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Biopolymeric composite materials for environmental applications

Abstract: The emerging phase of bioeconomy demands that human beings be concerned more with ecofriendly practices in every aspect of life. Thus, the demand for biopolymer/biopolymer-based composite materials has witnessed a surge in recent decades. Biopolymeric composites at macro, micro, and nano scales have various applications in environmental cleanup. Biopolymers from natural resources have established an important position owing to their easy availability, abundance, and biodegradability. This review reveals the advantages of biopolymer usage in the field of environmental remediation over conventional practices and also the advantages of biopolymer composites over general biopolymeric material. Further, it focuses on the recent rapid development of nanotechnology, which has led to significant advances in the design and synthesis of biopolymer-based nanocomposites, with higher specific surface areas that can be functionalized to strongly adsorb contaminants in comparison with conventional adsorbents. It also presents the biopolymer-based composite materials separated on the basis of scale commonly used for environmental applications such as the removal of dyes, oil–water separation, and air filtration. This review also summarizes the benefits and drawbacks on biopolymer composite usage along with future perspectives to give an idea on the areas for researchers to focus on in the future.

Keywords: biodegradability; biopolymers; environmental cleanup; nanocomposites.

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1 Introduction

Plastic, being an omnipresent material with high usage, has become a matter of serious concern as its negative impact is no longer restricted to the land but extended to water bodies, air, and the bodies of living organisms. According to statistics from around the world, 44% of seabird species, 86% of sea turtle species, and 43% of marine mammal species are at risk of consuming microplastic from marine waste [1]. Polymers provide a natural and greener solution to the aforementioned problem. Due to their variety, accessibility, and durability, polymeric materials, which have blossomed on world markets over the past 50 years, are essential to any product [2]. There are two types of polymers, i.e., biological polymers and synthetic polymers, both of which are helpful in making human life much better by providing comforts and facilitation to mankind. These are also responsible for leading a human life to the fullest via medication, nutrition, buildings, highways, transportation, drug delivery, etc. [3].

In this context, biopolymers made of lipopolysaccharides, polysaccharides, proteins, polyhydroxyalkanoates, or glycolipids that are obtained from microbial, plant, and animal sources have received a lot of attention in recent times due to the alarming issues caused by the use of petroleum-derived synthetic polymers and could be utilized for a variety of natural implementations [4]. Heavy metals and chemical dyes are two common contaminants that biopolymer materials are effective at removing. In conjunction with these, chronic contaminants such as nitrates, phosphates, perchlorates, fluorides, hydrocarbons, herbicides, and others have also been addressed. Additionally, biopolymers serve as naturally occurring coagulants and flocculants to cleanse storm water [5], minimizing the dependability on synthetic polyelectrolytes [6].

Natural fibers are widely utilized all over the world in a range of applications, including those in the aerospace and automotive industries, sporting events, the delivery of medical implants and drugs, garments, packaging, infrastructure, and construction, leathers and household equipment, and many housewares [7]. Plastic culture is a method that significantly utilizes plastic products for numerous uses in intensive farming [8]. Engineered biopolymers, including petroleum-based resins, castor oil–based nylons, vegetable oil–based polyesters, and soy oil–based emulsions, are manufactured to custom specifications designed for use in the automotive industry [9]. In the polymer industry, poly (lactic acid) (PLA) has attracted a lot of commercial interest among the natural polymers due to its unique mechanical qualities and biodegradability [10]. Biopolymers are involved in the development of antimicrobial textiles, as mentioned by Shahid and Mohammad [11]. For the environmental remediation of crude oil–polluted sites, biopolymers such as C8 (3-hydroxyoctanoate), C10 (3-hydroxydecanoate), C12 (2-hydroxydodecanoate), C14 (3-hydroxytetradecanoate), and C16 (3-hydroxydecahexanoate) can be widely used. Additionally, polyhydroxyalkanoate plays a vital role in pathogen survival and stress tolerance in hazardous conditions and low food supplies [12].

The presumed shortage of fossil resources is a major commercial driver for biopolymers, especially petroleum. Most conventional polymers currently available are made from crude oil [13], which acts as a pollutant for the environment. A major trend in recent years has been the substitution of bioplastics made from fossil fuels with compounds produced from renewable sources that are identical [14]. For example, poly (lactic acid), which is derived via fermentation from renewable sources like starch or sugar, is one of the most successful and popular bioplastics [15]. The low cost and reliable supply of fossil fuels can be achieved by biopolymers. In less than 20 years, petroleum-derived plastics have almost completely replaced plant-based materials [16].

In this context, bio-based plastics, polymers, and biocomposites can provide more environmentally friendly substances with a lower impact on the environment. The term "biopolymer composites" refers to biodegradable materials that are augmented with a range of fibers derived from plants and animals and/or natural and/or artificial biopolymers [17]. Further, biopolymers can provide unique qualities like increased rigidity and strength, which when merged with recycled polymers can result in completely bio-based and recyclable systems [18]. Composite materials, which are constituted of a matrix and an active ingredient, are exceptional sorbents because of their remarkable chemical and mechanical stability. The most desirable ingredients for composite sorbents include biopolymers like bentonite and chitosan [19]. Nanotechnologies in the field of industrial water remediation have emerged lately improving the overall efficiency, cost, eco- and environmental-friendliness, as well as providing a greener approach to treating wastewater. Nanoscale particles, platelets, and fibers range between 1 and 100 nm [20]. Nanomaterials offer superior selectivity, sustainability, stability, and adsorption capacities than other substances. Polymer science and nanotechnology are the other areas of interdisciplinary research that will have a direct impact on environmental protection. Environmental protection will be directly impacted through an interdisciplinary approach involving polymer science and nanotechnology.

Reddy et al. [21] deliberately explained the benefits of biopolymers, including reduced CO_2 emissions, alternative products at a cheaper price, minimizing the toxicity toward the environment, and benefitting to rural economy. Biopolymer composites are more attractive due to their sustainability, low cost, high stiffness, lightweight, higher strength, good thermal properties, eco-friendliness of renewable materials, and health and safety of the manufacturer and consumers [22]. Some of the commonly used biopolymers in composite making are illustrated in Figure 1. Since nothing in our world is perfect, biodegradable polymers, which are recommended for older systems, contain a few limitations, including it is not intended to recycle biodegradable plastic along with other types of plastic. Moreover, improper handling results in an inefficient decomposition of the plastic, which can discharge flammable gases and carbon into the atmosphere [21]. Currently, biopolymers are used to minimize the negative environmental impact of "used" plastic products.

This study aims to delineate the various biopolymer composites production methods in macro/micro/nano scale along with their applications in environmental clean-up. It also compiles their availability and abundance as well as their tuneable structural,

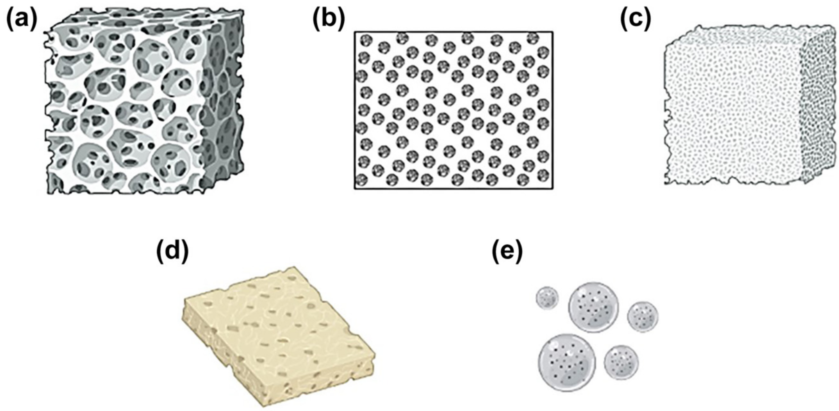

Figure 1: Structures of commonly used biopolymer. (a) Chitosan, (b) cellulose, (c) alginate, (d) starch, and (e) poly vinyl alcohol.

physicochemical, mechanical, and biological characteristics. The advantages, drawbacks, research gap, and future perspective visualizing the use of biopolymer composites in this field are the other aspects of this review.

2 Production strategies and characterization of biopolymers-based composites (macro/micro/nano level)

Due to its low cost and ease of use, the precipitation approach, such as chemical precipitation, has historically been used to remove pollutants. Its inability to remediate environments with high pollution concentrations, however, restricts its economic application. When not renewed, ion exchange systems that produce resins could result in secondary contamination. They are also not cost-effective for treating huge amounts of wastewater. Adsorption, advanced oxidation, membrane separation, and ozonation are a few examples of cutting-edge processes with great efficacy. The ease of use and low cost of operation of adsorption, on the other hand, make it a superior method for eliminating environmental toxins. The development of effective, stable, and affordable adsorbents for application in batch size clean-up methods is receiving increased attention [23]. In this aspect, bio-based and renewable sources have caught the attention of many researchers as they are eco-friendly and sustainable compared to traditional methods, which are no longer economically feasible. Based on their structural moieties, engineering properties like biodegradability, absorptivity, and hydrophilicity/hydrophobicity enable biopolymers to become potential alternatives to their chemical/synthetic/nonrenewable counterparts. Bio-based polymers or biopolymers may be derived from animals, plants, or microorganisms and can be composed of repeating monomers forming proteins, polysaccharides, lipopolysaccharides, glycolipids, or polyhydroxyalkanoates [6]. Biopolymers can have a well-defined macro, micro, or nanostructure compared to the random structure of synthetic polymers; they can be broken down into smaller chains or monomeric units by environmental factors, reducing the threat to environmental security [24].

In order to overcome some of the drawbacks of polymeric qualities, such as weak mechanical performance, low resistance, constrained processing capacity, and long-term stability, biopolymer composites were developed. They are produced by adding the right fillers, such as metal, metal oxides, and natural fibers, to biopolymers to strengthen them [25]. There are several ways to create biopolymer composites (as shown in Figure 2). Reinforcement materials can be introduced to the growth medium as polymers are formed through the fermentation process, and their polymerization in the form of fibrils occurs extracellularly. These additional components, such as nanomaterials and polymer solutions, can combine with the produced polymers to produce composites. Another production process is the postsynthetic composite synthesis, where the reinforcement elements are treated with prepared biopolymers before being inserted inside of or adhered to the surface of the polymer matrix to create composite structures. Another synthesis technique is polymer blending, which involves combining two polymer solutions in various ratios before casting to create materials like composite films or fibers. Degradability, physical characteristics, mechanical strength, thermal stability, and biocompatibility are just a few of the characteristics of composite materials that can vary greatly. By altering the ratio of the matrix and reinforcing components, these characteristics can be changed [26].

Alginate-based compounds have been proposed for a variety of uses in wastewater remediation for the adsorption of pollutants due to their benign nature, biodegradability, durability, and water permeability. The benefits of stable biohydrogel beads' network structure, surface moieties, and high surface area have led to their effective use as a

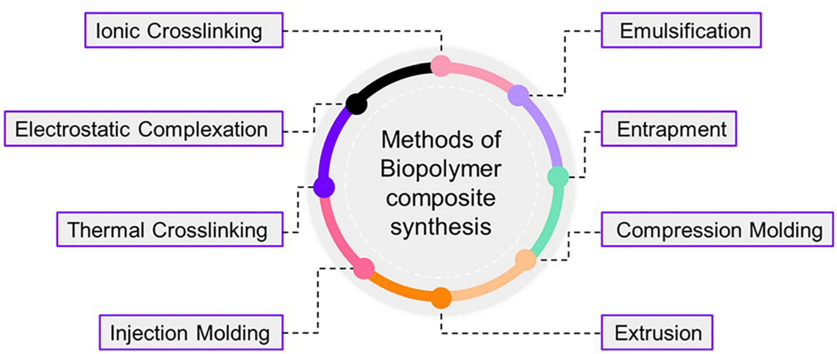

Figure 2: Various production strategies for synthesis of biopolymer composites.

catalytic support material [27]. Alginate-based composites' synthesis, or the physical and chemical cross-linking techniques used to create them, heavily influences both their properties and possible applications. Alginate-based composites have been created using four popular techniques: ionic cross-linking, electrostatic complexation, emulsification, and self-assembly. Ionic contact, crystallization, hydrophobized polysaccharides, stereo complex formation, protein interaction, and hydrogen bonding all contribute to the physical cross-linking of hydrogels. Contrarily, chemically cross-linked hydrogels are produced using gamma and electron beam polymerization, addition, and condensation polymerization and chain growth polymerization. These synthesis techniques each have advantages and drawbacks of their own. Physically cross-linked sodium alginate hydrogel is easy to make under mild circumstances; however, the gel strength is low [28].

Zhang & Chen [29] proposed that pH-dependent Pb (II) and Cu (II) ion sorbents were cross-linked starch graft copolymers with amine groups. This is because the amine groups on the surface undergo protonation and deprotonation. Guo et al. [30] developed cross-linked porous starch by hydrolyzing maize starch using α-amylase, cross-linking it with epichlorohydrin, and creating a brand-new biopolymer-based sorbent for removing methylene blue (MB) from water. Membranes for hemodialysis, distillation, micro-, nano-, and ultrafiltration based on cellulosic nano- and microfibers that are made from cellulose nanomaterial mats embedded in a polymer matrix (cellulose triacetate, poly (ether sulfone)), polypyrrole, poly (acrylonitrile), poly (vinyl alcohol), poly (ethylene oxide), poly (3-hydroxybutyrate), and poly (vinylidene fluoride) [27]. Iota-carrageenan and polyamidoamine dendrimers are physically cross-linked in the presence of varied magnetic nanoparticle (NP) concentrations.

Abdellatif et al. [31] created secure, environmentally friendly, and affordable magnetic aerogels (1%, 3%, and 5%). The aerogels' high removal effectiveness was demonstrated by the evaluation of their adsorption behavior for the metal ions Cr (VI), Cu^{2+}, Co^{2+}, Mn^{7+}, Cd^{2+}, and the fast blue dye Alphanol. Cañizares et al. [32] examined the active entrapment of spirulina maxima in kappa-carrageenan as a tertiary treatment for diluted aeration-stabilized swine manure. The immobilized algae were subjected to several iterations of the effluent cycles. Gopi et al. [33] reported on the efficient treatment of wastewater by multifunctional biohybrid aerogels constructed of cellulose nanofibers (CNFs) and adorned with carbon nanocellulose (CNC). By adjusting the ratio of CNCs used during the freeze-drying process, hybrid bioaerogels were created that were decorated on the CNFs and could be reused at least five times without losing activity or efficiency.

Thermal cross-linking between (2,2,6,6-tetramethylpiperidin-1-yl) oxyl (TEMPO)-oxidized cellulose nanofibers (TOCNF), branched polyethylenimine (bPEI), and citric acid has produced micro- and nanoporous sponge-like systems with demonstrated sorbent efficiency against various dyes (such as Cibacron Brilliant Yellow, Brilliant Blue R, Orange II, and Naphthol Blue Black) [27]. This work successfully treated cotton waste thermally to create unique carbon microtubes, which were then employed as tannic acid (TA) sorbents. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, zeta potentiometer, and N_2 adsorption and desorption techniques were used to examine the characteristics of carbon microtubes (CMTs). The temperatures at which CMT and TA were treated to produce the most stable solutions in water were 900 °C, 1300 °C, and 1100 °C, respectively. CMT treated at 1100 °C had the highest TA sorption capacity, which was found to be 596.5 mg/g [34]. Since the *Moringa oleifera* plant's seed extracts have coagulation qualities that are excellent for purifying water, they have been utilized extensively for this purpose, especially in impoverished nations. Additionally, because *M. oleifera* seed husks have an embedded microstructure and a high carbon content, they can be utilized to recover high-quality activated carbon that can be used to cleanse water instead of activated carbon [35]. Zeolites are crystalline, microporous aluminosilicates with ion exchange capabilities that can be used in a variety of catalysis and separation processes for liquid and gaseous mixtures. The diffusion outside of the zeolite crystals can be effectively controlled by incorporating in chitosan membranes, and correctly built composite systems can find a wide range of uses in wastewater treatment. Clinoptillolite microcrystals were disseminated in 3% chitosan in a 1% aqueous acetic acid solution. During the gelling procedure, the chitosan gel was created and the zeolite crystals were enclosed [36].

A bio nanocomposite is a form of hybrid material made up of a combination of an inorganic solid having at least one dimension at the nanometric scale and a natural polymer or biopolymer. Particularly, when compared to conventional microfillers, nanostructures can have higher specific surface areas, surface energies, and densities. This can result in materials with novel and improved properties because of synergistic effects that are superior to those brought on by the simple rule of mixtures [37]. However, the difficulties with NP separation during the process and their subsequent recycling limit their application as aqueous solutions. These NPs are consequently immobilized on a polymer matrix, which can be made of biopolymers such as resins, chitosan, carboxymethyl cellulose, and cellulose acetate. The material's mechanical, thermal, and biological properties are significantly improved by the integration of nanoparticles inside the polymer matrix. Over the past 20 years, a wide range of bio nanocomposites have been developed by intercalating high molecular mass biopolymers like alginate, cellulose, chitosan, starch, sacran, gelatine, zein, or polylactic acid into clay minerals like palygorskite, smectites, sepiolite, and micas.

To date, the removal of heavy metals, pesticides, reactive dyes, and even newly developing contaminants like bisphenol A from aqueous media has all been accomplished using this novel class of biohybrid materials. Additionally, when clays and polymers are combined to create bio nanocomposites, some of the individual drawbacks of each material (particle size, poor specificity, sensitivity to pH, as well as low wettability) are overcome [38]. Based on the intercalation of chitosan in organically or natively occurring vermiculite (with hexadecyltrimethylammonium (HDTMA)), Padilla-Ortega et al. [39] created functional bio nanocomposites (HDTMA) for cadmium uptake. The materials were homogenized using ultrasound, and low-density macroporous foams were created from them. The electrostatic connection between the protonated amino groups and the negative charge in the natural vermiculite layers was responsible for the intercalation of chitosan, as per Fourier transform infrared spectroscopy (FTIR) analysis. Salgueiro et al. [40] presented kappa-carrageenan–coated superparamagnetic iron oxide nanoparticles for enhanced removal of MB from aqueous solutions. The generated superparamagnetic composite nanoparticles demonstrated an MB absorption ability dependent on the pH of the solution and included about 12 wt percent carrageenan, making them potential eco-friendly materials for MB removal through magnetic separation. In their study, Saxena et al. [41] evaluated the effects of reinforcement on water transmission while reinforcing acacia fibers, bleached softwood kraft fibers, and nanocrystalline cellulose to xylan/sorbitol films. The results of the experiment showed that the nanocrystalline cellulose composite films have a more closed structure than the control film.

The most popular characterization methods for figuring out the interface of biopolymer composites include FTIR spectroscopy, laser Raman spectroscopy, solid state nuclear magnetic resonance (ssNMR) spectroscopy, ion scattering spectroscopy, Auger electron spectroscopy, X-ray photoelectron spectroscopy, wide-angle X-ray scattering (WAXS), and contact angle measurement. Microscopic visualization methods like the atomic force microscope (AFM), polarized optical microscope (POM), SEM, scanning tunneling microscope (STM), and field emission scanning electron microscope (FESEM) are used to examine the particle distribution, reinforcements in the matrix, surface interaction between the fiber and biopolymer, and voids. The necessary magnifications are used to capture the images for simple visualization and analysis. For the purpose of measuring the surface roughness of fibers or biopolymer composites, AFM uses high-resolution nondestructive analysis. The surface depth profile, surface morphology, physiochemical changes, and fiber–matrix interaction are also disclosed by these morphological approaches. The intensity of the band depends on the concentration of nanocellulose, and the FTIR analysis showed a significant interaction at the OH band, showing robust interfacial bonding between nanocellulose and the matrix surface. The effect of natural fiber on the crystallinity of biopolymer composites is researched using X-ray diffraction (XRD) analysis. The XRD data are mostly correlated with the FTIR analysis and the thermal, mechanical, and barrier properties of the composites. It is well known that adding natural fibers to biopolymer composites improves the interfacial bonding and crystallinity of the material, which in turn improves the mechanical properties [42].

3 Application of biopolymer-based composites

Many biopolymers and biopolymer composites have shown significant potential in tackling contemporary environmental issues and have been successfully used in a variety of areas. Applications for waste water treatment have come into focus as a result of the characteristics of biopolymers and their composites. The cost of the clean-up procedure is decreased with the use of economical polymers as an adsorbent. Pollutant adsorption has historically made extensive use of composites. The primary characteristics of biopolymer composites, such as higher durability, processing capabilities, high functionality, and a vast surface area, accelerate the removal of impurities or pollutants from the environment by adsorption [43]. The biopolymer composites utilized for different environmental applications are shown in Figure 3.

3.1 Biopolymer composite with macro particles

An aromatic polymer called lignin has a lot of active functional groups and fascinating electroactive redox characteristics. Using lignin and environmentally friendly methods, harmful colors can be effectively removed from wastewater effluents. Up to 10–25% of lignocellulosic biomass is composed of lignin. By using a solvent evaporation method, lignin-based chitosan composite membranes were created, which were then used to filter water of the MB dye [44]. With a 95% effectiveness, the membrane's adsorption kinetics mirrored Langmuir's adsorption kinetics. By repeatedly creating the membrane and assessing its adsorption performance, which remained unaltered from that of the fresh membrane, the reusability of the membrane was also investigated. Wang et al. [45] developed an environmentally acceptable nonsolvent-induced phase separation method for an antibacterial chitosan/polyvinyl alcohol blend system for air filtering. The membrane was made with a concentration of 30 wt% chitosan and a thickness of 300 μm. It had a gradient, interconnected porous structure without a skin layer that was 95.59% effective at filtering air. It was composed of pores of varying sizes, with the biggest pore being 467 nm in diameter and a surface porosity of 21.5%. It was determined that the thickness of the membrane was the most important factor in determining the filtering performance and that the direct interception of NaCl aerosol particles on the surface of the membrane was the most effective mechanism for their removal. Different applications of biopolymer macro composites are listed in Table 1.

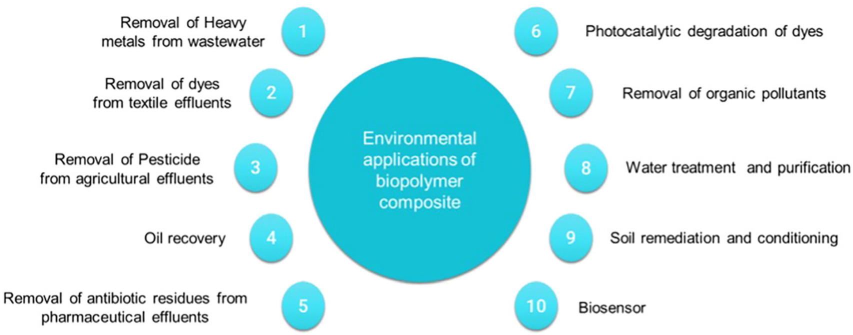

Figure 3: Applications of biopolymer composites in environmental remediation.

Table 1: Different biopolymer macrocomposites and their applications.

Biopolymer	Filler	Applications	References
Chitosan	Gelatin	Removal of Pb (II), Cd (II), Hg (II), and Cr (III)	[50]
Polyethylene oxide/ TEMPO-oxidized cellulose	Chitosan	Removal of Cu (II)	[51]
Carboxymethyl cellulose	Guar gum and graphene oxide	Removal of malachite green	[52]
Carboxymethyl cellulose	Acrylamide and graphene oxide	Removal of ionic dyes	[53]
Chitosan	Alginate	Removal of glyphosate herbicide	[54]
Cellulose nanofibril	Graphene oxide	Removal of broad types of antibiotics	[55]
Poly vinyl alcohol	Cellulose	Removal of ionic dyes from waste water	[56]
Cellulose	Graphene oxide	Removal of methylene blue	[57]
Cellulose	Graphene oxide/1-ethyl-3-methylimidazolium acetate	Removal of lead, zinc, cobalt, and nickel from wastewater	[58]
Cellulose	Graphene	Removal of oil from waste	[59]
Cellulose nanofibril	Graphene oxide	Removal of doxycycline, chlortetracycline, oxytetracycline, and tetracycline in pharmaceutical wastewater	[60]
Cellulose triacetate	Activated carbon	Ultrafiltration membrane for removal of uranium from water	[61]
Starch	Acrylic acid	Removal of ionic dyes	[62]

Zhu et al. [46] produced a magnetic composite made of polyvinyl alcohol and chitosan using the wet gel technique. This composite has a capacity for adsorption of 14.39 mg/g during 2 h, and it attained 97.5% adsorption efficiency. The inclusion of -NH_2 and OH groups in the composite was determined to be the cause of this composite's increased Co^{2+} adsorption value. Cu (II), Fe (II), and Cr (VI) can be extracted from hydrogels made of dextran and starch that were produced with the monomers of acrylamide, N-isopropyl acrylamide, and 2-acrylamido-2-methylpropanesulfonic acid and then cross-linked with N, N-methylene bis acrylamide [47]. Ion-exchange groups were included in the synthetic hydrogels, in addition to the hydrogels' high water absorption capacity. The impact of functionalization upon metal ion uptake has also been investigated. The findings of this research could aid in the advancement of hydrogel-based technologies for extracting and purifying metal ions from water.

An ultra-hydrophobic copper nanoparticle–coated cellulose aerogel (Cu/CEA) was created with the aim of separating oil and water. Li et al. [48] found that Cu/CEA has the potential to collect oily pollutants quickly and selectively. Furthermore, it has an excellent oil absorption capacity and good recyclability. The TiO_2 nanoparticles were used to create an aerogel that was generated from gelatin, and glutaraldehyde was used to cross-link the aerogel with bPEI. It has been determined that the hierarchical porous structure of the aerogel and its highly amphiphilic surface are responsible for the exceptional oil/water separation capacity that it possesses in free mixes and emulsions. In addition, aerogel demonstrated a high ability for adsorption of cationic and anionic organic dye. The capacity of composite aerogel to effectively absorb copper ions from aqueous solutions was noteworthy. Most importantly, aerogel can be rejuvenated by the use of methanol, ethylenediamine tetraacetic acid (EDTA), and copper (II), respectively [49].

3.2 Biopolymer composite with microparticles

Efforts to clean up the environment made extensive use of biopolymer composites based on the substance chitosan. Increasing chitosan's capacity to absorb inorganic nitrates from wastewater discharge, chitosan is often blended with synthetic hydrophilic polymers such as poly vinyl alcohol (PVA) and polyethylene glycol (PEG). To increase its propensity to interact with nitrates in wastewater, the chitosan-PVA/poly glycolic acid microcomposite is activated at acidic pH, ionizing the amine group on the backbone of chitosan. Rajeswari et al. compared the two microcomposites for their nitrate adsorption effectiveness and found that the chitosan/PEG microcomposite had a higher adsorption capacity (50.68 mg/g) than the PVA/chitosan microcomposite (30 mg/g) [63]. As for the adsorption kinetics, the Freundlich model revealed that the reaction was endothermic and had a high affinity for nitrate. In an alkaline solution, the chitosan microcomposite can be regenerated for further usage.

The adsorption of dyes and other colored substances from wastewater has become more common in recent years thanks to the usage of microhydrogels based on alginate. Although alginate by itself is an effective adsorbent for dyes, the use of composite micro hydrospheres comprised of alginate combined with other adsorbents has been shown to be a more effective method of removing dyes from wastewater. Beads made of calcium alginate and activated carbons were combined to make a composite material for the removal of MB from wastewater. When the pH was greater than 6, it was demonstrated that the adsorption of dye followed a pseudo-second order mechanism. In general, the study on thermodynamic parameters during the adsorption process, it was found that the adsorption occurred naturally and generated endothermic activity [64].

In addition, Benhouria et al. [65] synthesized an alginate-based microcomposite hydrosphere that was utilized for the process of removing MB from the wastewater. Simple synthesis is intended for the formation of a composite consisting of activated carbon, bentonite, and alginate. At a temperature of 30 °C, the maximum monolayer adsorption capacity of the hydrosphere for the adsorption of MB was measured at 756.97 mg/g. The application of the pseudo-second-order kinetic model was shown to be appropriate by the adsorption kinetics. The data on the equilibrium adsorption were a good fit for the Freundlich isotherm. After undergoing six rounds of regeneration, the composite demonstrated an adsorption absorption capability of greater than 70%. For the elimination of ionic dyes such as methyl orange and MB, a bioadsorbent was created by Sui et al. [66] employing the wet spinning approach. This bioadsorbent was made of calcium alginate and multiwalled carbon nanotube composite fiber. The adsorption efficiency for the elimination of ionic dyes has been improved by a factor of three as a result of the use of multiwalled carbon nanotubes. The composite behaved according to an adsorption isotherm of the second order. Further, they observed that the initial pH value is one of the most crucial elements that affects the dyes' capacity to be adsorbed onto the composite. Table 2 enlists the different biopolymer microcomposites with their application.

The leather manufacturing industries make heavy utilization of basic black dye, which is one of the most commonly used dyes in general. Aravindhan et al. [67] conducted research to evaluate the possibility of removing the basic black dye with calcium alginate microhydrogels. At an initial concentration of 300 mg/L, with 4 g/L of alginate dose, at a pH of 4.0, the maximum adsorption capacity of 57.70 mg/g was attained at room temperature. The Langmuir isotherm offers a better fit for explaining the adsorption of the dye by alginate beads, which implies that the binding surface is both homogeneous and monolayer, as was amply demonstrated by adsorption kinetics. The thermodynamic characteristics suggested a spontaneous endothermic adsorption mechanism, while the adsorption kinetics followed a pseudo-second order.

3.3 Biopolymer composite with nanoparticles

A novel graphene oxide/sodium alginate/polyacrylamide ternary nanocomposite hydrogel with excellent mechanical performance was created by the polymerization of acrylamide and sodium alginate by free radicals in the presence of graphene oxide in an aqueous environment before calcium ions were ionically cross-linked. The hydrogel was fabricated by using graphene oxide as a catalyst. Reinforcing the sodium alginate/

Table 2: Different biopolymer microcomposites and their applications.

Biopolymer	Filler	Applications	References
Chitosan	Carboxymethyl cellulose	Removal of ionic dyes	[68]
Cellulose and welan gum	Carbon nanotubes	Removal of methylene blue	[69]
Chitosan/hydroxyapatite	Manganese dioxide	Photocatalytic degradation of acid orange 7 dye	[70]
Chitosan	Loofah powder	Adsorption of surfactant, organic acids, and dyes	[71]
Chitosan	Bentonite	Heavy metal adsorption	[72]

polyacrylamide nanocomposite hydrogel with graphene oxide allows for an increase in the hydrogel's mechanical properties. Additionally, the nanocomposite hydrogels exhibit excellent elasticity. The robust interfacial interactions that exist between graphene oxide nanosheets and polymer chains are accountable too for this phenomenon. Because graphene oxide was included in the formulation, the composite hydrogels have excellent adsorption capabilities for both cationic and anionic dyes [73].

Zhuang et al. [74] created a brand-new class of porous graphene/alginate double network nanocomposite beads with a porous structure, larger surface area, and greater stability at higher NaCl concentrations. According to the Langmuir model of adsorption, the produced nanocomposite possessed a maximum adsorption capacity of 1.84 g/g even after undergoing 10 adsorption–desorption cycles. This was the case even though the material had been subjected to both conditions. The adsorption of Congo red 4B, acid red GR, and bright yellow K4G was investigated using material generated from cellulose by Jin et al. [75]. A nanocellulose/amphoteric poly-vinylamine nanocomposite microgel was formed in an acidic environment and found to be especially efficient at removing anionic dyes. It was shown that Congo red 4BS, acid red GR, and light-yellow K-4G each had maximal adsorption capacities of 869.1, 1469.7, and 1250.9 mg/g, respectively. In order to purify water using a thin-film composite membrane, silver and platinum nanoparticles were included into nanocellulose-derived composites as additives. These nanoparticles were used for the support layer of the membrane. Samples of nano-pure water, urea, and wastewater were used in the experiment to test the forward osmosis capability of the membrane. The research showed that altered composite membranes made of nanocellulose thin films for wastewater samples exhibited greater water fluxes and solute rejection compared to conventional membranes [76].

Microwave heating was utilized by Mostafa et al. for the synthesis of chitosan/zinc oxide (CS/ZnO) nanocomposite because of the reduced time required for reactions compared to traditional heating [77]. Composites made at 800 W of power for 10 min were discovered to be efficient at removing dye. Due to the presence of zinc cations on the surface, the nanocomposite additionally exhibited improved thermal characteristics and demonstrated better efficiency. According to the findings of the adsorption investigations, the optimal conditions for the removal of MB dye by CS/ZnO nanocomposite and CS were 20 mg/L and 60 mg/L at a pH of 9 for 60 min. The MB dye removal was improved from 81% to 96.7% under these circumstances attributable to the incorporation of ZnO nanoparticle in CS.

Activated carbon, chitosan, and polyvinyl alcohol were used by Akter et al. to synthesize CS-AC-PVA beads. At 25 °C and a pH value of 5, the synthesized beads demonstrated a strong affinity for removing Pb (II) from water [78]. In contrast to the usual pH-dependent activity of the sorption mechanism, the CS-AC-PVA beads had about the same affinity at pH 4–6. However, the adsorption capacity in CS-AC-PVA beads rose with increasing concentration, and the kinetics model of Pb (II) shifting onto CS-AC-PVA beads followed pseudo-second-order kinetics, showing that Pb (II) ion was largely adsorbed on the CS-AC-PVA surface via chemical interactions. The thermodynamic

Table 3: Different biopolymer nanocomposites and their applications.

Biopolymer	Filler	Applications	References
Phosphorylated nanocellulose	Chitosan	Removal of Cd (II) ions from aqueous solution	[79]
Sodium alginate	TiO_2/bentonite	Removal of methylene blue by photocatalysis	[80]
Carboxymethyl cellulose	Graphitic-carbon nitride and zinc oxide	Removal of methyl violet dye	[81]
Alginate	Au/Mica	Removal of Pb (II) and Cu (II)	[82]
Alginate	Montmorillonite	Removal of cationic pesticide – paraquat	[83]
Alginate	Maghemite (γ-Fe_2O_3) nanoparticles coated by citrate ions	Removal of a surfactant: cetylpyridinium chloride	[84]
β-cyclodextrin	Fe_4O_3–graphene oxide	Adsorption and removal of neonicotinoid insecticide pollutants from aqueous solution	[85]
Chitosan	Silver nanoparticles	Solid-phase extraction of metal pollutants from surface waters	[86]
Gum xanthan	Fe_3O_4 magnetic nanoparticles	Adsorption of malachite green	[87]
Cellulose	Titanium dioxide	Catalytic adsorption of methylene blue (MB) from aqueous solutions	[88]

analysis pointed to the exothermic character of chemical adsorption as the sorption mechanism. As a result of their high affinity for Pb adsorption in aqueous solutions and relatively straightforward production, CS-AC-PVA beads have emerged as a promising adsorbent for Pb removal in Pb-contaminated water environments. Biopolymer nanocomposites extends its application in various environmental remediation, few are listed in Table 3.

4 Benefits and limitations on the usage of biopolymers composites in environmental remediation

Materials generated from biopolymers are not only environmentally friendly and renewable but they also offer superior performance while leaving a smaller carbon footprint. These polymers are utilized mostly due to the benefits that they offer, which include being chemically inert, lightweight, long-lasting, and flexible in terms of shape and size. Composite materials have the advantage of being able to have a range of qualities designed for them, which can change depending on what the composite will be used for. This flexibility in design is one of the advantages of composite materials. The programmability of these materials is their primary benefit, which now enables them to be utilized in a variety of contexts.

Particularly, biopolymer-based nanocomposites offer advantages, including active functional moieties, dimensional change, and film formation, that make them suitable for usage as catalysts and adsorbent materials. Because they are less expensive, less likely to harm processing machinery, have good mechanical properties like tensile modulus and flexural modulus, improve the surface finish of molded composite parts, are produced from renewable resources, are flexible during processing, biodegrade, and present few health risks, natural fibers are preferable to synthetic ones.

It is challenging to use biopolymers in extensive commercial applications due to their inherent limitations, which include their poor processibility, brittleness, hydrophilicity, insufficient gas and moisture barrier, inadequate compatibility, and electrical properties. These barriers need to be diminished with the appropriate changes in order to be used commercially as photocatalyst supports. Low production rates, thermal stability, and physicochemical resistance limit the use of biopolymers as photocatalytic membrane materials. Depending on their concentration, these photocatalysts can occasionally have hazardous consequences. The two main challenges encountered during the manufacture of NPs loaded polymeric membrane are NP aggregation and pore clogging. TiO_2 clumping lowers the specific surface area, which leads to poor photocatalytic degradation efficiency. Although electrospinning is a simple method for creating membranes or nanofibers with a large surface area and high porosity, the membrane must be produced at a high voltage or the other hand low deposition rates and a reduced bombardment target area limits the sputtering process [89].

In comparison to activated carbons and zeolites, clay minerals are less effective at removing micropollutants from water due to their limited surface area. Additionally, after adsorption, it is challenging to remove clay particles from the solution, and the adsorption capabilities of the clay minerals are reduced during regeneration for reuse. Low water wettability, sensitivity to particle size, and pH dependence are some cons of polymeric resins, on the other hand. The main disadvantage of dried alginate beads is their weak porosity, which prevents the passage of heavy metals. After adsorption, tannin is challenging to separate since it is a molecule that is water soluble. Thus, one of the promising ways of overcoming these shortcomings is to prepare composites for improving their efficiency. Cross-linkers can also be used to compensate for inherent defects in biopolymers, such as insufficient mechanical stability, poor chemical and thermal resistance, and partial solubility in watery circumstances [90].

Different support materials have different shortcomings, such as (i) metals are expensive, thermally unstable with high mass loss and low reusability; (ii) issues with recovery and reusability exist for carbons; (iii) ceramics have low activity compared to the polymer; (iv) hydrophilicity of cellulose restricts the use of cellulose with hydrophobic pollutants; and (v) restrictions on the protonation of chitosan's NH_2 groups and dissolution in acidic medium, and moreover, polymers have low mass transfer [91]. The ability to synthesize and use nano, micro, and macro adsorbents for the removal of toxic metal ions and other toxic contaminants has been limited by the uncontrolled use of chemicals, catalysts, low yield, a series of by-products, and demanding experimental conditions. Environmental protection is a major concern despite the ability of ever-newer chemical strategies to produce precise structures with desirable properties [92].

5 Future perspectives

In order to develop a sustainable circular economy and gradually decrease the heavy dependence of humans on plastic usage derived from non–eco-friendly sources, considerable efforts and research still have to be put into adapting renewable alternatives such as biopolymers/biopolymer composites and recycling of plastic waste to regenerate the damaged natural system.

As most of the research is restricted to laboratory scale, the main constraints in the real time application of biopolymer composites for environmental applications lie in their inability to yield the same results as inside the laboratory and also in their incapacity to mimic real time conditions [93]. For example, at low pollutant concentrations, researchers have been able to specify a precise range of doses/parameters for ideal coagulation and flocculation, for effective wastewater treatment. But, when the volume increases at an industrial scale due to a lack of scale up data, the desired efficiency is not achieved [94]. Thus, further research needs to be carried out using the laboratory scale data for scaling up studies to achieve comparable efficiencies and reduce the risk of commercialization. Moreover, along with scaling up a process, the economical aspect also has to be taken into consideration. Further with the rapid urbanization and industrial advancement, the concentration and chemical nature of the pollutants keep changing, which requisites constant improvement in stability and chemical robustness of biopolymer composites as adsorbents. Newer biopolymer composites need to be developed with cost-effective green methods, with higher efficiency to reduce the dependence on conventional methods and also to remediate the newer pollutants. A better understanding of the mechanism and chemical structure of novel composites, along with the standardization of their synthesis methods, will help in better utilization. As most popular regenerating agents are harmful (e.g., EDTA) and/or harmful to biosorbent polymer backbones (like inorganic acids), researchers are yet to identify safer eluents and better regeneration procedures [95].

6 Conclusions

Polymeric materials have been thriving in global industries that are widely used in aerospace, sports, medical implant and drug deliveries, textiles, packaging, infrastructure and building, upholstery and furniture, and many household products.

Nondegradable synthetic polymer environmental pollution is a major global challenge that is only getting worse. This review discusses about the biopolymers, which has made an entry to minimize the downside characteristics of polymers on that account they have been a promising alternative for synthetic materials by being solitary solution to our mother planet. Biodegradability, sustainability, eco-friendliness, cost effectiveness, noncorrosive nature, and lightweight characteristics are the attributes of biopolymers along with significant strength of renewable materials by maintaining health and safety of manufacturer and consumers. The removal of heavy metal ions from industrial wastewater has been demonstrated to be a successful application of the bio nano-composite as an adsorbent. The qualities of these hybrid materials will improve with the continued development of more environmentally friendly biohybrid composites. Additionally, the creation of novel biocomposites with regulated breakdown at the conclusion of their life cycles will reduce the buildup of uncontrolled garbage in landfills.

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