The major concern about plasma arc technology is a significant investment cost. However, another issue of chief concern is ensuring that the gaseous emissions are kept to the minimum required values before being released to the atmosphere.

3.2 Autoclaving

Autoclaving is a technology that involves higher pressure sterilisation of the MSW by the use of super steam. This technology cooks the waste, in so doing killing all the bacteria's contained in the waste as well as reducing the moisture content of the wastes [24, 25]. The schematic of the working principle of autoclaving technology is shown in Fig. 4. Autoclaving technology is also another form of mechanical heat treatment (MHT) since it uses thermal and mechanical methods to treat wastes Fig. 6.

Municipal solid waste autoclaving is one of the waste treatment techniques being used to pretreat the recyclable component of the MSW and is often applied to the residual wastes after recycling. The autoclaving system uses a combination of heat, steam, pressure and mechanical rotation for the feed wastes in the chamber. The most common autoclaving systems employed in the treatment of MSW are the steam autoclaves. Steam autoclaves are steel horizontal-type devices that are designed to operate safely under high temperatures and pressures.

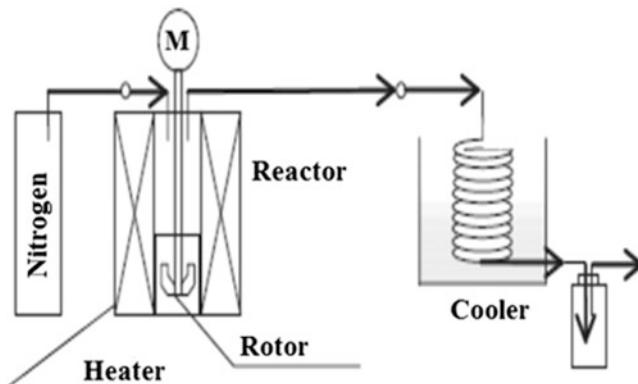


Fig. 6 Small-scale autoclave facility (With permission from: [4])

Table 1 Typical outputs and aggregates of the autoclaving process

Component	Percentage (%)
Organic fibre	64
Recyclables	17.5
Aggregate	2.5
Other materials suitable for landfill	16
Mixed plastics	9
Glass	4
Steel	3.5
Aluminium	1

In using the autoclaving systems in the treatment of MSW, the wastes may initially be screened for the removal of any large items and in some cases possibly shredded. The wastes components are then sealed in the autoclave chamber that rotates to agitate and mix the wastes. Because of the residence time of the wastes in the chamber and high temperature and pressure, all the bacteria content in the wastes will be destroyed, thereby sterilising all the wastes in the chamber. However, a significant reduction of up to 60% in the volume of the wastes can be achieved with a significant reduction of the moisture content of the wastes.

The cellulose of the organic components of the feed wastes including food, garden wastes, papers, cards and all sorts of organic components in the MSW stream is broken down to mush of fibre also known as floc or fluff. After the autoclaving process, the wastes are usually discharged for treatment using mechanical separation technologies. The typical outputs and aggregates of the autoclaving process are given in Table 1.

It is clear from the table that, the fibre is the main output of the MSW autoclaving process since biodegradables constitute the highest proportion in the MSW stream. Diverse applications are proposed for the recycling and recovering the fibre among

which includes composting, anaerobic digestion and refuse-derived fuel (RDF). The glasses and plastic components are separated for recycling and reuse as aggregates, while the metals are extracted for recycling. The water used in the system is usually trapped and recycled in the process, and the final wastewater is discharged as an effluent stream which removes pollutants from the process. The great advantages of this technology are its ability on the treatment of all form of wastes in the MSW stream, including those that are not recyclables like metals. The technology also enables the reuse option for plastics, as well as sterilising plastic wastes before the recycling. The metals and plastic wastes treated using this technology are always comparable to virgin materials. The autoclaving plants are modular in nature because they are made up of units which can be added or taken away based on changes of the waste stream or volume of the wastes. Huge development is witnessed in using the cellulosic pulps from the treated wastes using this technology in biofuel production.

3.3 Microwave Technology

Microwave technology is becoming widely used in the globe, in the treatment and remediation of environmental problems related to municipal solid waste. Since the first use of this technology in the 1940s by *Percy Spencer*, microwave heating is constantly getting serious attention by different researchers across the globe [26, 27]. In recent years, microwave technology is proven to be an attractive technology for the treatment of municipal solid wastes in addition to many astonishing applications in different areas of human life. Microwave technology operates by delivering direct energy to the microwave absorbing material for complete heating of the material from the outside and inside as shown in Fig. 7. Microwave operates in the region between the electromagnetic spectrum and infrared radiation region. Microwaves are defined as waves having wavelengths ranging from about 1 m to 1 mm, which correspond to frequencies between 300 MHz (1 m) and 300 GHz (1 mm).

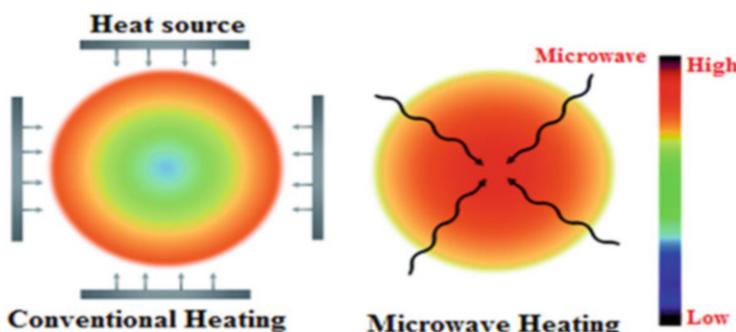


Fig. 7 Microwave and conventional heating patterns (With Permission from: [28])

Using microwave technology for the treatment of MSW, the issue of long heating periods energy lost to the environment and thermal gradients are minimised because the materials are heated from outside and inside different from the conventional heating as shown in Fig. 7. For the treatment of biodegradables in the MSW stream, since thermal and non-thermal impacts are created in the materials, this will lead to the rupturing of the crystalline structures of the lignocellulosic materials, thereby enhancing the reactivity of the materials.

The major advantages of using this technology include reducing the volume of wastes, selective heating of the wastes and ability to treat the waste *in situ*. Recent results on the use of this technology in biodegradable waste treatment show that 1 tonne of waste can produce reasonable barrels of oil, with a reasonable amount of carbon black. The oil generated can be used in the generation of green electricity and many other applications.

3.4 Biorefinery (*Bioconversion*)

Biorefinery (bioconversion) technology converts organic wastes or biodegradable fraction of the MSW to chemicals using the anaerobic digestion. This technology converts the biodegradables from the MSW to varieties of marketable products that can be used to generate fuels, chemicals, and fibres [29, 30]. The concept of the biorefinery is not different from the conventional refinery process which produces multiple fuels and products from crude oil as starting product. Biorefinery process utilises biomass from the municipal solid wastes for conversion to liquid and gaseous biofuels. Generally, in biorefinery facilities, the organics fractions of the MSW are usually converted into biogas, while the non-organic components are converted into solid refuse fuels (SRF) used in syngas production. Starting from the syngas, the fuel synthesis facilities such as in Fig. 8 will convert the syngas various fuels such as bio-jet fuel, bio-diesel, bio-ethanol, bio-methanol, dimethyl ether, etc. which can be used for various energy applications. It is worth noting that, in the process of syngas production from the SRF, several thermochemical steps are involved at different temperatures ranging from torrefaction, gasification and pyrolysis.

As depicted in Fig. 8, a sustainable biorefinery configuration must produce bio-products in conjunction with bioenergy and biofuels. To maximise the efficiency of the biorefinery process, most of the advanced biorefinery facilities are usually integrated with efficient and flexible biomass feedstock conversion systems which involves a combination of physical, chemical, biochemical, and thermochemical processes for the production of multiple products from the biomass. This technology is recognised as one of the most promising technologies for the effective implementation of modern sustainable energy policies, especially in the transportation sector.

Although biorefinery offers environmental benefits, it is important to consider prevention of biodiversity loss during the conception of a biorefinery by utilising

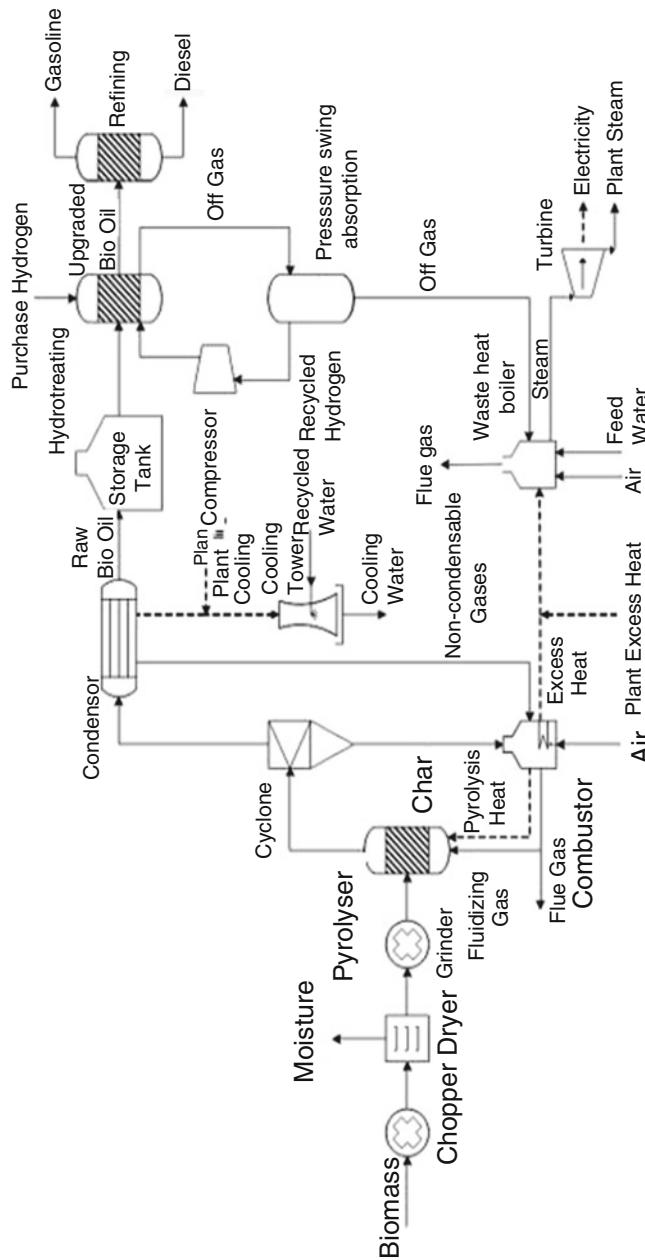


Fig. 8 Schematics of a generic advanced biorefinery (Adapted with Permission from: [31])

only the biomass components from the MSW or other sources that are not having the potential of causing issues in the food cycle.

4 Advanced Thermal Treatment (Hydrothermal Treatment of Municipal Solid Wastes)

Hydrothermal technology is specifically targeted technology for the treatment of organic wastes in both wet and dry forms, as well as the destruction of hazardous and chemical wastes. The use of hydrothermal technology in the treatment of biodegradable wastes in the MSW is increasing in global literature because it is believed to serve as a reliable solution to the issues related to fossil fuels and their emissions. This technology is believed to be the everlasting solution to the ever-increasing biodegradable wastes in the MSW stream across the globe. The technology is tested and proven to be an alternative solution in tackling the energy shortage and environmental pollution, as well as a potential alternative source of green fuels [32, 33].

4.1 *Hydrothermal Technology*

The term ‘hydrothermal’ is used to refer to any heterogeneous reaction in the manifestation of aqueous solvents or mineralisers, under conditions of high temperature and pressure, to dissolve and recrystallise materials that are relatively insoluble at normal conditions. Hydrothermal technology got its first successful commercial application in the extraction of ores in the twentieth century. In this century, hydrothermal technology has found many applications in the branches of science and technology in the production of environmentally safe and green energy, especially in waste biomass treatment [34, 35].

The application of hydrothermal technology in MSW treatment is aimed at solving the problem of organic wastes, which has the highest proportion in the MSW. However, the technology can also be used in the treatment of hazardous wastes, wastes with higher water contents, halogenated wastes and chemical wastes. The various chemistries involved in the treatment of organics using hydrothermal technology are highlighted in Fig. 9.

The hydrothermal technique has become the most popular, garnering interest from scientists and technologists of different disciplines, particularly in the last 15 years. It is worth noting that, despite the fact that this technology has made tremendous progress in all angles of science and technology, there is no unanimity about its definition. As shown in the figure, the hydrothermal technology involves subjecting the organic components of the MSW to the action of water at higher temperature considered as above critical temperature (370°C), and higher pressure is referred to as supercritical [34].

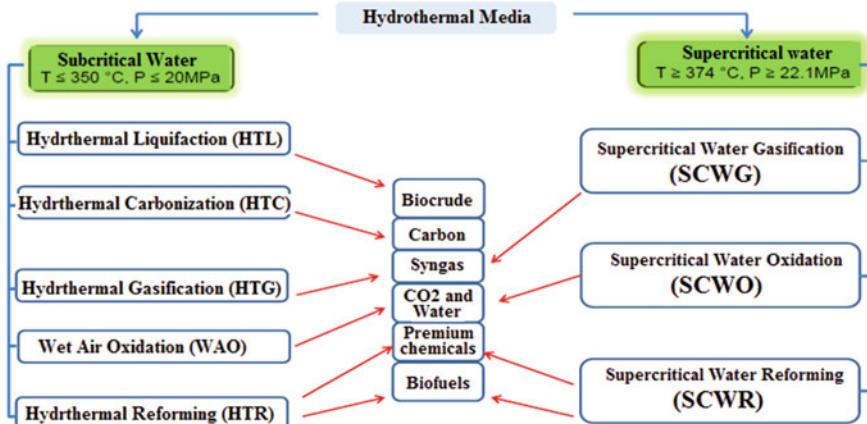


Fig. 9 Hydrothermal processing technologies (Original)

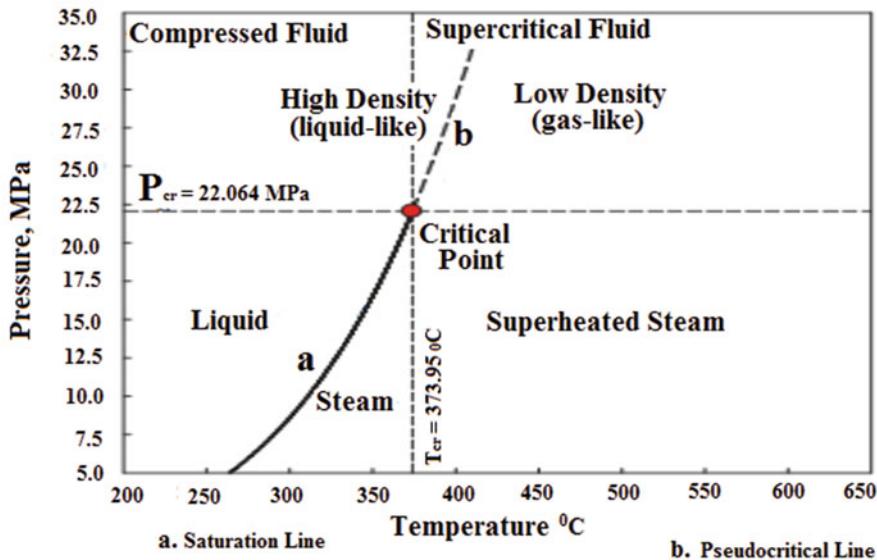


Fig. 10 Pressure-temperature diagram for water (With Permission from: [37])

4.2 The Basic Principle of Supercritical Water

The experiments conducted by Modell and Amin, to convert carbohydrates in supercritical water at Massachusetts in the mid of 1970s, encourage the development of this technology across the global laboratories [36]. The general basics of supercritical water are depicted in Fig. 10.

When the pressure and temperature of the water reach a critical point, the supercritical condition is achieved. The pressure and temperature at this level correspond to $P_c \geq 22.1$ MPa and $T_c \geq 374^\circ\text{C}$. At this point, all the physiochemical characteristics of water such as ion product, viscosity, water density and dielectric properties will be extremely higher. However, this will equally change the chemical properties like dipole moment, pH, polarity, etc. which will make water not only solvent for ionic species but for non-ionic species [38]. The property of water at this point makes it very attractive and environmentally potential reaction medium for organic and inorganic compounds. This draws the attention of the researchers looking for green and environmentally friendly solvents for chemical reactions without pollution to the atmosphere [39].

4.3 *Supercritical Water Gasification of Biomass (SCWG)*

The global energy crisis is the driving factor for the development of this technology, as hydrogen that can be used as fuel can be produced. In recent years, supercritical water at temperature 374°C and higher pressure of 221 bar is widely employed in converting biomass to liquid and gaseous fuels, which can be detached easily from the reacting phase (i.e. water) by simple cooling to ambient temperature [40].

Understanding the influence of this novel technology on biomass is a difficult task because of the different components available in the biomass structure. However as stated earlier, hydrogen which is crucial for the development of a bio-economy can be produced easily with this technology. Despite the prospect of the hydrothermal technology in hydrogen and other fuel production, the only workable biomass that can be sustainable for this technology is biomass source that avoided any potential competition with food cycle. In this context, the best biomass source that can serve this purpose is the biomass from MSW source.

Almost 90% of the available land biomass structure and cell walls of all terrestrial plants is made up of lignocellulose. Lignocellulosic biomass consists of 40–55% cellulose fibres and 15–35% hemicellulose surrounded in 20–40% of lignin. In the three components of lignocellulosic biomass, i.e. cellulose, hemicellulose and lignin, celluloses and hemicelluloses are polysaccharides of C6 and C5 monomers connected by β -(1-4)-glycosidic linkages. The main compounds in the lignin are polymers of para-hydroxyphenyl (H lignin), guaiacyl (G lignin) and syringyl (S lignin) alcohol as shown in Fig. 11.

Most of the cellulose in biomass is crystalline, although a small portion is amorphous. The crystalline cellulose is built up by 5,000–15,000 glucose units β -1,4 glycosidic and hydrogen bonds, while the amorphous hemicellulose consists of branched C5- and C6-sugars (xylose, manose, arabinose, glucose and galactose) linked by β -1,4 glycosidic bonds with a polymerisation degree of 100–1,000. Lignin is composed of p-hydroxy-propyl-benzene structures, namely, p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, connected by ether and C–C bonds to build a three-dimensional network, although the proportion of units in lignin varies from

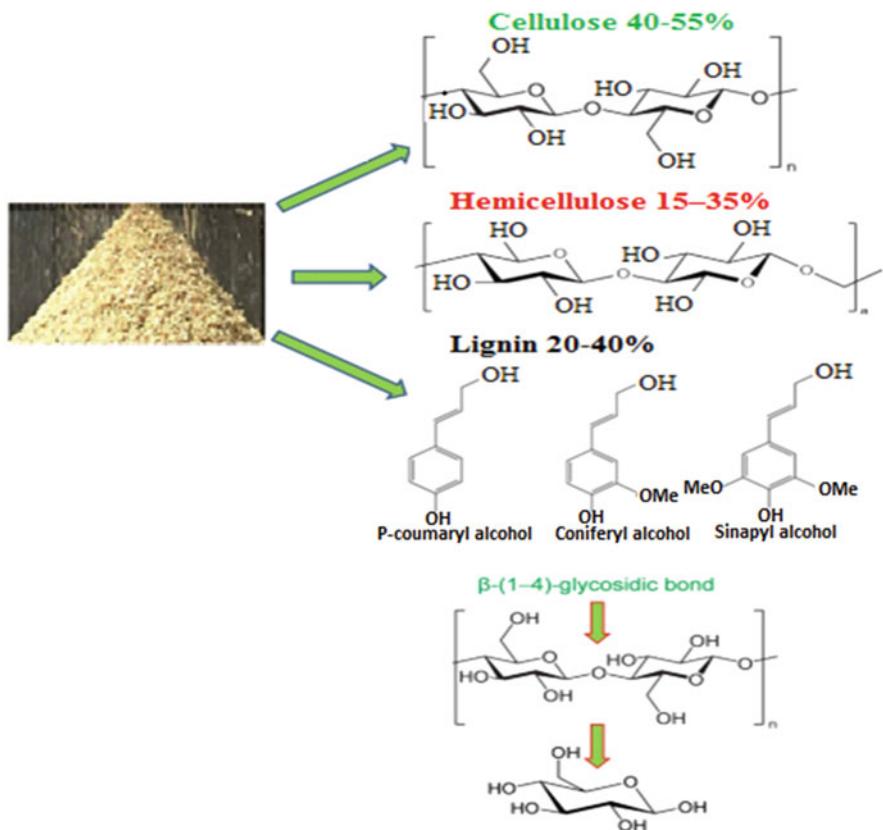


Fig. 11 Lignocellulose structure and constituents (With Permission from: [41])

biomass species to species. It is very clear that biomass consists of different components, and understanding the influence of the components during the gasification process is quite a complex task. Another complex issue in utilising this technology in the treatment of biomass from MSW is the higher water content. In this section, VERENA pilot reactor, a down flow reactor depicted in Fig. 12, is reviewed to explained the supercritical water gasification of biomass from the MSW.

The VERENA pilot reactor depicted in Fig. 12 has a total throughput of 100 kg/h (max. 20% dry biomass) and is designed to operate at a pressure of 35 MPa at a maximum temperature of 700°C. The plant is operated usually at a flow rate of 100 kg/h at a maximal reaction temperature of 660°C at a pressure of 28 MPa.

4.3.1 Feeds System

The biomass contained in the MSW constitutes different types of organics in both wet and dry forms. As highlighted, biomass contains cellulose, lignin and

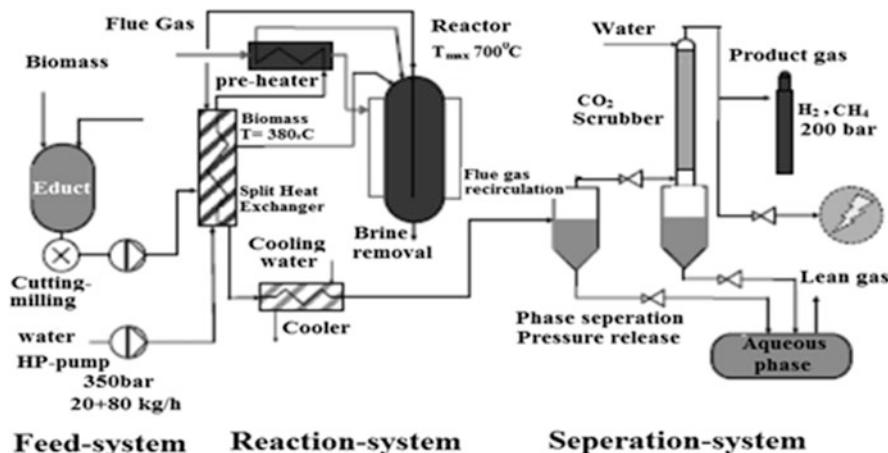


Fig. 12 The basic flow of supercritical gasification process (Adapted with permission from: [42])

hemicellulose. The cellulose and hemicellulose are carbohydrates types, while lignin contains aromatic derivatives, which when hydrolysed, products such as phenol and other carbohydrates derivatives are produced. The feeds system of the reactor contains enhanced setups, designed and developed to handle the common organics found in MSW. As part of the handling methods, the biomass size is reduced to a suitable size for the plant using the inbuilt cutting mill. The most common available reactors are designed to operate at a capacity of 100 kg/h, with a maximum of 20% dry biomass, at 350 bar and 700°C operating pressure and temperature, respectively. This means, it is enhanced to handle a high percentage of wet biomass, which are the most challenging components of MSW. The feed system of the reactor is dosed into the reaction chamber by a mass flow controlled, high-pressure metering pump serving as a heat exchanger.

4.3.2 Reaction System

As shown in the diagram, the VERENA pilot reactor depicted in Fig. 12 is a down flow reactor. The vessel in the lower part of the reactor takes the mixture from down through the head of the reactor and to the heat exchanger. The VERENA pilot reactor is generally a different supercritical reactor in the sense that heterogamous catalysts are not required for the production of gases. The system utilises the brine produced from biomass as a catalyst for the system. This makes it a promising MSW biomass treatment technology, as it can handle even biomass containing chlorine, sulphur, etc. which are the major challenges of other technologies [42].

The process of heating the biomass moderately to critical temperature helps in preventing the precipitation of inorganic salts in the heat exchanger. However, since the heating of the biomass to the working temperature takes place in the downstream

part of the reactor, the biomass wastes are then mixed with hot stream water and the salt transported downward by gravitational action. The excess salt produced from the process is then removed by the brine removal system. A typical overall reaction for glucose taking place in the process can be written as:



The end gases depend on the working temperature of the system. Based on the reaction pathway, three main pathways for the production of gases are highlighted which are:

- For substitute natural gas production, CO has to be minimised.
- For hydrogen production, H₂ has to be maximised.
- Synthesis gas production requires CH₄ to be minimised.

4.3.3 Separation System

At the supercritical working conditions, the gases are soluble in the working supercritical water and will leave the reactor and passes to the heat exchanger and cooler. After cooling, the gases are separated from the water phase which is equipped with CO₂ scrubber. The gasses separated are then stored in the storage containers for further treatments.

Figure 13 depicts the composition of the product gases. As shown in the figure, a significant percentage of important gases can be generated using this technology. However, it is worth noting that the composition of the product gases depends on the choice end gases as identified earlier.

4.4 Syngas Treatment Chain

After treatment, different products are obtained among which includes chemicals, diesel, coal, petcoke, natural gas and naphtha, methanol, dimethyl ether (DME, also known as wood ether), ammonia, Fischer-Tropsch liquid (renewable transportation fuels like Fischer-Tropsch diesel), etc. The treatment chain of the synthesis gas is shown in Fig. 14.

The different products from the process can be classified according to their uses as follows:

- Hydrogen – Hydrogen can be used in electricity generation in the form of fuel cells, as well as transportation fuel. Hydrogen technology is already well developed across the global transportation sector.
- Steam – The steam generated in the process can also be used to drive turbines for electricity generation.

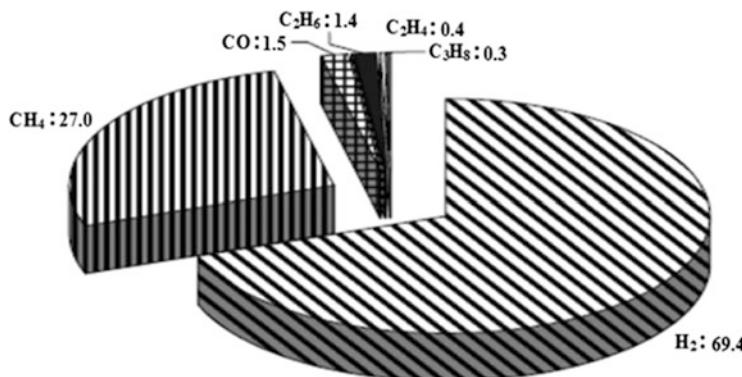


Fig. 13 Composition of product gases (With permission from: [42])

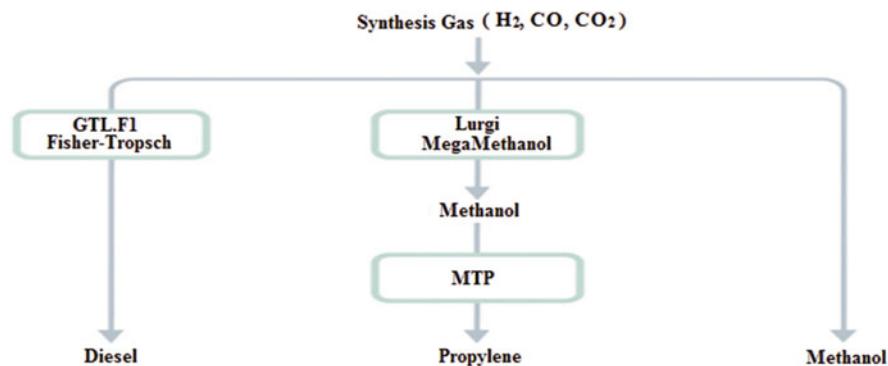


Fig. 14 Synthesis gas treatment schematics (Original)

- Carbon monoxide – Carbon monoxide is used in several chemical industries as feedstock for different applications and also as fuel.
- Carbon dioxide – Since the process is in control conditions and environment, the carbon dioxide can be easily captured for injection into the sequestration wells or for other applications.

4.5 *Advantages of Supercritical Water Gasification of Biomass (SCWG)*

The advantages of supercritical water gasification of biomass contained in municipal solid wastes cannot be overemphasised. The advantages of using this novel technology in MSW management include:

- This method requires no drying of wet biomass. This means the cost and the energy needed for MSW moisture evaporation can be avoided. In addition, another interesting feature of using this technology is that the water contained in the biomass is another important parameter for additional hydrogen formation in the system.
- CO_2 is separated in the easiest possible way because CO_2 is much more soluble in water at high pressure and ambient temperature than CH_4 and H_2 .
- In other reactors, salts or ash needs to be added to achieve low CO. However, this configuration saves the resources as it used the salt in the biomass for these reasons.
- The burnable product gas is gained at high pressure, and further compression does not consume much energy.

5 Conclusion

There is a serious need for curtailing the ever-increasing biodegradables in the global MSW using more viable and environmentally friendly techniques. This chapter highlighted conventional and advanced waste treatment technologies in details for sustainable waste management. The chapter embarks on more detailed and rigorous consideration of the fundamental principle of advanced thermal treatment using hydrothermal technology for gasification of organics in municipal solid wastes and methods involve in the supercritical water gasification (SCWG) process.

It is concluded that the recent struggle and efforts towards finding clean resources from MSW for sustainable development can be achieved with this technology. The technology can serve as a potential solution to fossil fuel consumption in the energy sector (electricity, heat and transportation). Meanwhile, with the wide varieties of sustainable fuels that can be generated from this technology, such as hydrogen (as automobile fuel), methane (for sustainable fuels and electricity generation), dimethyl ether (for blending with diesel), petcoke, natural gas and naphtha, methanol, etc., this technology can surely lead to zero carbon emission to the environment and hence help in building a greater sustainable environment.

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Hydrothermal Conversion of Biomass into Fuel and Fine Chemicals



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and Sathish Raam Ravichandran

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Abstract Hydrothermal conversion is an important thermochemical conversion technique that is used to convert waste biomass into valuable products or biofuel. The process is usually performed in the presence of water at high temperature and high pressures. The biomass is depolymerized to form three phases such as biocrude, biogas, and biocarbon into small components in water. Based on the process conditions (temperature, pressure, catalyst, and time), the yield of the phases varies accordingly. Comparing to other thermochemical conversion techniques like combustion, pyrolysis, and gasification, the hydrothermal conversion is highly appropriate for handling biomass with high moisture content. According to the physicochemical properties of water, the process can be classified as hydrothermal

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carbonization, hydrothermal liquefaction (at subcritical conditions T , 250–374°C, and P , 4–22 MPa), and hydrothermal gasification (at supercritical conditions $T > 374^\circ\text{C}$ and $P > 22 \text{ MPa}$). There has been significant research reported on the hydrothermal conversion of lignocellulosic biomasses, algal biomasses, and also co-utilization of these two with other waste materials. The interaction of water with the biomass results in formation of various chemicals like acids, alcohols, cyclic ketones, phenols, and methoxyphenols and more condensed structures like naphthols and benzofurans. This chapter focuses on the influence of the process parameters and types of biomass utilized on the hydrothermal conversion of biomass. Additionally, the use of biomass as not only an energy source but also as a viable source for value-added chemicals is discussed.

Keywords Biocrude, Biomass, Fine chemicals, Hydrothermal conversion

1 Introduction

Energy Alternatives India (EAI) estimates 450–500 million tons of biomass is produced from various sources in that 31.2% of it is highly utilized for production of bioenergy [1]. Bioenergy is one of the key renewable resources taken from different sources that is awfully heterogeneous. Bioenergy is the most suitable form of alternate energy that is derived from biological substances rich in organic substance – biomasses. For each generation of feedstock, the compositions vary broadly and are tedious to classify as most biomasses are wastes of various biochemical processes and are heterogeneous. The first-generation feedstocks are edible crops like sugarcane, palm oil, and rapeseed that were used for thermochemical conversion [2], whereas second-generation feedstocks are nonedible crops of lignocellulosic biomass like wood, straw, etc., used to avoid the shortage of food compared to first-generation feedstock [3]. In both generations, the plants or crops fix carbon through photosynthesis in the form of carbohydrates. When processed, they leave out carbon dioxide (CO_2), and thus the vent gas can be recycled by other plant. In the past few years, the third-generation feedstocks, i.e., algal biomasses, emerges loudly and attract the researchers than the first- and second-generation feedstocks [4]. They can be broadly classified into microalgae and macroalgae based on its size, and like plants, algae store energy in the form of carbon-rich lipids through photosynthesis.

In a crude point, the various classifications of biomass based on their primary source are given in Table 1.

The two major categories of biomass that are going to be discussed are lignocellulosic and algal biomass. The lignocellulosic plants belong to the division Spermatophyta of the subkingdom Phanerogame in the kingdom Plantae where the

Table 1 Biomass classification based on the source

Source	Type	Example
Forest	Forestry plantations from natural forests and woodlands	Wooden blocks, logs and sticks
	Forestry by-products	Wood chips; tree branches from thinning; bark
Agricultural wastes	Plants and agricultural residue	Cane trash; stover, straw, hay from small grains; cobs (corn, maize); stalk (cotton, jute, hemp, flax, kenaf); shells (almond, pistachio, walnut, pecan, macadamia, Brazil nut, hazelnut, peanut, olive); pith(coconut, palm, date, peach, <i>Sabal</i>); seed burs, pods, leaves, and roots
	Shrubs and herbaceous green residue	Garden wastes, shrubs, creepers, reeds, grasses (switch, canary, and Coastal Bermuda)
	Livestock waste	Animal waste (cattle, goat, sheep, pigs) and poultry
	Others	Weeds and aquatic plants
Algae	Fresh water and marine	Green algae (Chlorophyceae, Charophyceae, Micromonadophyceae, Pleurastrophyceae); brown algae (Phaeophyceae); dinoflagellates (Dinophyceae); diatoms (Cryptophyceae); red algae (Rhodellophyceae, Compsopogonophyceae); euglenoids (Euglenophyceae)
Industry	Wood and lumber industry residues	Waste wood residue from timber mills and saw mills (barks, chips, offcuts, and sawdust);
	Food industry residues	Sugarcane bagasse; starch residue (potatoes, yam, cassava, sugar beet, tapioca, sweet sorghum); fruit peels; residues such as husks, hulls, and shells (barley, cereal, rice, wheat, maize, rye, and oil seeds like cottonseed, linseed, sunflower, rape-seed, etc.)
	Meat processing industry waste	Poultry houses and slaughterhouse wastes, wastes from dairies and fisheries
	Others	Winery wastes, distillery ethanolic wastes, paper industry wastes such as pulp, black liquor, and cellulosic sludge
Domestic	Organic waste	Food waste materials, kitchen-generated vegetable wastes and used cooking oil; sewage sludge
	Municipal waste	Food waste, plastics, paper, rubber, leather, wood, cardboard, cloth rags, and inerts

algae belong to the division Thallophyta of the subkingdom Cryptogamae in the kingdom Plantae. There are major differences in the structure and composition of both biomasses. For a terrestrial lignocellulosic plant, the cell wall is made of uniformly arranged layers of cellulose, hemicellulose, lignin, and pectin [5]. It also contains smaller amounts of proteins, soluble extractives, sugars, nitrogenous amino compounds, resins, waxes, oils, chlorophyll, and ash [6]. While the main

composition of algae is proteins, carbohydrates, and lipids, their percentage might vary even in a single alga depending upon the conditions of growth and age of the culture, and there are some algal species like *Coleochaete thallus* which even contains lignin as well in smaller percentages [7].

Cellulose is a polymer of D-glucose subunits linked by α -(1,4)-glycosidic bonds throughout its length that forms the organized fibrous linear structure. These long fibrous polymeric chains are packed into bundles of microfibrils by hydrogen bonds and weak van der Waals bonds. These microfibrils are concealed by hemicelluloses and lignin, thereby adding additional strength to the cell wall. The hemicellulose is a heteropolymer made of short lateral chains and branches of sugars and polysaccharides linked by α -(1,4)-glycosidic bonds like cellulose and occasionally by α -(1,3)-glycosidic bonds. Xylose is the major sugar component, and it also includes arabinose, rhamnose, glucose, galactose, mannose, and other uronic acids like 4-O-methylglucuronic and D-glucuronic, and D-galacturonic acids [8]. Lignin has a complex cross-linked polymeric structure with large molecular weight which mainly constitutes coniferyl alcohol, p-coumaryl alcohol, and sinapyl phenyl propionic alcohols as monomers which are linked together by alkyl-alkyl, alkyl-aryl, and aryl-aryl ether bonds [9]. Extractives include some organic compounds like alkaloids, phenolics, glycosides, saponins, terpenes, pectins, waxes, gums, mucilages, resins, and oils. They act as plant's energy storage units and also as a defense against insects and microbes that take plants as food. They also contribute to the wood properties such as color, odor, and decay resistance. Ash is the inorganic final residue that remains after complete combustion of the biomass at a high temperature [10]. Proteins are made of one or more peptide chains with various percentages of amino acids, namely, lysine, cysteine, methionine, and tyrosine folded together into a solid or fibrous form. They act as the means of nitrogen storage for the algal cells which decreases as it grows with age [11]. Carbohydrates consist of starches and sugars that are formed as a result of energy absorbed by the chloroplasts and reduction of carbon dioxide into 3-phosphoglycerate in the presence of ribulose-1,5-bisphosphate carboxylase/oxygenase. They act as the structural part of the algal cell wall and provide energy needed for metabolism under dark conditions [12]. Lipids are long carbon chain molecules with carbon numbers 16–24 that consist of polar and neutral constituents of fatty esters, fatty acids, hydrocarbons, and triglycerides. They are formed in the inter-thylakoidal space of the chloroplast and stored inside the cytoplasm which serves as a structural component of the cell membrane. The increased lipid content in algae decreases the specific gravity, making the cells buoyant [13].

The chemical composition of the biomass varies from one plant species to another. The lignocellulosic and algal biomass compositions with their constituents of some of the feedstock are given in Tables 2 and 3, respectively.

The chemical energy stored in the biomass can be converted into energy and useful products by numerous ways. The two frequently and majorly used pathways are (a) thermochemical processes and (b) biochemical processes. Thermal conversion processes include combustion, gasification, pyrolysis, carbonization, and hydrothermal conversion techniques, while biochemical processes include anaerobic digestion, fermentation, transesterification, and biohydrogen production. Though

Table 2 Lignocellulosic biomass feedstock composition

Category	Feedstock	Constituents (wt% in dry basis)		
		Cellulose	Hemicellulose	Lignin
Woody biomass	Pine wood	45.3	22.5	26.8
	Oak wood	38.1	23	32
	Spruce wood	45.6	20	28.2
Agricultural residue	Rice straw	41.1	23.8	19.5
	Common reed	43.3	29.6	27.1
	Corn cob	38.8	33	13.1
	Cotton cocoon shell	32.6	10.2	48.7

Table 3 Algal biomass feedstock composition

Category	Feedstock	Constituents (wt% in dry basis)			
		Protein	Carbohydrate	Lipids	Others (ash and fibers)
Macroalgae	<i>Caulerpa serrulata</i>	14.48	45.6	4.24	27.66
	<i>Daviesia divaricata</i>	8.89	14.6	10.51	38.99
	<i>Padina tetrastromatica</i>	3.87	15.54	3.92	34.58
	<i>Turbinaria triquetra</i>	4.13	16.3	1.62	53.19
	<i>Sargassum subrepandum</i>	4.22	17.21	3.83	39.73
Microalgae	<i>Chaetoceros calcitrans</i>	34	6.0	16	44
	<i>Nannochloropsis oculata</i>	35	7.8	18	39.2
	<i>Dunaliella tertiolecta</i>	20	12.2	15	52.8
	<i>Chroomonas salina</i>	29	9.1	12	49.9
	<i>Isochrysis galbana</i>	29	12.9	23	35.1

there are many methods available, this chapter focuses on one of the fastest and cost-effective conversion methods, which is hydrothermal conversion.

2 Hydrothermal Conversion

The biomass is converted into biochar, biocrude, and biogas in the presence of subcritical or supercritical water at high temperatures and pressures. The three phases of water and various points can be identified from the phase diagram as given in Fig. 1. Water at subcritical conditions breaks the long chain macromolecules of the biomass into smaller fragments by acting as a catalyst due to its higher ionic product that favors acids or base-catalyzed reactions [14]. In general, hydrothermal conversion is further divided into three separate processes: (1) hydrothermal carbonization, (2) hydrothermal liquefaction, and (3) hydrothermal gasification depending on the severity of its operating conditions.

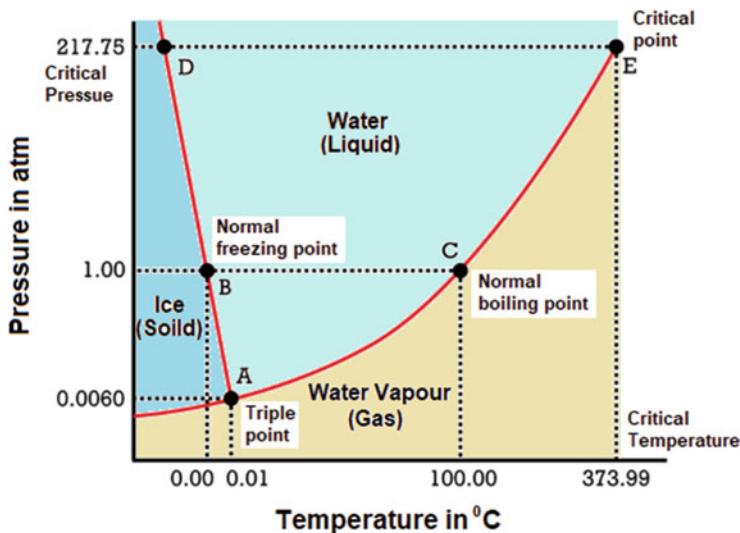


Fig. 1 Phase diagram for water

2.1 Hydrothermal Carbonization

This is a process in which the biomass is kept suspended in water at elevated operating temperature and pressure range of 180–350°C and 2–10 MPa, where high-potential solid chars of moderate calorific value are obtained. Generally, the process is exothermic since it utilizes the oxygen and hydrogen present in the raw material [15]. The reaction pressure is not actually controlled; rather presence of liquid in biomass helps to promote the pressure up to a maximum of 10 MPa [16]. Though the process is carried over at mild operating conditions, care should be taken in keeping the water under subcritical state. Sometimes the medium becomes alkaline due to the drop in pH, and this is because of the formation of by-products inside the reactor. The main advantage of HTC is handling of high moisture content feedstock; the solid char is highly sterilized (biologically) due to the thermal conversion, and energy incentive product is derived [17]. But still HTC was found to gain less interest among the researchers because of the datum that hydrochar possesses less energy-carrying space for solid products than liquefaction and gasification [18].

2.2 Hydrothermal Liquefaction

Biomass with higher percentage of moisture can be utilized for the liquefaction process. Unlike hydrothermal carbonization, liquefaction is carried out under lower temperature (250–450°C) and high pressure (4–20 MPa) in presence of water or

other organic solvents like hexane, methanol, acetic acid, acetone, etc. [19]. At this range the solvent behaves like a compressible fluid which generates high solvation environment, thus making the long chain hydrocarbons dissociate into the shorter chain [20]. A wide variety of raw feedstocks can be utilized for HTL conversion like lignocellulosic biomass, algal biomass, solid wastes that contain organic matters, etc. The primary product from HTL is the biocrude that should be further moved for upgradation. Along with the primary product, other by-products like hydrochar, aqueous, and biogas are produced. HTL finds its own place in attracting the research group because of its integrated characteristics of solvents like high ion product and low dielectric constant [21]. The major advantages of HTL than other thermochemical conversions are the following: effort for preconditioning of feed is not mandatory; it operates at moderate temperature; and heating rates can be slower than pyrolysis [22].

2.3 Hydrothermal Gasification

The other way of depolymerizing biomass is by hydrothermal gasification in which water reacts with biomass to produce gaseous hydrocarbon. Based on the operating conditions, they are classified into supercritical water gasification, near-critical water gasification, and low-temperature aqueous-phase reforming [23]. For low temperature HTG the sugar-like fructose or sugar alcohols like galactitol, sorbitol APR is considered as raw material. For high-temperature SCWG, raw materials like glucose, mannose, and fructose can be considered as good feedstocks [24]. To understand the background of HTG, the behaviors of solvents at high temperature and high pressure should be studied. The operating temperature for gasification ranges between 350 and 700°C which yields the gaseous products like H₂, CH₄, and CO₂ [25]. Unlike other hydrothermal conversions, HTG produces hydrocarbon gas that has high HHV and negligible percentage of tar that is considered as advantage over other hydrothermal processes.

2.4 Conversion Chemistry

It is necessary to understand the behavior and mechanism by which the lignocellulosic and algal biomass degrades in the subcritical and supercritical environment. In case of lignocellulosic biomass, the major constituents present are cellulose, hemicellulose, and lignin, which influence the yield and composition of the products formed. Likewise for algal biomass, the degradation of carbohydrates, proteins, and lipids is to be studied. Due to different structures and properties of the major constituents, the depolymerization reaction pathways are different in the hydrothermal environment as given in Fig. 2.

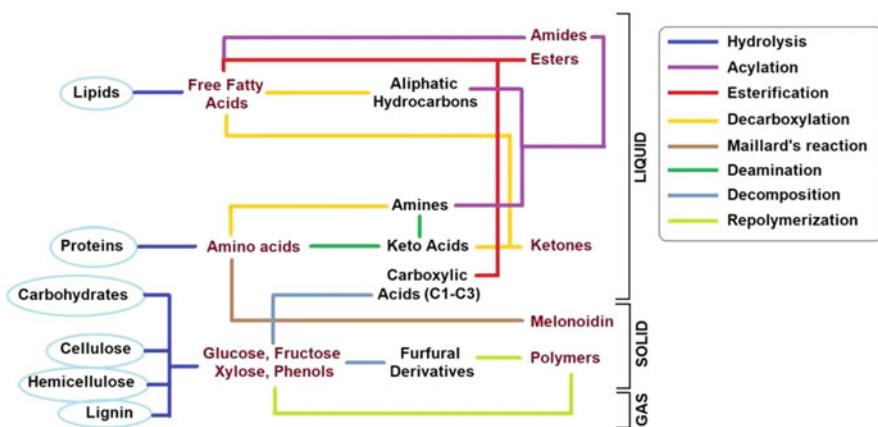


Fig. 2 Hydrothermal conversion reaction pathways

Conversion of Cellulose Hydrothermal depolymerization of cellulose involves several reaction pathways where linear bulk chain of molecules is fragmented into small fractions by hydrolysis and Lobry de Bruyn-Alberda van Ekenstein transformation. It was also observed that the molecular interaction was different in alkaline and acidic environments during the hydrothermal treatment. The alkaline environments led the products from hydrolysis to further degrade by retro-aldol transformation, followed by rearrangement of aldehydes, hydration, and dehydration into simpler acid and alcohols, while acidic environment resulted in the production of mostly 5-hydroxymethylfurfural (5-HMF) and its acid derivatives [26].

Conversion of Hemicellulose Hemicelluloses constitute about 20–40% of the total plant biomass, where during high pressure hot compressed water uncatalysed solvolysis on various wood and herbaceous biomass materials showed that 100% hemicellulose was hydrolyzed and selectively decomposed into saccharides at 230°C, 34.5 MPa at 200 reaction time of 2 min [27]. Sasaki et al. [28] experimented on D-xylose, which is a substitute compound for hemicellulose under subcritical and supercritical water extraction, which confirmed the same reaction pathway at lower temperatures. At higher temperatures and pressures of 360–420°C and 25–40 MPa with a time of 0.02–1 s, retro-aldol condensation and dehydration resulting in glycolaldehyde, glyceraldehyde, and dihydroxyacetone followed.

Conversion of Lignin Lignin consists of p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol units of p-hydroxy-phenylpropanoids held together by C-C or C-O-C bonds. Compared to cellulose and hemicellulose, lignin is relatively resistant to chemical or enzymatic degradation during hydrothermal conversion. In alkaline hydrolysis conditions of lignin, the C-O-C bonds result in phenols and methoxyphenols, where the condensation of these phenolic products resulted in significant amounts of solid residue.

Thus to reduce the solid residue and increase the yield of biocrude, the feedstock chosen must be in such a way that its lignin content is carefully balanced with cellulose and hemicellulose. The hydrothermal conversion of pure lignin at higher temperatures of 350°C, carried out by Wahyudiono et al. [29], resulted in products catechol, phenols, and cresols, which confirms the existence of secondary hydrolysis of methoxy groups. Similar results were found for hydrothermal conversion of Kraft pine resulting in major products as phenol, 4-ethylguaiacol, and methyl dehydroabietate [30].

Conversion of Carbohydrates The carbohydrates in algae mainly constitute polysaccharides, celluloses, hemicelluloses, and starches. They are hydrolyzed to form simple sugars with glucose as the main product; the glucose is then rapidly converted to fructose which in turn degrades with fragmentation to form carbon-carbon double bond components like aldehydes and phenols which are intermediates, thus converting into gaseous products like H₂, CO₂, CH₄, etc. [31].

Conversion of Proteins Proteins mostly consist of linear polymeric amino acids that are connected to carboxylic and amine group using C-N bond links. During the hydrothermal conversion process, these bonds get hydrolyzed to produce free amino acids which quickly undergo decarboxylation and deamination to produce hydrocarbons, amines, aldehydes, and acids [32].

Conversion of Lipids Lipids are mainly comprised of fatty acid triglycerides (TAG) which are nonpolar components with aliphatic characteristics. TAG is hydrolyzed to form fatty acids and glycerol, where glycerol readily gets converted into water-soluble components. Free fatty acids are pretty much stable but partially get converted into hydrocarbons via decarboxylation [33].

3 Hydrothermal Conversion Process Conditions

The hydrothermal conversion processes depend upon various parameters: temperature and heating rate, solvent or hydrothermal media, biomass to solvent loading, residence time, and catalysts. Once the reaction is over, the reaction products are taken out and filtered for the residual water. Then it is washed with extraction solvent to leach out the biocrude from the biochar, where the excess solvent is removed by vacuum evaporation. There are various methods by which the recovery of the products is calculated, and most widely used conventions are given below:

$$\text{Biocrude yield(wt\%)} = W_{\text{es}}/W_{\text{f}} \times 100 \quad (1)$$

$$\text{Biogas yield(wt\%)} = W_{\text{c}} - W_{\text{rp}}/W_{\text{c}} \times 100 \quad (2)$$

$$\text{Biochar yield(wt\%)} = W_{\text{r}}/W_{\text{f}} \times 100 \quad (3)$$

$$\text{Water Soluble Products yield(wt\%)} = 100 - (\text{Crude} + \text{Gas} + \text{Residue}) \quad (4)$$

where W_f is the weight of the biomass (dry basis); W_{es} is the weight of products soluble in extraction solvents (ether, acetone, acetone, dichloromethane, etc.); W_c is the charged weight (biomass + hydrothermal media); W_{rp} is the weight of reaction products; and W_r is the weight of solid residue, i.e., biochar.

Some of the woody and algal feedstock, their possible hydrothermal pathway, type of reactor and its specifications, hydrothermal media used, catalyst, and the extraction solvent used are listed Table 4.

3.1 Effect of Temperature

Temperature plays an important role in the hydrothermal processing irrespective of biomasses. The temperature for a typical hydrothermal conversion process ranges between 180 and 700°C, and it mainly depends on the type of feedstock and its constituent composition (Table 4). Under such given elevated temperatures, it shows symbiotic effect in the yield of resultant products (biochar, biocrude, and biochar) from the biomass. The increased temperature depolymerizes the long chain complex organic molecule of length 800–10,000 units into chemicals of C₁₅₊ to simple gases like H₂, CH₄, and CO₂. Such conditions not only improved the reaction rate but also created variation in reaction mechanisms. Tungal and Shende [34] explained the effect of temperature on pine sawdust under carbonization and liquefaction conditions, where the biocrude yield increased from 24.04 to 30.5% at 1:10 biomass loading and 90 min reaction time [34]. The tar formed during the hydrothermal conversion process is due to the impact of temperature under the subcritical condition, and its formation is extremely lowered under supercritical conditions. The two reasons that controlled this reaction are (1) reduced dielectric constant which led to free-radical reactions to leaving away with gaseous products and (2) under supercritical region tarry material which behaves like a solvent [51]. From studies it is observed that when operating temperature is elevated beyond 500–600°C, the depolymerization reaction occurs resulting in dissociation of complex bonds into simpler gaseous molecules [35]. Figure 3 shows the effect of temperature (225–600°C) on the yield of different hydrothermal products. This effect was also confirmed by a recent study by Alper et.al [38] on hydrothermal liquefaction of spruce wood at 250–300°C; the yield of biocrude increased slightly from 3.9 to 6.6 wt%. But beyond 300–350°C, the yield progressively decreased to 4.9 wt% due to the vaporization of biocrude at this temperature range [38]. Similar phenomena was observed beyond the supercritical condition (>374°C, 219 bar) in the case of algal biomass *Posidonia oceanica* due to the stimulation of steam-reforming and methanation reactions reducing the liquid and solid residue while increasing the gaseous products [50].

Table 4 Reaction parameters of different woody and algal species

Feedstock (possible hydrothermal routes)	Reactor specifications	Temperature range (°C)	Hydrothermal media	Catalyst	Extraction solvent	Ref
Pine wood (HTC, HTL)	300 mL SS316 PARR reactor with heating rate 5 K/min	200–275	Water	5 wt% Ni(NO ₃) ₂	Ethyl acetate, acetone	[34]
Pine wood (HTG)	100 mL SS 316 batch-type autoclave reactor with heating rate of 8–10 K/min	500–600	Water	10 wt% K ₂ CO ₃	—	[35]
Pine wood (HTC, HTL)	600 mL stainless steel autoclave reactor with heating rate of 10 K/min	200–350	50% aqueous EtOH, MeOH	—	Acetone	[36]
Oak wood (HTL)	10 mL AISI 316 tubular microreactor with heating rate of 60 K/min	260–320	Water	Fe, Fe ₂ O ₃ , Fe ₃ O ₄ (0.05–0.3 g/g biomass)	Acetone	[37]
Spruce wood (HTL)	600 mL Parr 4,848 high-pressure reactor with heating rate of 5 K/min	250–300	Water	KFAAl ₂ O ₃	Dichloromethane	[38]
Rice straw (HTC)	2 L stainless steel pressure reactor	180–300	Water	—	—	[39]
Rice straw (HTL)	1,000 mL GSHA-1 type autoclave with heating rate of 3 K/min	260–300	EtOH-water, 2-propanol-water	—	Tetrahydrofuran	[40]
Common reed (HTL)	250 mL SS316 autoclave reactor with heating rate of 3 K/min	250–290	EtOH, MeOH	10 wt% NaOH	Benzene, diethyl ether	[41]
Corncob (HTL)	250 mL Parr reactor with heating rate of 5 K/min	300–360	Water, EtOH	5–10% NaOH, KOH	Acetone	[42]
Cotton cocoon shell (HTL)	100 mL SS316 cylindrical autoclave reactor with heating rate 5 K/min	235–300	Acetone, water	NaOH, Na ₂ CO ₃ , KOH, K ₂ CO ₃	Benzene, acetone	[43]
<i>Nannochloropsis</i> sp. (HTC, HTL)	500 mL SS316 batch reactor (MMJ500) with heating rate of 6 K/min	210–250	Water	5 wt% Nano-Ni/SiO ₂ , synthesize zeolite, Na ₂ CO ₃	Dichloromethane	[44]
<i>Enteromorpha prolifera</i> (HTL)	1,000 mL stainless steel autoclave	250–310	Water	0.02 M H ₂ SO ₄ , 0.2 M CH ₃ COOH	Dichloromethane	[45]

(continued)

Table 4 (continued)

Feedstock (possible hydrothermal routes)	Reactor specifications	Temperature range (°C)	Hydrothermal media	Catalyst	Extraction solvent	Ref
<i>Chlorella pyrenoidosa</i> (HTL)	100 mL Parr 4,593 stainless steel reactor with heating rate of 6 K/min	240–280	Nanopure® water	Pd/C, Pd/Al ₂ O ₃ , Pt/C, Pt/Al ₂ O ₃ , Al-Ni, NaOH, Na ₂ CO ₃	Toluene	[46]
<i>Nannochloropsis gaditana, Chlorella sp.</i> (HTC, HTL)	PARR 4,593 stainless steel bench top reactor	180–330	Water	—	Dichloromethane	[47]
<i>Spirulina</i> (HTL)	100 mL 316 stainless steel batch reactor	230–290	Water	Ni/TiO ₂	Dichloromethane	[48]
<i>Tetraselmis</i> sp. (HTL)	7.5 mL micro-tubing reactor	250–350	Water	—	Dichloromethane, n-hexane	[49]
<i>Posidonia oceanica</i> (HTL, HTG)	100 mL batch-type reaction vessel	300–600	Water	—	—	[50]

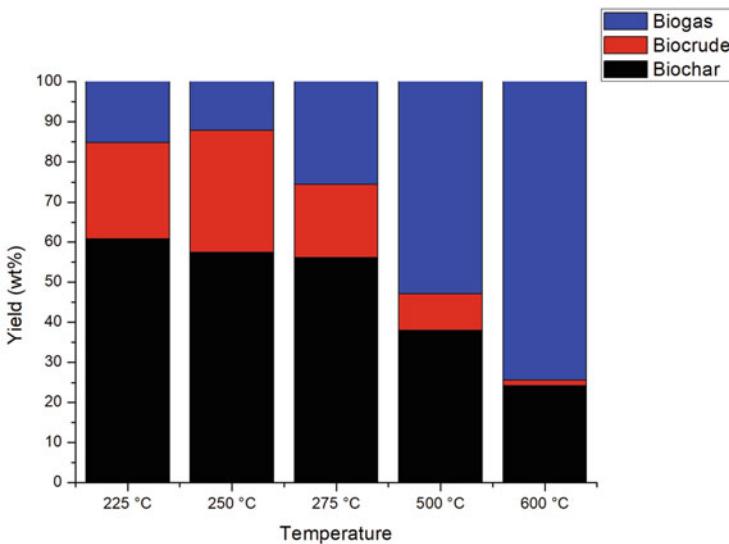


Fig. 3 Effect of temperature on yield of hydrothermal products

3.2 Effect of Hydrothermal Media

The hydrothermal media are generally called solvents, and they enhance the stability and solubility of the depolymerized macromolecules. Under subcritical conditions, these solvents act not as molecules but as radicals and induce the ionic reactions [52]. In most of the cases, deionized water is used as solvent, and sometimes Nanopure® water having ionic purity of 18.2 MΩ was used to eliminate any effects caused by the minerals present in tap water [46]. Few other studies [36, 40–43] revealed that replacing a portion of water with compounds like ethanol, methanol, acetone, and 2-propanol enhances the ionic product of the mixture yielding maximum biocrude and minimum biochar at 50:50 solvent to water ratio as shown in Figs. 4 and 5.

3.3 Effect of Biomass to Solvent Ratio

The amount of solvent/hydrothermal media present inside the reactor is very crucial for the process. If the quantity is very less, it enhances carbonization, and on excess it promotes gasification of all residual materials irrespective whether it is of lignocelulosic or algal origin. Hence the biomass to solvent ratio has to be maintained carefully. Tungal and Shende [34] explained the effect of biomass to solvent ratio on

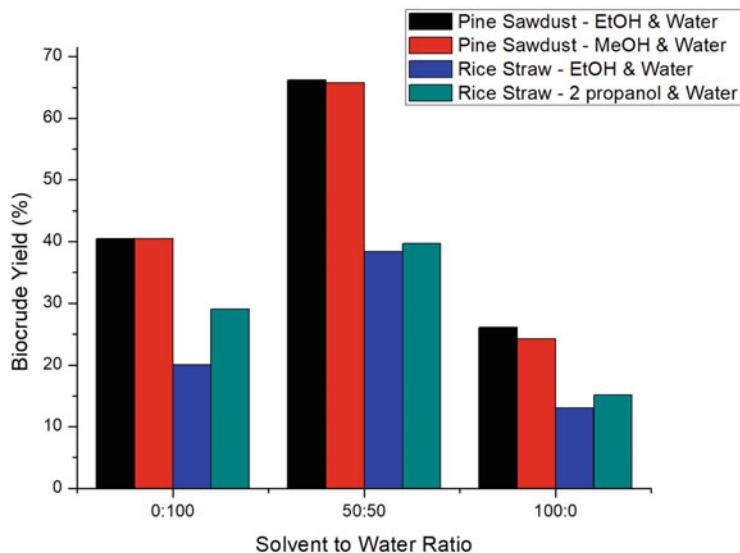


Fig. 4 Effect of hydrothermal media on biocrude yield

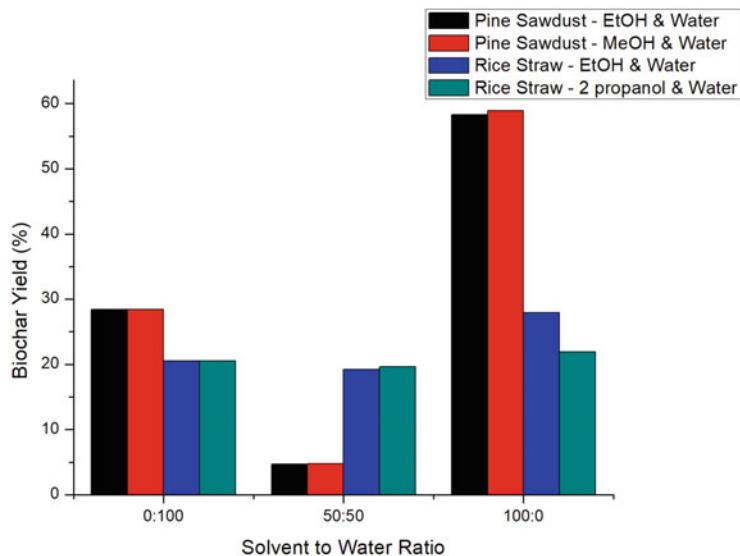


Fig. 5 Effect of hydrothermal media on biochar yield

pine sawdust under liquefaction conditions of 250°C, where the biocrude yield increased from 22.14 to 33.1% with catalyst loading of 5 wt% Ni(NO₃)₂ and 120 min reaction time [34]. This effect is shown in Fig. 6.

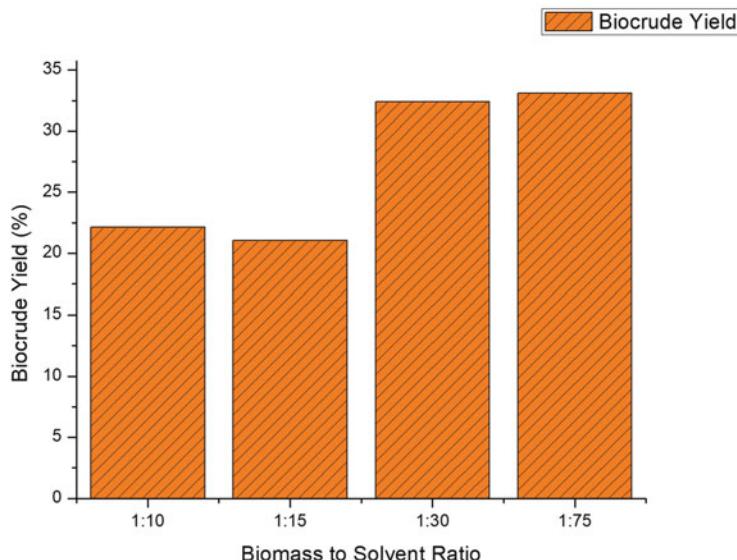


Fig. 6 Effect of hydrothermal media on biochar yield

3.4 Effect of Catalyst

Water acts itself as a catalyst during subcritical or supercritical hydrothermal conditions, and yet the products resulted with mostly oxygenated compounds with low high heating value (HHV). Thus to reduce the high O/H ratio in the resulting biocrude, it is required to add more catalysts into the reacting system. The addition of catalysts improves the gasification efficiency and reduces the solid residue (tar and char) by suppressing the condensation and repolymerization into stable macromolecules. Alkali salts and hydroxides have been frequently used as homogeneous catalysts, whereas Ni, Fe, Al, Pd, Pt, and Ti were used as heterogeneous catalysts, which were utilized to enhance the yield of biocrude.

Homogeneous Catalysts Homogeneous catalysts improve gasification by accelerating the water-gas shift reaction, thereby increasing the liquid product yields. They raise pH of the mixture to more alkaline, which in turn inhibits the dehydration of the cellulose, hemicellulose, and lignin; thereby increasing the H/C ratio in the biocrude and biochar. Alkali addition suppresses tar and biochar formation during the hydrothermal conversion process. It also prevents higher degree of oxygen removal in the biocrude, and instead of decarboxylation, it might result in the formation of unstable unsaturated compounds that can be easily polymerized into char and tar.

Küçük and Ağırtaş [41] investigated alkali-catalyzed hydrothermal liquefaction of common reed in subcritical water environment, where catalytic solvent (ethanol) + 10% NaOH resulted in high conversion of 57.6% at 290°C [41]. In another

study, Khampuang et al. [42] observed that liquefaction performed for 60 min at 340°C with a 1:1 (v/v) ethanol/water with addition of 10 wt% of NaOH resulted in oil yield of 50.2–57.2%; rather with no catalyst it was 49.0%. The oil yield with KOH addition (51.4–57.5%) was slightly higher than that with NaOH (50.5–56.4%) [42]. Similarly, alkali especially potassium in the form of K₂CO₃ exhibited a progressive effect on yield of biocrude. The hydrothermal treatment of cotton cocoon shell showed a catalytic activity which is as follows: KOH > NaOH > K₂CO₃ > Na₂CO₃ [43]. The alkali catalysts weaken the C-C bond, thereby decreasing the activation energy. It also triggers biomass swelling and increase in the surface area exposed, enhancing the retro-aldol cleavage. These alkali catalysts have the tendency to promote water-gas shift reaction during the hydrothermal conversion, thus favoring H₂ and CO₂ formation from CO. The resulting hydrogen gas in turn acts as a reducing agent, increasing the HHV and quality of the biocrude.

Heterogeneous Catalysts Heterogeneous catalysts have been mostly used in hydrothermal gasification process and low-temperature applications, where they enhance the quality of the biocrude obtained. de Caprariis et al. [37] investigated that HTL of oak wood with addition of Fe as a catalyst increases the quality and quantity of biocrude. Fe acts as a sacrificial catalyst, which in turn undergoes surface oxidation into Fe₂O₃, thereby reducing the acids and aldehydes formed during the process. Gasification is crucial to a certain extent for biocrudes containing higher percentages of oxygenated compounds. Few other studies show that by doping oxides like Al₂O₃ with active substance like KF, Pd, and Pt and using it as a catalyst, the yield of the biocrude increased significantly [38, 46]. However, extensive gasification will reduce the biocrude yield. Some of the other heterogeneous catalysts reported for hydrothermal conversion of lignocellulosic and algal biomass include Ni doped over SiO₂, TiO₂, and zeolite [44, 48].

4 Biomass to Fuel

The useful products obtained from the hydrothermal processing are biochar, biocrude, and biogas, which have their own significance. These products were always energy intensified compared to their feedstock. This was confirmed by elemental analysis of the feedstock and the resulting products. The biochar obtained is converted into pellets and used for various applications, whereas the biocrude and biogas are further purified to get fine chemicals. The main parameter that is to be noted for any fuel is its heating value. The energy density of products can be compared by calculating the HHV using the united formula by Channiwala and Parikh [59] that can be used for both feedstock and the resulting products [59]:

$$\text{HHV}(\text{MJ/kg}) = 0.3491(\text{C}) + 1.1783(\text{H}) + 0.1005(\text{S}) + 0.1034(\text{O}) + 0.0151(\text{N}) + 0.021(\text{A}) \quad (5)$$

$$\text{O} = 100 - (\text{C} + \text{H} + \text{N} + \text{S}) \quad (6)$$

$$\text{Energy Densification(ED)} = \text{HHV}_{\text{(Biochar or Biocrude)}} / \text{HHV}_{\text{Biomass}} \quad (7)$$

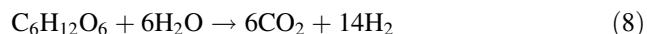
The elemental composition of the raw material, biochar, and biocrude obtained from the hydrothermal carbonization and liquefaction process is given in Table 5.

The high heating value (HHV) of the hydrothermal products compared to the feedstock is increased significantly due to the carbonization. It is observed from Table 5 that the hydrothermal products (biochar and biocrude) have a high energy densification ratio higher than 1, which proves the decarboxylation and deoxygenation reactions were involved during the hydrothermal carbonization and liquefaction. Table 6 shows the elemental composition of reference feedstock. Figure 7 depicts the van Krevelen plot, and it shows that the lignocellulosic feedstock is converted to products similar to that of lignite and liquefaction of algal biomass resulted in biocrude that resembles petroleum crude. The only disadvantage is the high nitrogen content in the biocrude.

Compared to other energy intensification processes, the hydrothermal processes have higher ratios and also low heat of reactions as the subcritical and supercritical water lowers the activation energy. Additionally, the mechanical dewatering or any other preheating is not required, as the feedstock of the process is moist biomass.

Hydrothermal coal is also called biocoal and has ash melting point similar to lignite, although in the case of algal biomass, the minerals in the solid product fuse together to form a sticky dense slurry-like material that changes the behavior of biochar entirely compared to lignocellulosic biochar. The algal biochar and solid residue are hygroscopic, and they are difficult to separate. Materials that are obtained from hydrothermal carbonization also have shown promising properties with varying functionalities, morphologies, and porosities [60]. They have important applications in a variety of modern fields such as electrode materials in superior performance supercapacitors, Na-based batteries, Li-ion batteries, and fuel cells [14].

At supercritical conditions, hydrogen and methane from biomass can also be manufactured from single-step hydrothermal gasification process without the formation of any solid residue:



Thus, Table 7 shows promising results that both lignocellulosic and algal biomass can be used for hydrogen gas production.

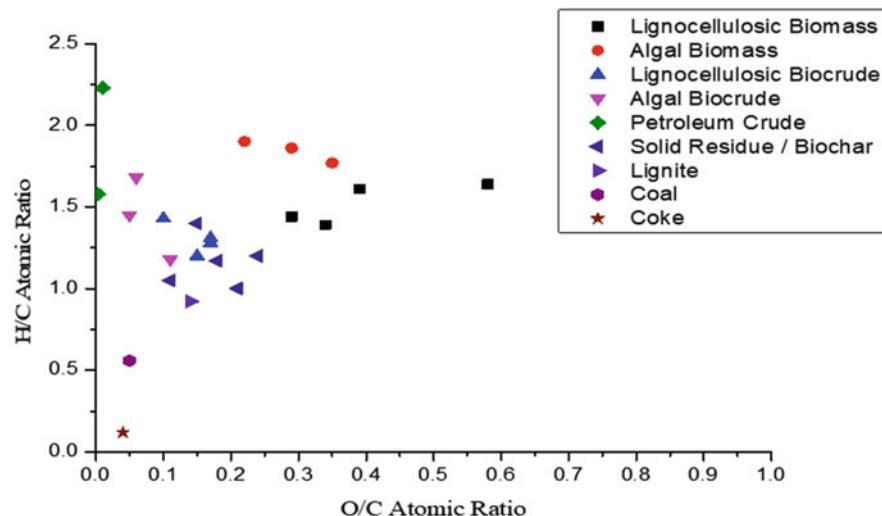
Table 5 Energy intensification of woody and algal species

			Temp (°C)	C	H	N	S	O	H/C	O/C	HHV MJ/kg	ED	Ref
PS	Raw		52.5	6.32	0.10	0.05	40.6	1.44	0.29	29.98			
	Biochar	HTL	250	72.4	6.31	0.78	–	20.51	1.05	0.11	34.84	1.162	
	Biocrude	HTL	250	63.5	6.78	0.65	–	29.07	1.28	0.17	33.17	1.107	
RS	Raw		36.81	5.025	1.059	0.416	56.69	1.64	0.58	24.69			
	Biochar	HTC	220	45.50	4.43	1.56	0.15	21.59	1.17	0.18	23.37	0.947	
	Biocrude	HTL	300	71.34	8.509	1.451	0.211	18.489	1.43	0.10	36.89	1.494	
BW	Raw		49.1	5.7	0.3	0.05	44.5	1.39	0.34	28.47			
	Biochar	HTC	210	56.9	5.7	0.3	0.2	36.9	1.20	0.24	30.42	1.069	
	Biocrude	HTL	300	68.2	6.8	–	–	27.3	1.20	0.15	34.64	1.217	
CC	Raw		43.1	5.8	0.23	0.12	44.6	1.61	0.39	26.51			
	Biochar	HTC	210	56.7	4.72	0.53	0.06	31.5	1.00	0.21	28.63	1.080	
	Biocrude	HTL	280	63.0	6.87	0.42	1.31	28.82	1.31	0.17	33.21	1.253	
NS	Raw		49.93	7.91	6.33	0.64	28.71	1.90	0.22	29.88			
	Biochar	HTC	210	54.89	6.42	5.98	0.50	21.79	1.40	0.15	29.12	0.975	
	Biocrude	HTC	250	72.65	10.19	5.13	0.42	10.88	1.68	0.06	38.61	1.292	
EP	Raw		35.20	5.20	2.10	–	32.98	1.77	0.35	21.86			
	Biocrude	HTL	290	69.2	6.8	3.9	–	20.1	1.18	0.11	34.31	1.570	
	Raw		46.16	7.14	10.56	0.74	35.44	1.86	0.29	28.43			
SP	Biocrude	HTL	350	73.73	8.90	6.30	0.90	10.17	1.45	0.05	37.46	1.318	
												[58]	

PS pine sawdust, RS rice Straw, BW beech wood, CC Corn cob, NS *Nannochloropsis* sp., EP *Enteromorpha prolifera*, SP *Streptomyces platensis*

Table 6 Elemental composition of reference feedstock

	C	H	N	S	O	H/C	O/C	HHV
Coke	87.91	0.88	1.19	0.66	9.36	0.12	0.04	32.78
Coal	83.02	3.89	1.59	1.03	10.47	0.56	0.047	34.78
Lignite	67.8	5.2	0.8	0.8	25.4	0.92	0.14	32.51
Petroleum crude 1	79.5	14.8	3.5	0.1	2.1	2.23	0.01	45.47
Petroleum crude 2	87.1	11.5	0.1	0.5	0.8	1.58	0.003	44.09

**Fig. 7** van Krevelen plot for biomass and hydrothermal products**Table 7** Gaseous product composition result of hydrothermal conversion from woody and algal biomass (yield moles/kg biomass)

Feedstock	Temperature (°C)	H ₂	CO	CH ₄	CO ₂
Pine sawdust	225	1.32	2.85	0.03	7.80
	275	12.26	6.03	0.44	8.36
	500	15.52	7.12	2.25	13.81
	600	26.15	8.90	2.41	23.32
<i>Enteromorpha prolifera</i>	300	0.15	0.6	—	8.9
	400	0.9	0.5	0.3	10.2
	500	3.2	—	2.4	8.4
	600	10.2	—	6.1	6.7

Table 8 Essential chemicals from hydrothermal processing

Feedstock	Compounds	Relative area %	Significance
Beech wood	Guaiacol	26.4	Flavoring agent in baking industry
	2,6-Dimethoxyphenol (Syringol)	18.6	Food industry to artificially produce smoky aroma to food items
	2-Methyl-2-cyclopenten-1-one	7.89	Ketonic group added as ingredient in fragrance
	Acetic acid	4.41	Production of vinyl acetate monomer, as solvent in recrystallization to purify organic compounds
Pine wood	2-Furancarboxaldehyde/furfural	77.68	Herbicide, solvents in agricultural preparations
	1-Hydroxy-2-methoxybenzene	42.99	Herbicide and also in biomedical applications
	5-Methyldihydro-2(3H)-furanone	8.85	Flavor and fragrance agents that give the caramel-like odor and brown-type flavor
	2-Oxo-3-cyclopentene-1-acetaldehyde	7.61	Solvent for extraction due to its high polarity
	Acetic acid, butyl ester	2.22	Solvents, flavoring agents
Corncob	p-Xylene	6.65	Polymer industry for production of polyethylene terephthalate
	Naphthalene, decahydro-	6.57	Solvent
	Ethylbenzene	3.60	Manufacturing products such as inks, insecticides, and paints
	Benzene, 1,3-dimethyl-	2.85	Smaller proportion in making resins, rugs, rubber lubricants, etc.
<i>Nannochloropsis</i> sp.	n-Hexadecanoic acid (C16:0)	23.45	Ingredient in soaps, cosmetics, etc.
	cis-9-Hexadecenoic acid (C16:1)	19.49	Disinfectants in water treatment
	Docosahexaenoic acid	8.50	Food industry as supplements
	Oleic acid (C18:1)	5.72	Manufacture of soaps as an emulsifying agent
	Tetradecanoic acid (C14:0)	5.68	Medicine preparation
	Pyrrolidine derivative	5.00	Pharma industry to produce tolmetin
<i>Enteromorpha prolifera</i>	1,4-Pentadiene	20.12	Paints, flavors, perfumes, varnishes as odor-causing agents
	3-Methyl-2-cyclopenten-1-one	10.26	Food additives, flavors, colorings, etc.
	Palmitic acid	9.78	Saponification of soaps

(continued)

Table 8 (continued)

Feedstock	Compounds	Relative area %	Significance
	2,3-Dimethyl-2-cyclopenten-1-one	7.77	Solvent in many extraction process
	3-Methyl-1,2-cyclopentanedione	6.68	Ketonic group added as ingredient in fragrance

5 Biomass to Fine Chemicals

The primary objective of any hydrothermal processing is to derive value-added products (biochar, biocrude, and biogas) in which biocrude on further processing results in a significant amount of fine chemicals. All these years many researchers have confirmed the presence of various fine chemicals in the biocrude through GC-MS analysis. The chemicals identified in biocrude obtained from the hydrothermal conversion of few woody and algal biomass feedstock and its commercial significance are listed in Table 8.

6 Conclusion

The hydrothermal conversion of both lignocellulosic and algal biomasses was studied with the help of predefined reaction mechanisms of their respective constituents. This chapter briefly explained about the advanced technologies that are adapted in generation of energy-intensified fuels and value-added fine chemicals. The hydrothermal technologies with biorefinery would be a promising solution for sustainability as it can be implemented with minor modifications to the current industrial infrastructure. In the energy sector, the biocrude in addition to the natural crude can be used as such as the feed to existing refinery equipment, and there is no need for modification or retrofitting. Thus this technology is yet to be explored, and more value-added chemicals can be obtained from the hydrothermal conversion of lignocellulosic and algal biomass, thereby maximizing the yield of products with commercial significance.

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Biopolymer-Based Nanofibrous Membrane for Water Purification Treatment



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Abstract The availability of the resources is limited due to ever increasing population, unplanned urbanization, industrialization, and improper waste management. Currently, one of the most important environmental issues is water pollution. The bacteria, viruses, intestinal parasites, and other pathogenic microorganisms mainly contaminated the drinking water and it causes the diseases such as diarrhea, dysentery, and typhoid. In 2015, the World Health Organization has reported that 321 children were killed every day by diarrhea. Globally, every year 1.8 million people mostly under 5 years died due to diarrheal diseases alone which is mainly related to water. At present, chemical disinfectants (e.g., chlorine) and polymer membrane-based water filtration system are employed to manage microbial pathogens in the water. The by-products of the chemical disinfectants are highly harmful and problematic. The major concerns in the water filtration of polymer membranes are biofouling and virus penetration. Furthermore, the membrane-based water filtration

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has several challenges including membrane permeability, lifetime, and energy costs. Therefore, interconnected, highly porous nanofibrous polymer membrane filtration could be used to overcome these technical challenges. Owing to lightweight, high permeability, and small pore size, nanofibrous polymer membranes can be potential candidates to remove unwanted smaller particles in the water. The performance of the nanofibrous membrane depends on their fiber thickness, distribution, pore size, porosity, and tortuosity factor. Nanofibrous membrane with desired properties can be obtained for water filtration by electrospinning technique. The antimicrobial activity of the polymer nanofibrous membrane can be further improved by the incorporation of metal oxide nanoparticles because of their good antimicrobial effects. Due to the high antimicrobial effect, zinc oxide nanoparticles have been widely incorporated with polymer to produce nanofibrous membrane for water filtration. In particular, zinc oxide nanoparticles incorporated with bio-based polymer (cellulose acetate) nanofibrous membranes showed potential material for water filtration to ensure safe and easy access drinking water.

Keywords Cellulose acetate, Electrospinning, Nanofibrous membrane, Water purification treatment, Zinc oxide nanoparticles

1 Introduction

Water is a basic resource and it occupies more than 70% of the earth's surface, but its pollution causes millions of people to drink impure water [1]. Around the world, there are 80 countries facing numerous problems in water shortage, and 25% of the population do not have access to fresh drinking water. Therefore, the quality of drinking water is extremely important to avoid waterborne diseases. There are two major types of water pollution, namely, organic and chemical pollution. Organic water pollution is caused by excrement, animal, and vegetable wastes. On the other hand, the household products, heavy metals, drugs, nitrates, phosphates, pesticides, acids, and hydrocarbons used in industries are the main sources for chemical water pollution. In addition, the human activities such as modern agricultural practices, industries, marine dumping, radioactive wastes, urbanization, deforestation, and sewage and waste water are mainly responsible for water pollution. There are many strategies available to purify the water including waste water treatment, desalination, membrane bioreactor, membrane distillation, and heavy metal ion adsorption. Currently, human being is facing three major challenges such as water treatment for drinking purpose, sewage treatment infrastructure, and extreme use of water in agricultural. Water is abundant and accessible, but it is not used for drinking purpose by humans due to its unhealthy condition. In particular, the availability of fresh water for drinking purpose is in great demands in the developing countries. Many studies have reported the effect of various environmental factors of physical

and chemical parameters on the water pollution [2]. Therefore, it is necessary to understand the pathogen concentrations in the water and their treatment process to enhance the purity of water for drinking purpose. It was identified by American Academy of Microbiology that storing and aging are the main reasons to increase the contamination of water in urban areas [3]. A simple in-house water purification is greatly increased due to increasing environmental awareness. The drinking water is one of the main vehicles of pathogen transmission by the fecal-oral route [4]. Enhancing the water quality is the only way to reduce the fecal-oral disease transmission. Many researchers have been developing water treatment process to remove waterborne pathogens from drinking water. There are a variety of process to produce nanofibrous membrane which involves the removal of contaminants from drinking water, namely, synthetic templates, nanoparticles' self-assembly, phase separation and, electrospinning. In these, most of the nanofibrous materials are produced by electrospinning method due to its unique properties. Electrospinning is one of the proficient techniques to develop interconnected porous nanofibrous structure for filtering the microorganisms present in contaminated water [5]. The production of nanofibrous membrane by various biopolymers, namely, cellulose acetate, polysulfone, poly(vinyl alcohol), polyacrylonitrile, polyurethane, and poly(vinylidene fluoride), are commonly used for water purification [6]. The polymers like polyacrylonitrile, polysulfone, polyethersulfone, and poly(vinylidene fluoride) are hydrophobic polymers with excellent physical, chemical, and mechanical properties. However, they are required to have some kind of modification in order to be used in water purification [7]. For this reason, hydrophilic polymers like cellulose acetate is used in all commercial water filtration membranes especially in reverse osmosis process. However, the electrospun cellulose acetate nanofibrous membrane alone has no antibacterial activity which has limited its application including water purification. Consequently, it is necessary to incorporate antibacterial agents in the electrospun nanofibrous membrane to destroy the bacteria in the drinking water during filtration [8, 9]. The electrospun nanofibrous membrane suffers from fouling during electrospinning process [10, 11]. For this reason, there are many surface modification strategies available, namely, grafting, coating, blending, and interfacial polymerization, respectively. For example, Gentamicin is used to eradicate the microorganism, and it reduces fouling. The additives and antimicrobial agents are used to modify the surface of the electrospun membranes to reduce the biofouling during water filtration [11].

2 Influence of Microorganisms in Drinking Water

The World Health Organization (WHO) reported that approximately 663 million people around the world have the problem to access the pure drinking water due to polluted water. According to the Environmental Protection Agency (EPA), there are more than 500 waterborne pathogens present in the contaminated water [1]. These pathogens are the main sources for various chronic and acute level illnesses to the

Table 1 Microorganisms and its health problems.

S. No.	Microorganisms	Health problems
I.		
1.	<i>Escherichia coli</i>	Hemolytic uremic syndrome, nausea, vomiting, severe bloody diarrhea, and abdominal cramps
2.	<i>Salmonella typhi</i>	Typhoid and gastrointestinal problems
3.	<i>Legionella pneumophila</i>	Legionnaires disease
4.	<i>Mycobacterium tuberculosis</i>	Tuberculosis
5.	<i>Vibrio cholera</i>	Cholera and gastrointestinal problems
6.	<i>Shigella</i> spp.	Diarrhea and gastrointestinal problems
7.	<i>Campylobacter jejuni</i>	Enteritis – cramping, diarrhea, fever, and malaise
8.	<i>Salmonella enteritidis</i>	Severe diarrhea
9.	<i>Salmonella choleraesuis</i>	Severe diarrhea
II.		
10.	<i>Adenoviruses</i>	Bronchitis, pneumonia, infections in the respiratory, and intestinal tract
11.	<i>Rotaviruses</i>	Diarrheal disease for infants and young children
12.	<i>Astroviruses</i>	Diarrhea to encephalitis
13.	<i>Enteroviruses</i>	Infect the central nervous system
14.	<i>Noroviruses</i>	Gastroenteritis
15.	<i>Hepatitis A virus</i>	Dark urine, jaundice, stomach pain, fever, and fatigue
16.	<i>Hepatitis E virus</i>	Liver disease
17.	<i>Sapoviruses</i>	Stomach flu
III.		
18.	<i>Cryptosporidium parvum</i>	Severe painful diarrhea, stomach cramps and gastrointestinal problems
19.	<i>Toxoplasma gondii</i>	Toxoplasmosis
20.	<i>Giardia lamblia</i>	Giardiasis
21.	<i>Dracunculus medinensis</i>	Guinea worm disease
22.	<i>Entamoeba histolytica</i>	Amebiasis – amebic dysentery

human [1]. For instance, about 30 million Americans per year are affected by a gastrointestinal illness because of the contaminated drinking water [12, 13]. Some of the harmful microorganisms which are present in the water and its effect on health are summarized in Table 1 [1, 14–17]. The prevention of waterborne infection by such microorganism is of supreme importance.

Microsporidia and *Helicobacter pylori* are emerging pathogens which could be present in drinking water [18]. These pathogens are mostly dangerous because it can cause chronic level diseases and even lead to cancer [19, 20]. *Microsporidia* are

unicellular parasites which causes severe diarrhea and systemic illness in person with acquired immunodeficiency syndrome (AIDS) [21]. *Helicobacter pylori* are intestinal bacteria which have been classified as carcinogenic pathogen by WHO [22]. The microorganism, namely, *Legionella*, grows in piped water distribution systems, whereas guinea worm (*Dracunculus medinensis*) occurs in many water sources [23]. The water contaminants are not easily detected through naked eye, odor, and taste. The microorganisms which are present in water may be beneficial or harmful to human health [1]. Sometimes the very tiny level of microorganisms (*Escherichia coli*, *Giardia*, *Cryptosporidium*) is more dangerous [24–26]. All peoples are not equally affected from the contaminated water; it may depend on the individual health conditions. People with weak immune system particularly infants, young children, pregnant women, old age people and immune suppressive therapy patients, AIDS patients, cancer patients, and organ transplant patients are more vulnerable to the waterborne pathogens [27].

In general, the bacteria are consisting of cell membrane, cell wall and cytoplasm. Gram-positive and gram-negative bacteria are the two major types which presents in the contaminated water. The gram-positive bacteria have one cytoplasmic membrane with a multilayer of peptidoglycan polymer and a thicker cell wall (20–80 nm), whereas gram-negative bacteria wall is composed of two cell membranes, an outer membrane, and a plasma membrane with a thin layer of peptidoglycan with a thickness of 7–8 nm. The bacterial cells range from about 1–10 μm in length and 0.2–1 μm in width, while the viruses are 100 times smaller than bacteria at 0.004–0.1 μm in size. The protozoan cysts are approximately 2–50 μm in diameter [1]. The microorganisms present in the drinking water can be removed or destroyed by various water purification techniques.

3 Water Purification Techniques

There are many well-established techniques available to purify the water, namely, chlorination, membrane distillation, ultraviolet light, ozonation, electrodialysis, ion exchange, etc. [28]. The chlorination process is inexpensive, is easy to handle, destroys the bacteria, and gives long-term protection. The main disadvantage of using chlorine for water treatment is that it easily reacts with organic matters like iron and manganese, even at low concentration which leads to form carcinogenic by-products [29]. The chlorination process destroys the bacteria only at higher level concentration of chlorine which may lead to unpleasant odor and taste of water. The distillation process is one of the most effective methods to purify the contaminated water. The distillation process involves no chemicals but is expensive and has longer process, and mainly the storage of distilled water affects its quality. Ultraviolet light disinfection unit is not used separately; it may be used with mechanical filters, activated carbon filters, reverse osmosis, and water softeners. In ozonation process, ozone is unstable, and it also provides more powerful disinfectant than chlorine. The water treatment process includes sedimentation, precipitation,

adsorption, oxidation, photocatalysis, multistep coagulation, and flocculation [30]. In the 21st century, membrane technologies have been used for water purification due to its high stability, high separation efficiency, and high selectivity. The different types of membranes are available in the market to purify the water, namely, microfiltration, ultrafiltration, reverse osmosis, and nanofiltration, respectively. Generally, the microfiltration membrane pore size ranges between 0.1 and 10 µm which are mainly rejecting the small particles and microorganisms [31, 32]. The ultrafiltration membranes can filter the bacteria and soluble macromolecules such as proteins because it has smaller pores (0.01–0.1 µm) than the microfiltration membranes. Particularly in the reverse osmosis process, the cellulose acetate membranes are used, but it is nonporous, and, therefore, it eliminates the particles, salt ions, organics, etc. [33] The nanofiltration membranes were often called as loose reverse osmosis membranes, and it is porous in nature, but the pores are on the order of ten less; they behave as both reverse osmosis and ultrafiltration membranes [34]. In many countries peoples are using the reverse osmosis process for removing the impurities from water, but unfortunately it reduces the number of beneficial minerals in the drinking water. Therefore, drinking water purified by reverse osmosis process can create heart and muscle health disorder. The microorganisms in water are usually removed by boiling the water, but it is limited to use in all places. The microfiltration membrane fails to eliminate the small-size viruses, while it eliminates the bacterial pathogens. On the other hand, the nanofiltration membranes have a positive charge which can selectively reject the viruses and bacteria. The identification of the microorganism's presence in the water is expensive, and practically it is impossible to do all the time before drinking water. Recently, the polymeric membranes have gained a great attention for water treatment due to its good thermal, mechanical, and chemical properties [35]. There are many methods to develop the polymeric membranes such as interfacial polymerization, phase-inversion, self-assembly, stretching, track-etching, spin coating, and electrospinning [33]. Among them, electrospinning is one of the simple and versatile methods which can be used to produce nanofibrous membrane for water purification [36].

4 Electrospinning Process

The world is facing serious concern in safe drinking water; the electrospinning-based advance nanotechnology could be a promising strategy to purify the water in the near future. Electrospinning-based nanotechnology is playing a vital role in water purification because it can be used to produces innovative structured membrane compared to conventional membrane technique [37]. Electrospun nanofibrous membrane-based water purification can offer a high-standard water quality, viability, low cost, and accessibility of drinking water. Purifying the contaminated water by using electrospun nanofibrous membrane is a simple method to prevent drinking waterborne illness. In addition, the electrospun nanofibrous membrane can provide long-term protection, operated properly, and also remove the turbidity from the

contaminated water [37]. Electrospinning is one of the versatile methods to produce interconnected porous structure which has been useful for many commercial applications. The interconnected porous structure is beneficial for filtering the microorganisms from the contaminated water. Nowadays, the electrospun polymeric nanofibrous membranes have been used for different areas of water treatment process especially for removing the microorganisms and separation of oil-water emulsion [38]. It has been established that high voltage should be applied to the polymer solution during the electrospinning process which leads to the formation of a higher electrostatic field and eventually produces the nanofibers [39, 40]. The opposite charges are connected to the metal collector which is wrapped with aluminum foil. The environmental condition (temperature and humidity) and the electrospinning parameters influenced the quality of the resulting nanofibers. The syringe needle, polymer solution, flow rate, and collector are the important electrospinning parameters which can influence the nanofibrous properties. The bead-free nanofibrous membrane can be obtained by optimizing spinning solution viscosity, concentration, molecular weight, and tip to collector distance [40]. The low-density and interconnecting open-pore nanostructures of the electrospun fibrous membrane are the main advantages of using water purification treatment. The electrospun nanofibrous membrane in filtration application has some other advantages, namely, high flux, low operating pressure, low cost, light weight, textile-like structure, good retention of multivalent anions salts, and cost-effective maintenance.

5 Cellulose Acetate Nanofibrous Membrane for Water Treatment

Cellulose acetate is one of the best biocompatible Food and Drug Administration-approved polymers and has drawn great attention for water filtration applications [41]. The electrospun cellulose acetate nanofibrous membrane not only filters the microorganisms, but it may also remove the chromium, metal ions, and toxic organic hydrocarbons [42]. The magnetic nanoparticles immobilized on cellulose acetate nanofibrous membrane have been fabricated for the removal of lead from polluted water [43]. The highly interconnected porous cellulose acetate nanofibrous membrane with uniform distribution is observed in Fig. 1a. The average fiber diameter of the cellulose acetate nanofibrous membrane is found to be 110 ± 30 nm. Hence, uniform, continuous, smooth, and interconnected porous nanosized fibers are present in the electrospun cellulose acetate membrane which is mainly suitable to filter the microorganisms present in the water. Flux and selectivity are the two factors to analyze the functionality of the membrane. The above two factors are mainly depends on the wettability, pore size, porosity, pressure drop and thickness of the electrospun membrane [44]. The wettability of the solid surface plays a main role in water purification treatment. The electrospun cellulose acetate nanofibrous membrane contact angle is found to be 50.2° in 0 s as seen in Fig. 2. Increasing the time

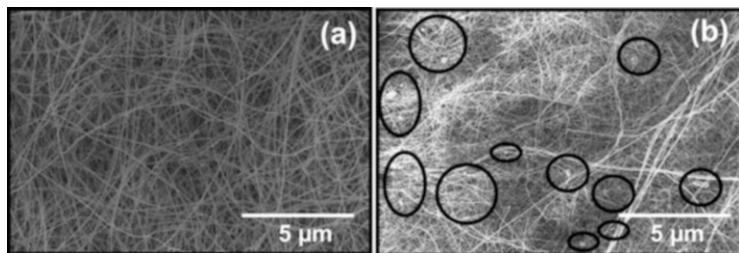


Fig. 1 Scanning electron microscopic images of the electrospun cellulose acetate nanofibrous membrane **(a)** before filtration and **(b)** after filtration

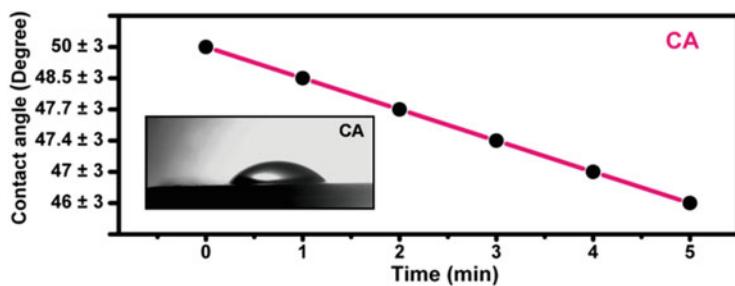


Fig. 2 Contact angle measurements of the electrospun cellulose acetate nanofibrous membrane

decreases the contact angle which is also seen in Fig. 2. Hence, this result clearly gives that the hydrophilic nature of the electrospun cellulose acetate nanofibrous membrane is suitable for water filtration applications.

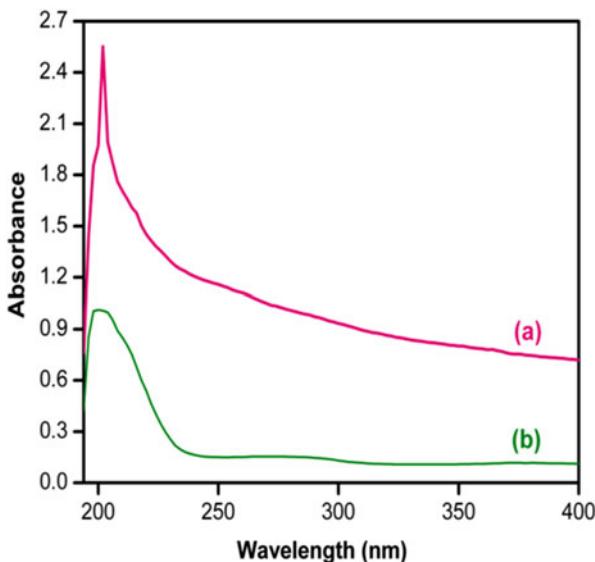
After filtering the piped river water using the developed electrospun cellulose acetate nanofibrous membrane morphology is as seen in Fig. 1b. The microorganisms are filtered and stayed in the surface of the electrospun cellulose acetate nanofibrous membrane which is clearly seen in Fig. 1b. Similarly, the electrospun cellulose acetate nanofibrous membrane was used to filter the bacteria, sand, coal particles, yeast, viruses, and few metal ions [39]. Therefore, the prepared electrospun cellulose acetate nanofibrous membrane is undoubtedly filtering the microorganisms which are present in water. The prepared electrospun cellulose acetate nanofibrous membrane filters the bacteria, but it does not completely destroy the bacteria which are stayed in the surface of the membrane. To overcome the above problem, the antibacterial agent is essential to prevent the growth of bacteria and reduce the harmful effects. In recent years, the metal oxide has been frequently used as antibacterial agents namely zinc oxide, titanium oxide, copper oxide, aluminum oxide, silicon oxide, iron oxide, and cerium oxide, respectively. Of these, zinc oxide has excellent antibacterial activities, and its application is versatile in nature. Hence, the antibacterial rich material like zinc oxide nanoparticle is incorporated into the cellulose acetate and develops the zinc oxide-cellulose acetate nanofibrous membrane.

6 Zinc Oxide Nanoparticles

Zinc oxide is one of the Food and Drug Administration-approved nanomaterial, and it is used as many ways in food additives [45]. Although, zinc oxide is a source of zinc which serves as an essential micronutrient in day-to-day life and behaves as a significant role in the growth and development of children and adult health. Zinc oxide nanoparticles are non-toxic and good biocompatibility to human cells but it is harmful to microorganisms due to its excellent antibacterial activity. The zinc oxide nanoparticles have excellent antimicrobial activities compared to bulk zinc oxide; the nanozinc oxide particles easily interact with the surface of the bacteria or core of the bacteria where it passes through the cell and then establishes the numerous bactericidal mechanisms. Due to these advantages, zinc oxide nanoparticles have been widely investigated and used in various fields, namely, wound dressings, cosmetics, tissue engineering, drug delivery, and food packaging. In recent years, zinc oxide nanoparticles have been used mainly for waste water treatment. The nanostructure zinc oxide loaded activated carbon-coated cloth is applied for the removal of copper from the waste water treatment [46]. The zinc oxide-incorporated poly(vinyl alcohol) nanofibrous membrane removes the uranium with copper and nickel from the contaminated water [47]. The synthesized zinc oxide nanoparticles which incorporated activated carbon nanocomposites has excellent hydrophilic properties [43]. In addition, it has excellent adsorption capacity at 92 mg/g within a short period of time (45 min) and may be used for the removal of lead ions from wastewater treatment. The zinc oxide-loaded montmorillonite clay nanocomposite has been developed for the removal of lead and copper from the aqueous solution. Its adsorption capacity is observed at 99.22 mg/g within 90 min [48]. Zinc oxide has exhibit excellent mechanical properties, good chemical stability, and heat resistance which have been proven to be a promising material for antibacterial agent. Increasing the weight percentage of zinc oxide nanoparticles in cellulose composite is greater than the antibacterial activity. The core shell of the electrospun zinc oxide-nylon 6,6 nanofibrous membrane has been used as a water treatment for the removal of organic pollutants due to their good photocatalytic properties, structural flexibility, and stability [49]. The incorporation of inorganic nanofillers like zinc oxide can enhance the polymer membrane properties. The inorganic fillers are added directly to the polymeric solution and electrospun to produce the single hybrid structure which enhances the characteristic properties and strength of the electrospun nanofibrous membrane [50].

Zinc oxide nanoparticles can be synthesized by many methods to control the synthesis parameters. Depending upon the application, various types of protocols are used, and the properties can be tailored by the shape and size of the zinc oxide. The significant parameters like chemical and physical parameters, namely, the solvent type, precursors, pH, and the temperature, are highly considered. A variety of zinc oxide morphologies such as nanorods, nanosphere, nanotubes, nanowires, nanoneedles, and nanorings have been successfully synthesized and used in many commercial applications. Each zinc oxide nanostructure has specific structural,

Fig. 3 UV Spectrum of synthesized zinc oxide nanoparticles (a) 3% dilution (b) 1% dilution

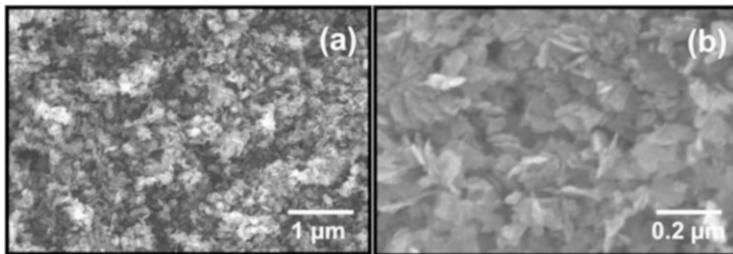


optical, electrical, and physicochemical properties using remarkable applications. These zinc oxide nanostructures have been developed by a variety of physical and chemical techniques; however, the chemical techniques offer better control of the particle size and morphology. The most approved synthesized methods include thermal evaporation of zinc oxide powders at 1400 °C, hydrothermal synthesis, sol-gel technique, simple thermal sublimation, self-combustion, polymerized complex method, vapor-liquid-solid technique, double-jet precipitation, and solution synthesis. The solution processes are used by few researchers to yield selective zinc oxide nanostructures. Normally, the antibacterial tests are done in aqueous media or cell culture media. Zinc oxide is known as nearly insoluble in water, and it agglomerates immediately with water during synthesis due to the high polarity of water leading to deposition. The matters of accumulation, re-precipitation, settling, or non-dissolution are delaying the synthesis processes.

The zinc oxide nanoparticles are prepared from the aqueous solution of zinc sulfate and sodium hydroxide in the ratio of 1:2. Initially, the synthesized zinc oxide nanoparticles are identified by UV–Visible spectroscopy. The synthesized zinc oxide nanoparticles are observed by UV–Visible absorption spectrophotometer as shown in Fig. 3. The spectrum shows a peak at 210 nm formed due to the conversion of bulk zinc oxide particles to nanozinc oxide particles. The bulk zinc oxide particles lies the bandgap wavelength of 388 nm while the nanozinc oxide particles bandgap wavelength at 210 nm due to the interband transition of copper electron from deep level of the valence band [51]. The particle size analyzer also confirms that the synthesized zinc oxide nanoparticles are in nanosize at about approximately 296 nm as seen in Table 2. The average size of the synthesized zinc oxide nanoparticles are further confirmed by SEM analysis (Fig. 4). The surface morphology of the

Table 2 Particle size analyzer data for the synthesized zinc oxide nanoparticles

Z-Average (d. nm)	Size (d. nm)	% Intensity	Width (d. nm)	Pdl
295.7	207.6	100	39.6	0.460

**Fig. 4** Scanning electron microscopic image of synthesized zinc oxide nanoparticle (a) magnification at 1 μm and (b) magnification at 0.2 μm

synthesized zinc oxide nanoparticles is found to be 150 nm–300 nm respectively. Therefore, UV-visible spectra, particle size analyzer, and scanning electron microscopy images confirm that the synthesized zinc oxide particles are in nanoform and it is fit for use in water purification treatment.

7 Zinc Oxide Nanoparticle Dispersed Cellulose Acetate Nanofibrous Membrane

Electrospinning is one of the direct processes to produce nanofibrous membrane due to its easy incorporation of additives into the homogeneous polymer solution. The zinc oxide nanoparticles (0.5 wt %) are dispersed into the homogeneous 10 wt % cellulose acetate solution using sonicator for 4 h at room temperature. The electrospun zinc oxide nanoparticle dispersed cellulose acetate nanofibers are continuous, bead free, smooth, uniform in nature, and interconnected porous structure, and the average fiber diameter is found to be approximately 130 ± 30 nm as seen in Fig. 5. The average fiber diameter is increased from 110 ± 30 nm to 130 ± 30 nm which confirms the uniform distribution of zinc oxide nanoparticles in to the cellulose acetate nanofibrous membrane. The smooth, continuous, uniform distribution of zinc oxide nanoparticles in to the cellulose acetate nanofibrous membrane is once again clearly confirmed by transmission electron microscopy as seen in Fig. 6a. No other impurities are present in the electrospun zinc oxide nanoparticle dispersed cellulose acetate nanofibrous membrane which is confirmed by energy-dispersive X-ray (EDX) spectrum (Fig. 6b). The theoretical expected stoichiometric mass percent value of the zinc is 80.3% and oxide is 19.7%, respectively [50]. The EDX spectrum result confirms the presence of zinc oxide nanoparticles, uniform distribution, and excellent purity (zinc content – 63.65% and oxygen content –

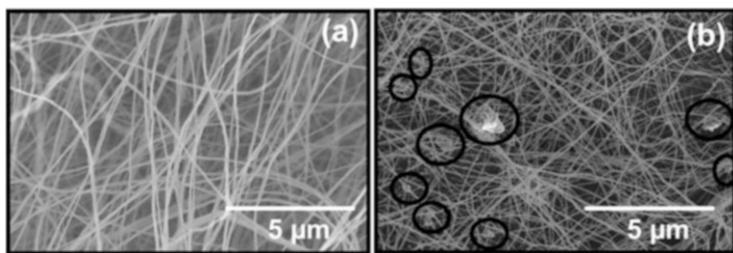


Fig. 5 Scanning electron microscopic images of electrospun zinc oxide nanoparticles dispersed cellulose acetate nanofibrous membrane **(a)** before filtration and **(b)** after filtration

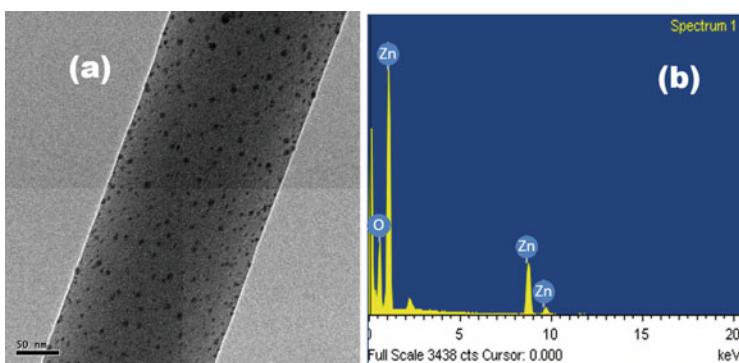


Fig. 6 Electrospun zinc oxide nanoparticle dispersed cellulose acetate nanofibrous membrane in **(a)** transmission electron microscopic image and **(b)** EDX Spectrum

Table 3 EDX data of zinc oxide nanoparticles

Element	Spectrum type	App conc.	Intensity corn	Weight %	Sigma %	Atomic %
O K	ED	29.67	1.3361	46.05	1.19	77.72
Zn K	ED	22.79	0.8763	53.95	1.19	22.28

36.35%) as seen in Fig. 6b and Table 3. After filtering the piped river water using the electrospun zinc oxide nanoparticle dispersed cellulose acetate nanofibrous membrane filtered the microorganisms (black circles) which is clearly seen in Fig. 5b. Therefore, the prepared electrospun cellulose acetate nanofibrous membrane is not only filtering the bacteria, but it also destroys the bacteria which creates biofouling and harmful in water.

Fouling is one of the main disadvantages to use as electrospun nanofibrous membrane in water filtration applications. Therefore, the surface modification is essential to achieve the better mechanical stability. The zinc oxide nanoparticle dispersed cellulose acetate nanofibrous membrane does not need surface modification because the zinc oxide nanoparticles could modify the surface, and fit for water filtration applications.

The electrospun zinc oxide nanoparticle dispersed cellulose acetate nanofibrous membrane offers free of microorganisms, is reliable, and is a good drinking water for human consumption.

8 Conclusion

In the 21st century, the contaminants present in the valuable drinking water lead to enormous health problems, particularly in developing countries. Even in the developed countries, the consumption of drinking water is not microbial safe. The domestic animals and human activities are the main source of introducing water-borne pathogens. Electrospun nanofibrous membranes have an excellent higher surface-to-volume ratio than conventional micro- or nanofibers as long as efficient separation of particulate matters. The electrospun zinc oxide nanoparticle dispersed cellulose acetate nanofibrous membrane is used to filter the microorganisms present in the piped river water, and the surface morphology is confirmed by scanning electron microscopy.

Hence, the overall studies show a simple, rapid, and economical route to develop the zinc oxide dispersed nanoparticle cellulose acetate nanofibrous membrane. The smooth, continuous nanofibers with interconnected porous structure have the advantage to filter the microorganisms present in water. Further, this study mainly confirms to facilitate to water filtration applications due to their good antibacterial activity and interconnected porous structure. The electrospun zinc oxide nanoparticle dispersed cellulose acetate nanofibrous membrane could be used in the future because it is cheap, simple, safe, more efficient, and biocompatible in nature.

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Material and Process Selection for Biosorption



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Abstract Pollution in all the essential elements such as air, water and land is a serious environmental problem for the last few decades. Among various methods for

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removing pollutants from environment, adsorption is the most economic and eco-friendly method. Nowadays, the use of biosorption process for removal of pollutants has been increased due to its efficiency, reusability of biosorbents and low cost of operation. The rate and efficiency of biosorption depend on the selection of suitable biosorbent and the process. To select an effective biosorbent for any process, the characteristics such as porosity, surface area and other chemical natures need to be studied. This chapter describes the various types of biosorbents, treatments applied to biosorbents, techniques and methods to study the characteristics of biosorbents, mechanisms, modes of operation, recovery and regeneration of biosorbents, kinetics, and modelling studies. Microscopic techniques such as electron microscopy (SEM and TEM) and atomic force microscopy (AFM) can be used to reveal the surface characteristics of the biosorbents. Pore volume and surface area of the biosorbent can be determined by Brunauer–Emmett–Teller (BET) analyser. Other characteristics such as thermal stability and particle size can be measured by instruments such as thermogravimetric analyser (TGA), differential scanning calorimetry (DSC) and particle size analyser. The mechanisms of biosorption at various locations (intracellular, cell surface and extracellular) are also discussed in detail in this chapter. The biosorption process can be performed in a batch and continuous modes depending on the type of pollutant removed. The selection of suitable mode of operation for different pollutants is emphasized. This chapter also covers the different factors influencing the biosorption process.

Keywords Biosorbents, Biosorption, Characterization techniques, Kinetics and modelling, Process selection

1 Introduction

Release of various pollutants into the water resources has been increased in recent times as a result of increasing industrialization and globalization. There are several methods such as precipitation, membrane separation, oxidation and chemical treatments available for removal of pollutants from aqueous solutions. Adsorption is a simple, eco-friendly and economically feasible method for large-scale removal and purification of aqueous solvents. According to De Gisi et al. [1], “Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid or liquid–solid interface”.

The substance being adsorbed is the *adsorbate* and the adsorbing material is termed the *adsorbent*. If the adsorbate and adsorbent have a physical interaction, then the adsorption is called as *physisorption*. If there is a chemical bonding between the adsorbate and adsorbent, then it is called as *chemisorption*. Adsorption involving biological materials as adsorbents is called as *biosorption*. The adsorbents used in

such process are called as *biosorbents*. Both physical and chemical interactions happen in biosorption.

Commonly adsorbents are carbon-based materials, zeolites, clay, alumina, sand and natural oxides. Carbon-based materials include activated carbons, carbonized materials, graphene-based adsorbents and carbon nanotubes.

Physisorption	Chemisorption
Non-specific	Highly specific
Occurs due to van der Waals's force	Occurs due to chemical bonds
Activation energy is not essential	Activation energy is essential
No electron transfer, while polarization of adsorbate occurs	Electron transfer leading to bond formation between adsorbate and adsorbent
Rapid process	Slow process
Reversible	Irreversible
Non-surface specific	Surface specific
No dissociation of adsorbed species	May involve dissociation
Mono layer or multilayer	Monolayer only
Only significant at very low operational temperature (at higher temperature, the process of physisorption decreases)	Possible over a wide range of temperature (with increasing temperature, chemisorption first increases and then decreases)
Enthalpies are in the region of -20 kJ/mol	Enthalpies are in the range of -200 kJ/mol
More liquefiable gases are adsorbed readily	Gases which form compounds with adsorbent alone undergo chemisorption
High pressure favours the process and low pressure causes desorption	High pressure is favourable, but low pressure does not cause desorption

2 Biosorbents

Biosorbents are called so attributing to their biological nature. Bacteria [2], fungi [3], algae [4, 5], agricultural wastes [6, 7], seed husks [8–10], leaves [11], stems [12], animal shells [13], scales [14], bone powders [15] and biopolymers [16] are few of commonly used biosorbents. Another widely used biosorbent to remove environmental pollutants is biochar which is derived from the pyrolysis of substrates including food waste, agricultural wastes and saw dust. Biosorbents can be used as such available (native biosorbents) or modified by physical and chemical methods (modified biosorbents). Usually unicellular organisms are used as available [2–5]. Agricultural wastes [7], rice husk and wood wastes [17] can be burned and used as biochar.

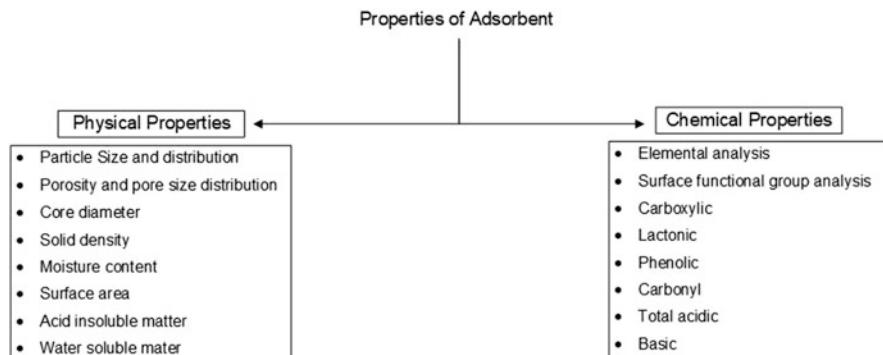
Usually dead biomass is preferred over live biomass as it does not require growth medium and growth can cause increase in the biological and chemical oxygen demand. Also, dead biomass can be modified through various activation processes. Regeneration of dead biomass can also be done easily. Modified biosorbents can

facilitate more surface area and a fine porous structure which has a large number of functional groups.

Some biomaterials like plant and animal tissues require a series of preliminary processing to make them more available as biosorbents. Properties of adsorbents depend on the raw material selected and the activation process applied. The physical and chemical treatments for the activation of adsorbent have effects on the properties of the adsorbents. Certain biomass has adsorption capacity higher than commercially available activated carbon, ion exchange resins and zeolites.

The following criteria should be considered while selecting a biosorbent for the biosorption process:

1. The biosorbent should be less expensive.
2. It should be reusable and the regeneration process should be less tedious.
3. Kinetics of the adsorption should be fast.



2.1 Physical Characteristics

2.1.1 Pore Size and Surface Area

IUPAC has classified the pores into three types based on the pore size, namely, microporous (<2 nm), mesoporous (2–50 nm) and macroporous (>50 nm) [18]. The size of the pores has a direct impact on the surface area available for adsorption. The surface area is defined as the area available on the surface of the adsorbent for the adsorbate to get adsorbed. It is expressed in m^2/g . The smaller the pore size, surface area will be more. As the surface area increases, the amount of adsorbate adsorbed on to the adsorbent increases.

In the selection of an adsorbent for a process, the size of the adsorbate is taken into consideration to select appropriate pore size adsorbent. For larger adsorbates, macroporous and mesoporous adsorbents are used, while for smaller adsorbates,

microporous adsorbents are used. Microporous adsorbents have more surface area than that of mesoporous and macroporous adsorbents.

2.1.2 Iodine Number

The ability of the biosorbent to take up smaller molecules is denoted as iodine number. It is defined as the mg of iodine adsorbed per g of adsorbent and is expressed in mg/g of adsorbent. Generally the iodine number varies in the range of 500–1,200 mg/g for activated carbon adsorbents [1].

2.1.3 Point of Zero Charge

Another important characteristic of biosorbents is the point of zero charge (pH_{PZC}). It is defined as the pH at which the adsorbent surface has no charge, i.e. net electrical neutrality. When pH is greater than pH_{PZC} , adsorbent surface has a net negative charge and favours the uptake of cations, and when pH is lesser than pH_{PZC} , the surface will have a net positive charge and have higher affinity towards anionic particles.

The point of zero charge can be determined by the series of adsorption experiments with 0.01 mol/L of NaCl conducted at different pH ranges from 2 to 12. The zeta potential was measured and the graph of zeta potential versus initial pH is used to determine the pH_{PZC} (Fig. 1).

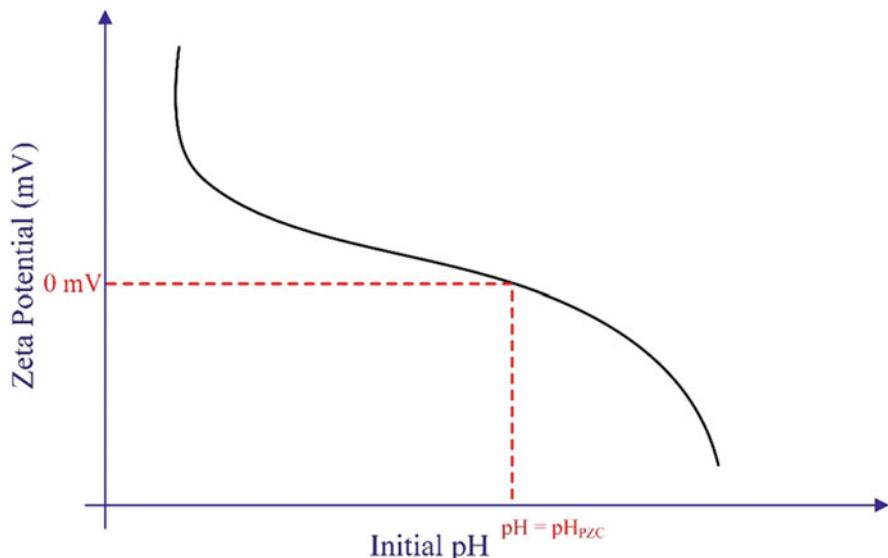


Fig. 1 Calculation of point of zero charge (pH_{PZC})

2.2 Chemical Characteristics

The surface of the biosorbents consists of functional groups such as amino, carboxyl, amide, carboxylate, thio-ether, thiols, sulphhydryl, imidazole, phenolic, phosphate and hydroxide from the biomolecules on the cell wall. These functional groups react with the pollutant and form covalent bond with them thus adsorbing them on the surface of the biosorbents.

Polyelectrolytic components of algal cell walls consist of peptidoglycan and teichuronic acid have specific charged groups with them. The pollutants in the aqueous solution will have ionic interaction with these charged groups and adsorb onto the cell surface [5].

3 Processing of Biosorbents

Pre-treatment of biomass to be used as adsorbents can involve physical treatments like grinding and chemical treatments such as alkali treatment, acid treatment, detergent treatment and treatment by organic solvents. These treatments increase the pore size, making functional groups available for adsorption.

When biomass is used as biosorbent, the cells are collected, dried and powdered and used as such. When live cells are used for biosorption, they can be used as such or can be immobilized on solid surfaces. This helps in creating adsorbent with properties necessary for the unit operations.

Burning of waste material in high temperatures decreases the oxygen and hydrogen contents and decreases the H/C and O/C ratio of the biochar. This increases the capacity of adsorption of aqueous contaminants. Also increasing temperatures leads to the increase in the surface area of the biochar [7]. Carbonized biomaterials by heating them in a furnace (up to 600°C) in the presence of nitrogen can also be used as biosorbents. This leads to the enrichment of carbon by decreasing the oxygen and nitrogen composition. Carbonization is also effective in opening the pores as a result of elimination of oxygen and nitrogen, thus increasing the surface area of the adsorbent [14].

Fe_3O_4 nanoparticles are incorporated into biosorbents to produce magnetic biosorbents which can help in the easier phase separation process. Chelating groups such as ethylenediaminetetraacetic acid (EDTA), diethylenetriamine (DETA), polyamidoamine (PAMAM) and diglycolic amic acid (DGAA) offer strong binding sites for metal ions when incorporated into the biosorbents by chemical processes [19].

Different biosorbents used in water treatment and their pre-treatments are listed in Table 1.

Another most important pre-treatment in the processing of biosorbents is the immobilization of biosorbents. Also, immobilization of biosorbents has an advantage of increasing the reusability of biosorbent. Immobilization is done by mixing the biosorbents with alginate or agar and forming small beads with them.

Table 1 Comparison of pre-treatment methods for various biosorbents and adsorbate

Biosorbent	Adsorbate	Pre-treatments	Reference
<i>Bacteria</i>			
<i>Micrococcus luteus</i>	Thorium and uranium	No pre-treatment	Nakajima, Tsuruta [20]
<i>Bacillus</i> sp. (ATS-1)	Copper and Lead	Drying at 80°C and screening particle size to 150 µm	Tunali et al. [21]
<i>Pseudomonas putida</i>	Lead and copper	Drying	Uslu and Tanyol [22]
<i>Bacillus licheniformis</i>	Chromium	Drying at 80°C	Zhou et al. [23]
<i>Streptomyces rimosus</i>	Lead	Drying at 50°C and size reduction to 50–160 µm. 0.1 M NaOH treatment for 30 min	Selatnia et al. [24]
<i>Fungi</i>			
<i>Aspergillus niger</i>	Chromium	Size reduction (grinded); 0.01 N NaOH, 0.1 N H ₂ SO ₄ , 50% v/v acetone, 10% v/v formaldehyde, 5% w/v CTAB, 1% w/v PEI, 3% v/v APTS	Mungasavalli et al. [25]
<i>Aspergillus niger</i>	Mercury	Size reduction (grinding)	Khambhaty et al. [26]
<i>Aspergillus fumigatus</i>	Chromium	Size reduction (grinding and sieving through 150 µm)	Dhal et al. [27]
<i>Algae</i>			
<i>Sargassum oligocystum</i>	Mercury, cadmium and copper	Carbonization at 350°C for 2 h and size reduction to 0.074 mm	Delshab et al. [28]
<i>Oedogonium hatei</i>	Nickel	0.1 M HCl treatment for 8 h and size reduction (150–250 µm)	Gupta et al. [29]
<i>Anabaena sphaerica</i>	Lead, cadmium	Size reduction (0.2 mm)	Abdel-Aty et al. [30]
<i>Jania rubens</i>	Lead	36% v/v formaldehyde and 0.1 M HCl for 1 h followed by 0.2 M sodium carbonate solution	Hanbali et al. [31]
<i>Pelvetia canaliculata</i> <i>Ochrophyta</i>	Nickel	0.5 M NaCl treatment	Bhatnagar et al. [32]
<i>Cystoseira indica</i>	Lead, uranium	0.1 CaCl ₂ treatment for 3 h and size reduction (1 mm – 2 mm)	Moghaddam et al. [33]
<i>Chlorella vulgaris</i>	Nickel	Size reduction	Aksu [34]
<i>Others</i>			
Rice husk	Levofloxacin	Pyrolysis at 300 and 600°C	Yi et al. [17]
Rice husk and snail shell composite	Brilliant green	Dried, size reduced to 400 µm, mixed and calcinated at 681.1°C for 2.6 h	Popoola et al. [35]

(continued)

Table 1 (continued)

Biosorbent	Adsorbate	Pre-treatments	Reference
Bengal Gram Seed husk	Congo red	Size reduction (grinding and sieving between 53 and 75 µm mesh)	Somasekhara Reddy et al. [9]
Wood chip	Levofloxacin	Pyrolysis at 300 and 600°C	Yi et al. [17]
Fish scales	Orange 16	Carbonization in the presence of N ₂ at 600°C, washing by 1 M HCl, drying t 105°C and ground to a mesh of 250–500 µm	Marrakchi et al. [14]
	Lanthanum	Size reduction to 425–600 µm size	Das et al. [36]
Animal bone meal	Rhodamine – B	Size reduction (grinding to powder)	El Haddad et al. [15]
Sorghum straw, oats straw, agave bagasse	Chromium (III)	Size reduction to 1 mm diameter, acid treatment by 0.01 N hydrochloric acid and drying at 50°C for 24 h	Bernardo et al. [6]
Potato plant leaves and stem	Methylene blue and malachite green	Boiling to separate fibres, size reduced by grinding to 100–150 µm	Gupta et al. [37]
<i>Haloxylon recurvum</i>	Methylene blue	Drying and size reduction by grinding	Hassan et al. [12]
Neem saw dust	Lanthanum	Size reduction to 425–600 µm size	Das et al. [36]

4 Characterization of Biosorbents

The physical nature of the biosorbents such as size, shape, surface area, pore size and chemical nature such as functional groups can be characterized by different methods. Some of the methods are listed below.

4.1 Microscopy

Physical structure and surface morphology of the adsorbent can be studied using scanning electron microscopy (SEM). Pores in the surface of the biosorbent can be visualized by the SEM. Also the metal binding to the surface of the adsorbent can be visualized by the SEM images taken before and after the adsorption [21].

4.2 Spectroscopy

Fourier transform infrared (FTIR) spectroscopy and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy are the methods to identify the functional groups and the bonding between the atoms in a compound. By analysing a

biosorbent by FTIR, the functional groups in the material can be revealed. The free functional groups in the adsorbent before treatment and after treatment and the functional groups after adsorption can also be studied using FTIR to elucidate the mechanism of biosorption [25].

X-ray photon spectroscopy is used to find the elemental composition of the biosorbents present. It is also helpful in deducing the empirical formula, electronic state and chemical state [19]. Energy dispersive X-ray spectroscopy (EDX or EDAX) is also used for elemental analysis of the material. EDS when used along with SEM gives the quantitative estimation of the metal adsorbed into the surface of the adsorbate.

X-ray fluorescence (XRF) spectroscopy and energy dispersive X-ray fluorescence (EDXRF) spectroscopy are also used to determine the elemental composition of the biosorbents. The secondary X-rays emitted from the sample when excited by a primary X-Ray are measured to determine the elemental composition. The metals adsorbed on the surface of the adsorbent are revealed by XRF and EDXRF spectroscopy.

Another technique used for elemental analysis is inductively coupled plasma atomic/optical emission spectroscopy (ICP-AES/ICP-OES). The inductively coupled plasma produces excited atoms that emit characteristic electromagnetic radiation which is used to determine the presence of the element.

4.3 Surface Area and Pore Size

Surface area (m^2/g) is determined by nitrogen adsorption-desorption studies at 77.3 K by Brunauer, Emmett and Teller method (BET analysis) [38], density function theory (DFT) methods and BJH methods [39]. BET analysis is the common method for determining the porosity and surface area of a material, while DFT and BJH methods are used to determine the pore volume (cm^3/g) of a material. Micrometrics® is one of the leading manufacturers of machines that can be used for BET analysis.

4.4 Thermal Stability

Thermal stability of the material is generally analysed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). In TGA, the sample is heated with a programmed heating rate, and the weight of the sample is monitored from time to time. Graph is plotted between temperature and weight loss. The sample is thermally stable till the temperature at which the weight loss begins.

5 Mechanism of Biosorption

Biosorption can be classified based on the metabolism dependence and on the location of the adsorption. Biosorption takes place either extracellular or intracellular. Extracellular biosorption may be precipitation or cell surface adsorption with the help of physical forces.

The cells produce compounds that can precipitate the metal pollutant and precipitate them around the cells or on the cell membrane. This process can be either metabolism dependent or due to chemical interaction between the cell surface and the adsorbate. Some bacteria are capable of secreting ligands, phosphates, acids and extracellular polymeric substances (EPS) including proteins, polysaccharides, nucleic acids, lipids and glycoproteins. These EPS have a large diversity in the functional groups and are capable of sequestering heavy metals and precipitating them. *Pseudomonas stutzeri*, *Pseudomonas aeruginosa*, *Paenibacillus jamiciae* and *Bacillus firmicus* are capable of sequestering and removing lead from environmental samples [40]. *Arthrobacter* and *Pseudomonas* remove cadmium by detoxification system that precipitates cadmium on cell surface [41].

Physical forces involved in the cell surface adsorption include van der Waal's forces, electrostatic interaction and ion exchange. As microbial cell wall contains a large number of binding sites for metals in the form of carbonyl, phosphoryl, sulfhydryl and carboxyl groups, the adsorption can also take place through the chemical adsorption. The cell wall structure of fungi, algae and bacteria can adsorb metals such as copper, zinc, cadmium, lead, cobalt and even uranium. Fungal cells have chitin on their cell wall which can have electrostatic interaction with the adsorbate and adsorbs them. The natural polysaccharides on the cell wall of these biomasses have bivalent metal ions like K^+ , Na^+ , Ca^{2+} and/or Mg^{2+} which exchanges counter ions such as Co^+ , Cd^+ , Cu^+ and Zn^+ . The polysaccharides on the cell wall are also capable of forming complexes with metal ions and thus adsorbing them on their cell surface. This process is called as complexation [42].

Intracellular biosorption requires the adsorbate to be transported into the cell. Heavy metals are taken into the cell by the same mechanism involved in transport of metabolically important ions. After transfer of the adsorbate into the cell, it can go through three processes: (1) binding to inner membrane of cell wall, (2) uptake as nutrient and (3) formation of complexes with adsorbate and precipitating them inside the cell. This kind of biosorption involving transport across cell membrane requires cells metabolism and takes place only on viable cells.

6 Modes of Operation

Biosorption for the removal of pollutants from water can be carried out in batch and continuous modes.

6.1 *Batch Mode*

The batch mode adsorption is carried out by putting the adsorbent in the solution and allowing it to adsorb for a specified period of time. Shift in the adsorption equilibrium due to the influence of various parameters such as temperature, pH, concentration of the adsorbate and adsorbent and time can be studied in batch mode. Agitated batch adsorption is recommended for efficient adsorption processes as it makes the biosorbent available throughout the reactor vessel. Small flasks can be agitated by placing them in a rotary shaker incubator or by using impellers or turbines.

6.2 *Continuous Mode*

Continuous mode of biosorption is carried out in columns packed with biosorbents. The raw or processed biosorbents are packed tightly inside a glass column, and the adsorbate is passed continuously through the column. The effluent concentration is monitored, and breakthrough curve is plotted to evaluate the effectiveness of the biosorption process. Mode of operation of column may be either top to bottom or bottom-up process. Flow rate of the adsorbate is maintained throughout the process.

The column may be a fixed bed [31] column in which the adsorbent is tightly packed or a fluidized bed column in which the adsorbent is loosely packed or immobilized in beads. When fluidized bed column is used, adsorbate is sent in through the bottom and collected at the top.

7 Factors Influencing Biosorption

In the treatment of waste water containing ions of minerals, there are various factors that influence the equilibrium of the biosorption process.

7.1 *Temperature*

Effect of temperature on biosorption is inconsistent with different authors. Some reported increase in the rate of adsorption with increase in temperature [34], while some reported decrease in rate of adsorption with increase in temperature [29]. From most of the works, temperature is not known to affect the biosorption equilibrium [43–46].

7.2 pH

Biosorbents are rich in carboxylic, amine, hydroxyl and thiol groups. These groups contribute to the characteristic acid–base property of the biosorbent. Hence, pH of the solution can alter the chemical nature of the functional groups present in the biosorbent and also the affinity of these groups towards metal ions. Some biosorbents and adsorbates have a buffering effect which can neutralize the effect of pH changes in the system [7, 17]. In many occasions, the change in pH alters the equilibrium of the biosorption process.

7.3 Biomass State and Concentration

The concentration of biomass in the solution directly constitutes the amount of surface area and functional groups available for the adsorption of the pollutants. Also, the state of biosorbent whether dead or alive also influences the rate of adsorption. At lower concentrations, the amount of adsorption doesn't seem to be affected, while in higher concentrations, the dead biomass adsorbs more than the live biomass [2].

7.4 Coexisting Ions

When biosorption is applied to treat waste water, the waste water may contain more than one ion in the solution. Presence of other coexisting ions can also influence the rate of biosorption. Fe^{2+} and Zn^{2+} can affect the adsorption of heavy metals by microorganisms. The microorganisms that uptake heavy metals such as uranium and thorium are found to be not affected by the presence of coexisting ions, while the presence of uranium and thorium might affect the adsorption of other metals [42].

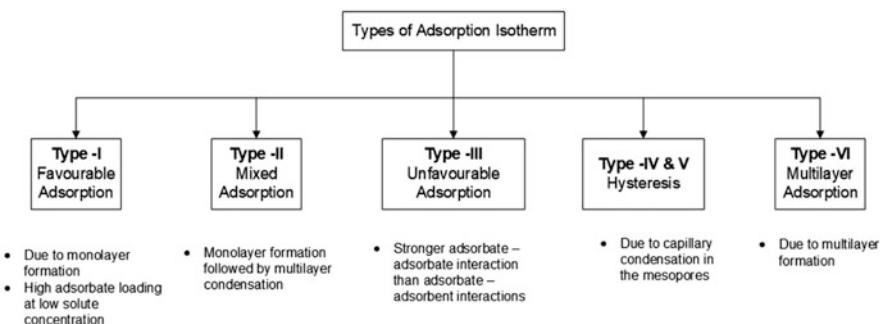
7.5 Contact Time with the Adsorbent

The rate of adsorption also depends on the contact time for adsorbate and the biosorbent. Increase in contact time leads to the increase in the percentage removal of the biosorbent. However, the adsorption rate will be maximum initially and then slows down and reaches the equilibrium. This is due to the presence of more vacant sites for adsorption at the start than at the end of adsorption.

8 Recovery and Regeneration of Biosorbents

The major advantage of using biosorbents is its reusability. As the adsorbent is insoluble in the solution, it can be filtered or centrifuged to separate it from the solution. Then the adsorbate can be separated from adsorbent by desorption process. As the adsorbate and adsorbent are held together only by temporary interaction, they can be easily released by reversing the physical or chemical reactions. Alteration of pH to desorb the adsorbate from the adsorbent is common method used for desorption. The pH is altered from a range of 2–12 for a given period of time to desorb the adsorbate [9]. Addition of chemicals which have functional groups that react with the adsorbate will desorb the adsorbate from the adsorbent. This will return the adsorbent to its previous state in which it can be used for adsorption again. Acids, bases [25], chelating groups such as EDTA [6] and organic solvents [8] can be used to recover the adsorbate and regenerate the adsorbent. Regenerated adsorbent can be used for adsorption process again.

9 Kinetics and Models for Biosorption



For the representation of results, equilibrium data need to be analysed and an equation is needed to be developed for design purposes. For this, there are several equilibrium models and isotherms are available. Common isotherms include Freundlich, Langmuir and Redlich–Peterson isotherms. The common isotherms, their equation and the graph are presented in the below table [19, 35].

Equation	Plot
<p><i>Langmuir model</i></p> $\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0}$ <p>C_e (mg/L): equilibrium conc. of adsorbate q_e (mg/g): amount of adsorbate adsorbed onto biosorbent at equilibrium. q_0(mg/g): adsorption capacity of adsorbent for adsorbate. b (L/mg): Langmuir isotherm constant</p>	<p>A graph showing the Langmuir isotherm. The y-axis is labeled C_e/q_e and the x-axis is labeled C_e. A red line starts at a positive intercept on the y-axis and passes through the origin, extending upwards and to the right. A vertical dashed line from the y-axis to the line is labeled "Slope = 1/q_0". A horizontal dashed line from the line to the x-axis is labeled "Intercept = 1/(q_0 b)".</p>
<p><i>Freundlich model</i></p> $\ln(q_e) = \ln(K_f) + \frac{1}{n} \ln(C_e)$ <p>K_f (mg^{1-(1/n)} L^{1/n} g⁻¹): Freundlich isotherm constant n: Freundlich exponent</p>	<p>A graph showing the Freundlich isotherm. The y-axis is labeled $\ln(q_e)$ and the x-axis is labeled $\ln(C_e)$. A red line starts at a positive intercept on the y-axis and passes through the origin, extending upwards and to the right. A vertical dashed line from the y-axis to the line is labeled "Slope = 1/n". A horizontal dashed line from the line to the x-axis is labeled "Intercept = \ln(K_f)".</p>
<p><i>Redlich–Peterson (R-P) model</i></p> $\ln\left(K_{RP} \frac{C_e}{q_e} - 1\right) = \ln(a_{RP}) + g \ln(C_e)$ <p>K_{RP} (g/L): Redlich–Peterson isotherm constant a_{RP} (L/mg): Redlich–Peterson constant g: Redlich–Peterson exponent (values between 0 and 1)</p>	<p>A graph showing the Redlich–Peterson isotherm. The y-axis is labeled $\ln(K_{RP}(C_e/q_e)-1)$ and the x-axis is labeled $\ln(C_e)$. A red line starts at a positive intercept on the y-axis and passes through the origin, extending upwards and to the right. A vertical dashed line from the y-axis to the line is labeled "Slope = g". A horizontal dashed line from the line to the x-axis is labeled "Intercept = \ln(a_{RP})".</p>
<p><i>Dubinin–Radushkevich (DR) model</i></p> $\ln(q_e) = \ln(X_m) - \beta \epsilon^2$ $\epsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$ $E = \frac{1}{-\frac{2\beta}{X_m}}$ <p>X_m (mg/g): maximum adsorption capacity β (KJ² mol²): activity constant ϵ: Polanyi potential E (KJ/mol): mean free energy of adsorption</p>	<p>A graph showing the Dubinin–Radushkevich isotherm. The y-axis is labeled $\ln(q_e)$ and the x-axis is labeled ϵ^2. A red line starts at a positive intercept on the y-axis and passes through the origin, extending upwards and to the right. A vertical dashed line from the y-axis to the line is labeled "Slope = \beta". A horizontal dashed line from the line to the x-axis is labeled "Intercept = \ln(X_m)".</p>

(continued)

Equation	Plot
<p><i>Temkin model</i></p> $q_e = \frac{RT}{b} \ln (A_T) + \frac{RT}{b} \ln (C_e)$ <p>A_T(L/g): Temkin equilibrium binding constant b (J/mol): Temkin isotherm constant R (8.314 J/Mol.K): gas constant T (K): absolute temperature</p>	
<p><i>Sips model</i></p> $\ln \left(\frac{q_e}{X_m - q_e} \right) = m_s \ln (C_e) + \ln (b_s)^{m_s}$ <p>m_s: Sips exponent b_s: Sips equilibrium constant</p>	
<p><i>Koble–Corrigan (K-C) model</i></p> $\frac{1}{q_e} = \frac{1}{A_{KC} C_e^p} + \frac{B_{KC}}{A_{KC}}$ <p>A_{KC} (L^p mg$^{1-p}$ g$^{-1}$): Koble–Corrigan isotherm constant B_{KC} (L/mg)p: Koble–Corrigan isotherm constant p: Koble–Corrigan exponent</p>	
<p><i>Harkin–Jura model</i></p> $\frac{1}{q_e^2} = \frac{B_{HJ}}{A_{HJ}} - \left(\frac{1}{A_{HJ}} \right) \log C_e$ <p>A_{HJ} and B_{HJ}: Harkin–Jura adsorption constants</p>	

10 Summary

Selection of materials and process for the removal of pollutants from environment starts with the selection and processing of the biosorbent used. Even though living microorganisms can be used, dead biomass is usually preferred to be used as biosorbents. Modification of biosorbents for better adsorption is not possible in living organisms. The biomass used for biosorption should have appropriate pore size, surface area, charge and appropriate functional groups on the surface to readily adsorb the pollutant passed through them. These properties can be incorporated into the biomass by various pre-treatment processes.

Pre-treatment process used should make the biosorbent more available to the adsorbate. The pre-treatment process should not complicate the recovery and regeneration process. Pre-treatment process should be determined according to the mechanism of biosorption involved and the type of material adsorbed. Some biosorbents does not require pre-treatment for removal of some materials. Treatment process includes drying and grinding, alkali or acid treatment, detergent treatment, carbonization process, boiling and pyrolysis. Grinding to a specific size makes the surface area of the material appropriate for the biosorption process. Alkali, acid, detergents and other chemical treatments will enhance the availability of the functional groups on the surface of the biosorbent for the adsorption process. Boiling helps in the separation of fibres from plant parts. Pyrolysis makes the biomass into biochar. Carbonization process removes moisture content and increases carbon content in the biosorbent used.

Visual characterization of the biosorbent can be done by scanning electron microscopy. FT-IR can be used to analyse the functional groups and to analyse the mechanism of the biosorption. X-ray photon spectroscopy, EDAX and ICP-AES/ICP-OES can be used to estimate the elemental composition of the adsorbent. The metals that are adsorbed onto the surface can also be estimated by above mentioned methods. Nitrogen adsorption/desorption studies are used to determine the pore size and surface area by BET, DFT and BHJ methods.

Mechanism of biosorption also plays a major role in the selection of material for biosorption. In whole cells used as biosorbents, the biosorption may be intracellular or extracellular. In case of physical and chemical attraction of the metals to the cell surface, dead cells can be used as biosorbents. Extracellular polymeric substances produced by microorganisms have a large diversity of functional groups that can adsorb various heavy metals and removes them by precipitation or complexation. The organisms that are capable of sequestering metals by precipitation and complexation can be used alive. Intracellular biosorption requires active metabolism and thus requires a live cell. Live cells thus used may take the pollutant as nutrient or might require separate nutrition provided in the feed.

Biosorption can be carried in either batch mode or continuous mode. Batch mode is suitable for all types of biosorption process. Advantage of the batch biosorption process is that the biosorbent along with the pollutant adsorbed on the surface can be removed easily from the feed. Continuous mode can be used for live cells which can

be immobilized and used for biosorption. The column for continuous biosorption may be fixed bed or fluidized bed.

Factors influence the biosorption such as temperature, pH, Biomass concentration, contact time influences the selection of process. These parameters can be optimized by statistical methods such as response surface methodology, etc. When contact time and biomass concentration needs to be high, batch process can be selected. Continuous process can be selected when the biomass concentration required is less so that it can process more feed.

The biomass can be regenerated by reversing the biosorption conditions. Alteration of pH by adding acids or bases and addition of chelating groups and organic solvents are common methods for the desorption of the adsorbate from the adsorbent. The biosorbent free of adsorbate can be reused for further processes.

The adsorption equilibrium can be analysed by various adsorption isotherm models such as Freundlich, Langmuir, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Sips, Koble–Corrigan and Harkin–Jura models.

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Removal of Acid Magenta Dye by Fly Ash: A Sustainable Tool for Textile Effluent Treatment



Riti Thapar Kapoor

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Abstract The pollution caused by industrial waste has become a major problem for most of the countries. The present paper deals with the effect of activated carbon and fly ash on removal of acid magenta dye from aqueous solution under different experimental conditions such as exposure time, pH, temperature, and different amount of adsorbent. Maximum 85% and 91% acid magenta dye (20 ppm) removal was observed at low pH (pH 2) with activated carbon and fly ash treated dye solution, respectively. The phytotoxicity study exhibited that *Vigna radiata* seeds showed better response in the fly ash treated dye solution in comparison with the

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activated carbon. The results revealed that fly ash, one of the industrial wastes, can be used as low-cost and effective adsorbent for the removal of acid magenta dye from aqueous solution.

Keywords Acid magenta, Activated carbon, Fly ash, Wastewater treatment

1 Introduction

Water, food, and energy are the three main components which ensure human survival. The access to adequate power supply is essential for socioeconomic development of a country. In India, approximately 70% electricity is generated through the coal-based thermal power plants. According to Jambhulkar et al. [1], coal fly ash is produced in India approximately 120 million tons/year from more than 85 thermal power plants which may increase to 442 million tons/year by the year 2035. The management of huge quantity of fly ash is a challenging task for thermal power plant. Fly ash is used as a supplementary material in the production of cement [2], aerated concrete [3], clay bricks [4], etc. It can also be used as an agricultural fertilizer and soil conditioner due to its high water retention capacity [5]. Although the use of fly ash has been significantly increased from 8 to 70% from 1997 to 2010, still approximately 40% of the fly ash remain unused [6]. Fly ash pollutes water resources and soil if it is directly dumped into the environment [7]. Fly ash contains many heavy metals and trace elements which enters in the food chain and adversely affect human health [8]. Fly ash causes various disorders in human beings such as asthma, bronchitis, silicosis, allergy, fibrosis, cancer, etc. [9].

Dyes are extensively used in textile, paper, leather tanning, printing, plastic, cosmetic, and pharmaceutical industries [10, 11]. Dyes are undesirable type of pollutant, and presence of dye even at very low concentration (1 mg/L) in the effluent is visible [12]. The discharge of dye-contaminated effluent into the water bodies may cause oxygen depletion, eutrophication, and adverse impact on entire aquatic ecosystem. Synthetic dyes adversely affect human health due to their acute or chronic toxicity and mutagenic, carcinogenic, genotoxic, cytotoxic, and immune suppression effects [13, 14]. Many physical and chemical techniques such as photocatalytic degradation [15], nanofiltration [16], coagulation/flocculation [17], electrochemical treatment [18], and ozonation [19] have been developed for the removal of dyes from industrial effluent. The drawbacks associated with the abovementioned techniques are long operation time, high cost of application, intensive energy requirement, complex procedure, unable to completely remove the dyes, and waste generation. Activated carbon is capable of adsorbing dyes due to its high adsorption capacity, but it is in limited use due to its high cost [20]. The application of fly ash as an adsorbent in treatment of industrial effluent not only removes dye but also eliminates the problem of fly ash disposal. Fly ash is available at zero cost, and it

can be used as a low-cost and efficient adsorbent for treatment of industrial effluents due to its high porosity and large surface area. Therefore, present investigation was conducted to compare the adsorption capacity of activated carbon and fly ash for removal of acid magenta dye from aqueous solution and their impact on *Vigna radiata* growth parameters.

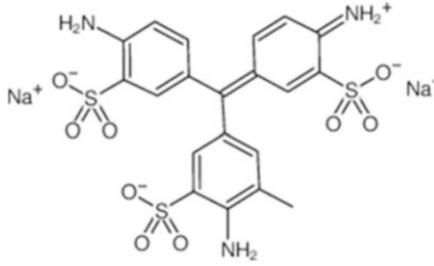
2 Materials and Methods

The present investigation was conducted in the Plant Physiology Laboratory, Amity Institute of Biotechnology, Amity University, Noida. Fly ash was collected from Badarpur Thermal Power Station, Delhi.

2.1 Preparation of the Dye Stock Solution

Activated carbon and acid magenta dye were procured from Sigma Aldrich, India. It is an anionic dye. The stock solution of acid magenta dye (1,000 ppm) was prepared initially, and it was diluted appropriately to produce acid magenta dye solution of desired concentrations. A calibration curve was plotted by analyzing different concentrations of acid magenta dye solution by using UV-Visible double beam spectrophotometer at 541 nm (Table 1).

Table 1 Details of acid magenta dye used in the experiment

Dyestuff	Acid fuchsin, acid violet 19
Appearance	Dark green
IUPAC name	Disodium 2-amino-5-[(Z)-(4-amino-3-sulfonatophenyl)(4-imino-3-sulfonato-2,5-cyclohexadien-1-ylidene)methyl]-3-methylbenzenesulfonate
Empirical formula	C ₂₀ H ₁₇ N ₃ Na ₂ O ₉ S ₃
Molecular weight	585.538 g/mol
Molecular structure	
λ_{max}	541 nm

2.2 Adsorption Studies

The experiments were conducted in a batch mode to check the applicability of activated carbon and fly ash as an adsorbent for the removal of acid magenta dye from aqueous solution. The effect of different parameters such as contact time (30–150 min), dye concentration (20–60 ppm), adsorbent dose (0.5–2.5 g), pH (from pH 2 to 10), and temperature (30–70°C) was investigated for the removal of acid magenta dye. In the batch adsorption study, 100 mL of acid magenta dye solution of different concentrations (50, 100, 150, and 200 ppm) was placed in four different Erlenmeyer flasks (250 mL capacity) with different amount of activated carbon and fly ash (0.5, 1.0, 1.5, 2.0, and 2.5 g), respectively. The mixture was placed in an incubator shaker at 120 rpm until equilibrium was observed to be attained. The conical flasks were withdrawn at regular time interval, and analysis of the sample was made by following standard procedure. The pH of the solution was maintained by using 0.1 N HCl and 0.1 N NaOH solution.

Removal efficiency was calculated by the following formula:

$$\text{Removal of Acid magenta dye (\%)} = C_0 - C_t / C_0 \times 100$$

where C_0 and C_t are initial and final concentrations of acid magenta dye at time t in mg/L in the sample, respectively. All the measurements were done for three times, and mean values were presented.

2.3 Phytotoxicity Study

The toxicity of acid magenta dye before and after the treatment with activated carbon and fly ash was studied on the seeds of mung bean (*Vigna radiata*). Maximum concentration (60 ppm) of acid magenta dye was used to determine the toxicity.

2.4 Seed Germination Test

The empty and undeveloped seeds of *Vigna radiata* were discarded by floating in tap water. Seeds of *Vigna radiata* were thoroughly washed with tap water to remove dirt and dust for 5 min. The seeds were surface sterilized with 10:1 distilled water/bleach (commercial NaOCl) solution for 5 min for inhibition of microbial infection and then washed six to seven times with distilled water. Mung bean seeds were soaked in acid magenta dye solution before and after the treatment with activated carbon and fly ash for 4 h, respectively. The filter paper was placed in sterilized Petri dishes (20 cm diameter) and mung bean seeds which were soaked in dye solution transferred into Petri dishes. The Petri dishes were covered with sterilized polythene bags and kept in

a seed germinator for 8 days under 70% relative humidity at $25 \pm 2^\circ\text{C}$ with 12 h photoperiod following guidelines of ISTA [21] in three replicates with completely randomized block design.

Seed germination and different growth characteristics such as radicle and plumule length and vigor index were determined in control and treatment by the following methods:

2.5 Germination Percentage

Total number of seeds germinated/total number of seeds taken for germination $\times 100$.

2.6 Seedling Length

After 8 days of seed sowing, radicle and plumule length of the mung bean seedlings was measured as per standard methods of ISTA [21]. The radicle and plumule length was measured with a measuring scale, and values were expressed in centimeters.

2.7 Vigor Index

Vigor index of the mung bean seedlings was estimated according to the formula:

$$\text{Vigor index} = \text{Total seedling length (mm)} \times \text{germination percentage}$$

[22].

2.8 Results and Discussion

In the present study, various parameters such as contact time, initial dye concentration, pH, adsorbent dose, and temperature were analyzed to study the effect of activated carbon and fly ash on the adsorption of acid magenta dye.

2.9 Effect of Contact Time

The batch experiments were carried out to study the effect of activated carbon and fly ash on various concentrations of acid magenta dye (20–60 mg/L) under different exposure period (30–150 min). Results showed that the adsorption capacity of activated carbon and fly ash increased rapidly with increasing contact time for the first 120 min (Fig. 1a, b). The 120 min was considered as the optimum exposure

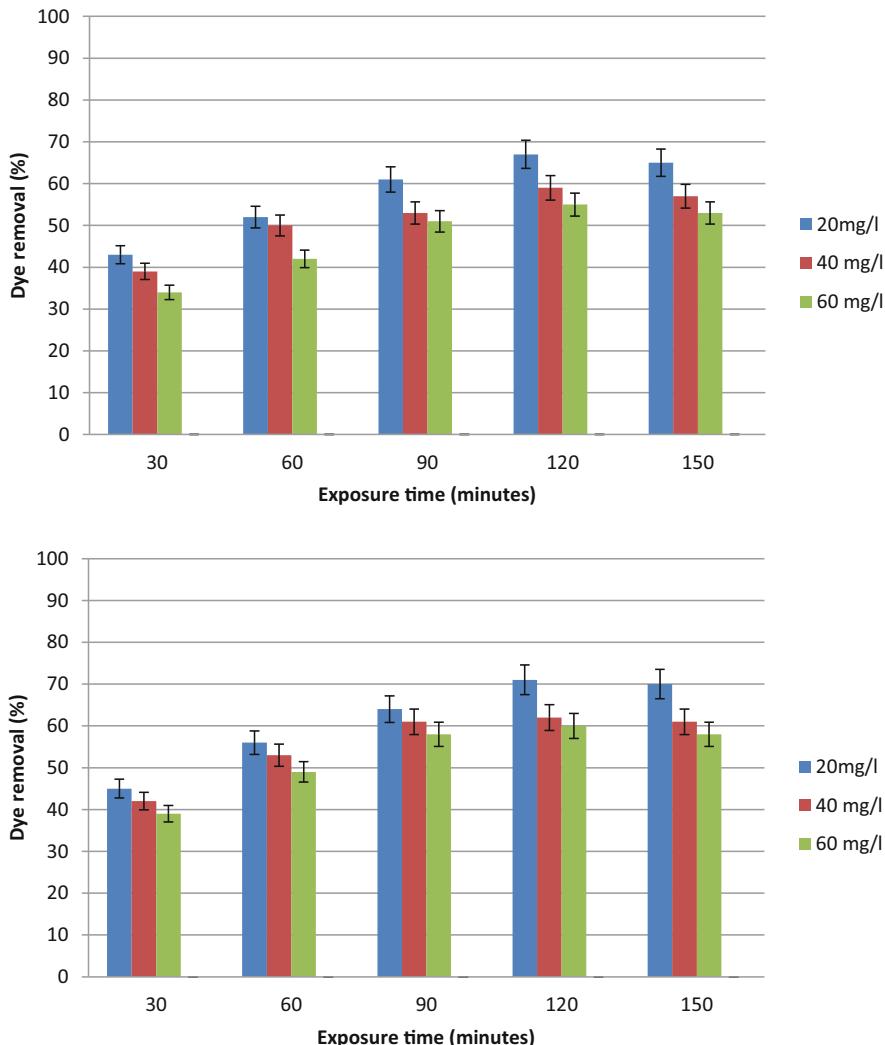


Fig. 1 (a) Adsorption of acid magenta dye by activated carbon at different exposure period. **(b)** Adsorption of acid magenta dye by fly ash at different exposure period

period for acid magenta dye removal for both of the adsorbents. Fly ash exhibited better adsorption capacity in comparison with activated carbon.

2.10 Effect of Adsorbent Dose

The different amount of activated carbon and fly ash (0.5, 1, 1.5, 2, and 2.5 g) was taken in the experiment to evaluate their adsorption capacity for the acid magenta dye. The increase in rate of adsorption of acid magenta dye was observed with increase in the adsorbent amount and exposure time (Fig. 2). The adsorption capacity of activated carbon and fly ash showed the following trend: 2 g > 1.5 g > 2.5 g > 1 g > 0.5 g. The results of the present study indicated that fly ash was effective in removal of acid magenta dye from aqueous solution in comparison with activated carbon. It may be due to increased surface area and availability of more adsorption sites on the fly ash [23].

2.11 Effect of pH

The percentage of acid magenta dye adsorbed by the activated carbon and fly ash at different pH is shown in Fig. 3. It was observed that with decrease in the pH of the acid magenta dye solution, more dye molecules are protonated and get adsorbed on the surface of fly ash. At pH 2, maximum dye removal 85% and 91% was observed

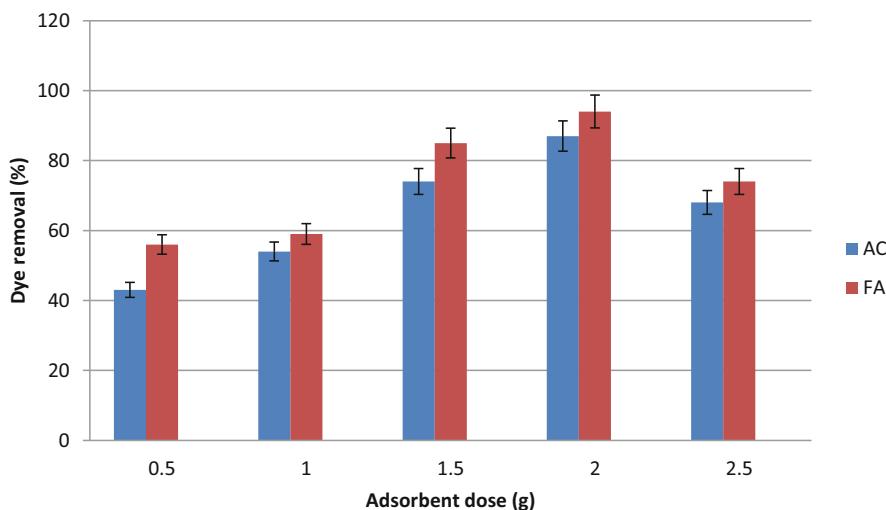


Fig. 2 Adsorption of acid magenta dye by different adsorbent dose

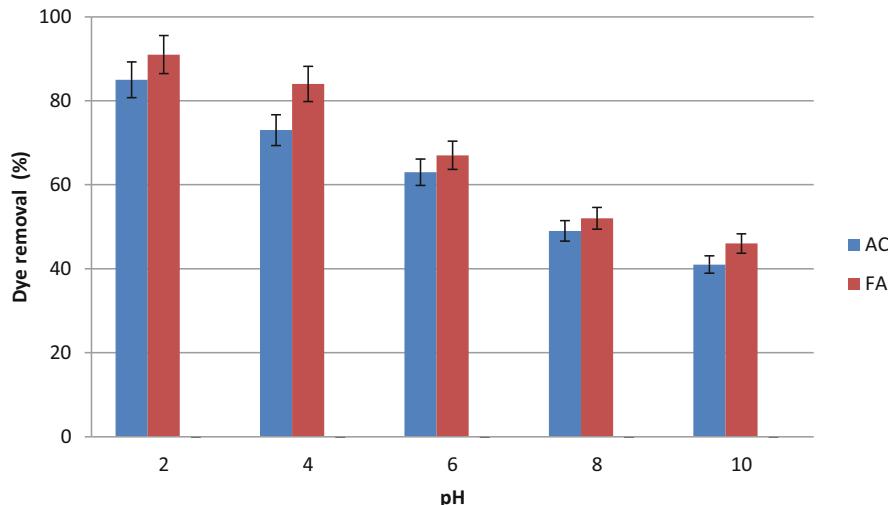


Fig. 3 Adsorption of acid magenta dye at different pH by different adsorbents

with activated carbon and fly ash, respectively, for an initial dye concentration of 20 mg/L.

2.12 Effect of Temperature

The adsorption of acid magenta dye on the activated carbon and fly ash was carried out at initial acid magenta dye concentration (20 mg/L) at different temperature. The dye adsorption increased on the activated carbon and fly ash with a rise in temperature from 30 to 60°C (Fig. 4). This is mainly due to the increased surface activity at high temperature, suggesting that adsorption of acid magenta dye on activated carbon and fly ash obeys an endothermic process. Maximum removal of acid magenta dye 71 and 67% was observed with activated carbon and fly ash, respectively, at 50°C.

2.13 Phytotoxicity Study

The phytotoxicity test with seeds of *Vigna radiata* showed toxicity of acid magenta dye. The significant differences were observed among various treatments for all the parameters studied, i.e., seed germination and other growth characteristics such as length of plumule and radicle and vigor index of the mung bean seeds. In control 97% seed germination was observed, whereas dye (20 ppm) treated seeds of *V. radiata* exhibited only 40% germination [24]. The germination of mung bean

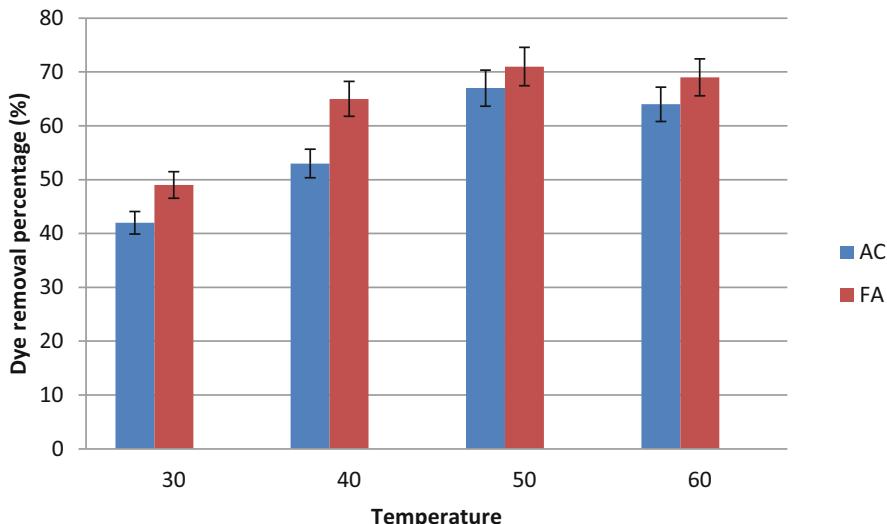


Fig. 4 Adsorption of acid magenta dye at different temperature

Table 2 Phytotoxicity comparison of acid magenta dye before and after treatment on seed germination and other growth parameters of *Vigna radiata*

Treatment	Seed germination (%)	Plumule length (cms)	Radicle length (cms)	Vigor index
Control	97 ± 0.65	10.8 ± 0.45	3.4 ± 0.21	13,774
Acid magenta dye (20 mg/L)	40 ± 0.18	2.7 ± 0.04	0.30 ± 0.01	1,200
Activated carbon treated dye solution	62 ± 0.31	6.4 ± 0.71	1.8 ± 0.14	5,084
Fly ash-treated dye solution	84 ± 0.52	8.7 ± 0.64	2.9 ± 0.23	9,744

seeds significantly increased from 62 to 84% in dye solution treated with activated carbon and fly ash, respectively. In control, the plumule and radicle lengths were 10.8 and 3.4 cms which were significantly reduced to 2.7 and 0.3 cms in acid magenta dye solution. Fly ash-treated dye solution showed increase in plumule and radicle length in comparison with activated carbon. The vigor index of *Vigna radiata* seeds showed the following trend: control > fly ash-treated dye solution > activated carbon treated dye solution > acid magenta dye (Table 2).

3 Conclusion

The present study revealed that the removal of acid magenta dye by using fly ash is a simple, low-cost, and environmentally benign technology. The phytotoxicity test on mung bean seeds revealed the less toxic and growth-promoting nature of fly

ash-treated dye solution as compared to the toxic acid magenta dye. The present investigation may be useful in fabrication of economically viable treatment system by utilization of fly ash for the removal of acid magenta dye from textile effluent.

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