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Recent advances and future prospects of electrochemical processes for microalgae harvesting

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ABSTRACT

Over the years, algae have found wide scope of utility in a variety of environmentally beneficial processes like biofuel production, removal of heavy metals from wastewater sources for potential bioremediation, monitoring water pollution and source of animal nutrition. However, the conventional harvesting methods pose a set-back in terms of energy, cost and operational complications due to the small size of microalgae. Of all the processes, harvesting alone corresponds to approximately 30% of the total production costs. Recent advancements in the microalgal technology have brought many efficient techniques into use for improved recovery of microalgae. This review comprehends the development, principle, influencing parameters and directions to future research of one of the state-of-the-art approaches for harvesting microalgae, electrochemical technology. Though this area was previously explored for its application in wastewater treatment, it has lately gained momentum in the field of microalgae due to its economic efficiency. This paper highlights the three prime processes used to yield microalgae namely electroflocculation, electroflotation and a combined electrocoagulation-flotation (ECF) system. Several encroachments and strategies among these techniques have also been elucidated. The review focusses on the effect of most significant process controlling parameters such as reactor and electrode design, various surface properties of microalgae, current, pH, salinity and agitation that influence harvesting. In addition, the economy and energy aspects that emphasize the welfares of this technology over others have been extensively discussed. The overall work aims to provide an insight into the electrochemical methods, their challenges and opportunities that might be beneficial for carrying out further research and scope for industrial applications.

1. Introduction

Due to the increasing population, the world is facing several encounters related to insufficient diet and energy supplies. Likewise, the uprising of greenhouse gases (*e.g.* CO_2) is also a potential threat [63]. Microalgae can provide prospective answers to these issues efficiently. Their elevated nutritional composition in terms of proteins, carbohydrates and lipids make them employed as an alternative source of food [53]. They can synthesize high amounts of lipid (10–100 times) compared to the terrestrial oil plants mainly due to their rapid growth rates. The value-added products produced by microalgae serve great applicability to the pharmaceutical, food and biofuel industries [46,54]. For instances, the carotenoids present in *Dunaliella sp*. and *Spirulina* sp. are known to possess anticancer properties. Other applications include the use of microalgae as biostimulants [57,58] or biofertilizer [21] in the natural or pyrolyzed form as biochar catalyst for biodiesel / biofuel production [7,55]. They also help in mitigating the atmospheric CO_2 levels by capturing them for survival. Several authors have reported that for obtaining 1 kg of dry microalgal biomass, approximately 1.8 kg of CO_2 is required. Thus, their carbon fixation capacity is relatively 10–50 times higher than terrestrial plants [4–6].

Microalgae possess the ability to adapt themselves to adverse

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environmental conditions which confers them a significant role in bioremediation and wastewater treatment. In addition, they can eliminate the dissolved heavy metals in their surroundings [4]. Though this technology is progressing fast from the laboratory to commercial pilot standards, the drawback lies in the harvesting of microalgal species [47,50]. Microalgae are typical ~5–50 μm in diameter and have a density equivalent to that of water (1020 kg/m^3) [13]. Thus, the harvesting step alone adds up to 20–30% of total production costs. The equipment used solely may represent up to 90% of the total cost in the case of microalgal cultivation in open ponds [10,26]. The methods of harvest currently in use are energy-intensive which is considered as the major bottleneck in the economy of the microalgal industry. Hence, advances in the technique of separating and dewatering microalgal biomass towards the cost and energy-efficient downstream processing technologies will improve the prospects of microalgal oil and related value-added products.

The choice of harvesting technique can depend on various factors, including the physical features of microalgae employed such as size, shape *etc.* that varies with species and majorly on the kind and value of the desired end product. Most microalgae in use are very small in size and are non-filamentous which demand effective ways of separation [38,50]. The steps in the harvesting process can be largely classified into two categories- Bulk harvesting & thickening. The method of bulk harvesting is involved in the separation of microalgal cells from the diluted suspension. This mainly depends on the concentration of initial biomass. The purpose of thickening is to concentrate the biomass further. The latter is considered the most energy-demanding step in harvesting [63].

Based on the mode of separation, the microalgal harvesting techniques can be commonly classified as mechanical, biological, chemical and electrical (Fig. 1). These methods can be applied either individually or combined. Almost all the techniques (except chemical flocculation and electrochemical methods) mentioned above are energy and cost-intensive. Though traditional coagulation might diminish pH and disuse alkalinity, it might lead to the introduction of more chemicals to re-equilibrate a neutral pH prior to distribution. An additional problem of concern with the conventional methods is the treatment of sludge. Chemical coagulants like alum and ferric chloride [6] cause several issues in the treatment plants due to lack of proper sludge management [3,54]. Recently, natural plant based coagulants were explored to complement the conventional inorganic coagulants [6].

As algal cells contain a negatively charged surface, they can be easily played by movement in an electric field. Many effective electric techniques are being used in the algal industry, including pulsed electric fields (PEF), electroporation, ultrasounds and low or moderate electric fields (MEF). The use of the electric field to influence or modify the surface charge of the microalgal cells to induce flocculation holds great potential to improve harvesting. This process can be mainly suggested for harvesting marine microalgae as it markedly decreases the electric energy consumption [28]. Additionally, electrochemical techniques do not destroy alkalinity and concurrently generate lower sludge waste. It potentially offers to be cost-effective, environment-friendly and highly selective of dewatering [47,56]. Harvesting of a microalgal consortium containing *Chlorella vulgaris* and *Scenedesmus obliquus* with electrocoagulation resulted in an energy saving of 89% on par with centrifugation alone [26]. The use of electrolytic flocculation technique for harvesting has revealed huge capacities and elevated performances [23,59].

In comparison with other techniques, electrochemical methods seem to offer exciting advantages such as low energy input, low dose, high recovery efficiency, wide-ranging working pH and lack of coupled anion contaminants in the biomass. This technology might attempt to fill the research gap between cost and environmental impacts caused due to existing microalgal harvesting technologies. In this context, the following review paper beholds various aspects of electrochemical techniques for harvesting technologies such as working principles, novel strategies adapted for improvisation, factors that have significant effect on algal recovery like reactor design, pH, current and duration of supply, conductivity, surface properties of microalgae, agitation rate and superior features compared to other technologies. It further deals with the challenges associated with electrochemical techniques, solutions to overcome the issues as well as successive perspectives.

2. Electrochemical processes

Electrochemical processes are being used for a wide variety of applications in the algal industry. Upon polarization of electrodes, these processes can occur, leading to electrolysis of water by electrode corrosion and gas bubble emanation. Depending on the application, their mechanisms vary. The three main electrochemical processes concerning the algal industry include 1. Electro-oxidation, 2. Electroflocculation, 3. Electroflotation. Electro-oxidation is mainly used for electrolytic removal or disinfection of algae in wastewater and drinking water treatment plants. It uses an electrochemically non-dissolving anode, which in the presence of chlorine produces toxic oxidants that can destroy algal cells. In the case of electroflocculation, an electrochemically dissolving polyvalent metal anode is used to release metal ions (Fe^{3+}, Al^{3+}, *etc.*) that can neutralize the algal cells and form aggregates. Electroflotation uses inactive metal cathodes (*e.g.,* carbon) to release air or gas bubbles (*e.g.,* hydrogen) which when in contact with microalgal cells, trap them and upswing them to the surface. The pictorial representation of these mechanisms is shown in Fig. 2. Among

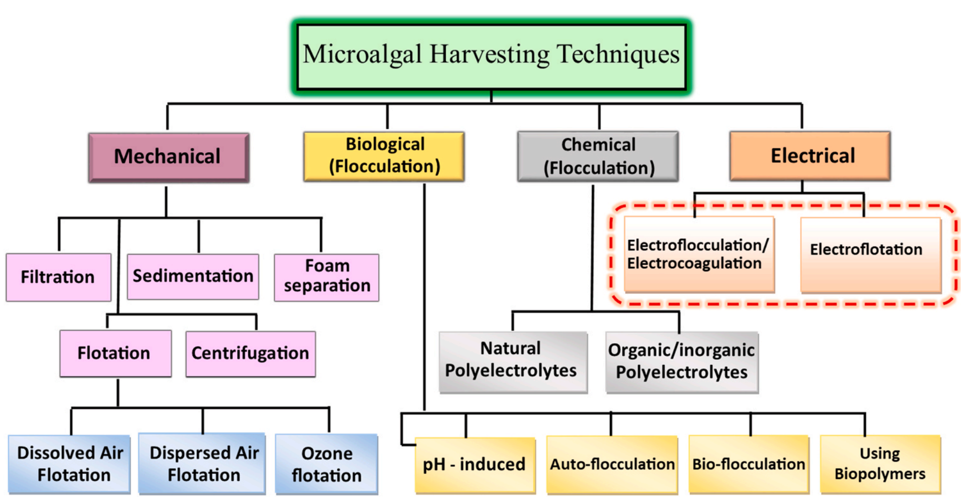

Fig. 1. Various microalgal harvesting techniques.

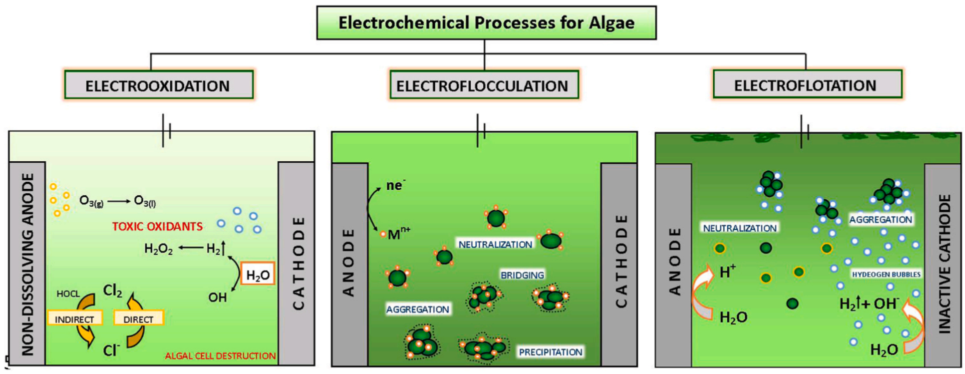

Fig. 2. Mechanisms of the three main electrochemical processes employed in algal industry

them, electroflocculation and electroflotation mechanisms are mainly used for microalgae harvesting purposes [21,68].

2.1. Electroflocculation

Electroflocculation is regarded as a promising technique for harvesting microalgae in terms of cost-effectiveness within the downstream processes. The biomass can be recovered with high efficiency without notable changes in the quality of the biomass in terms of pigment and fatty acid profiles. This approach lies in the border between the chemical and physical methods of harvesting. Electroflocculation is influenced by various parameters such as cell concentration, surface properties, pH of the environment and ionic strength. The majority of the harvesting procedures involve the application of direct current (DC) which renders the flow of electric charges in a unidirectional manner from one electrode to another [21,60].

2.1.1. Principles and mechanisms

In electroflocculation, metal ions are released from the sacrificial metal anodes into the water. These ions then act similar to the chemical flocculants of destabilizing the negatively charged surface of suspended microalgal cells with the use of electricity [9,10]. On the application of current, the electronegative microalgal surface moves become electropositive. The primary mechanism behind flocculation includes neutralization of negative charge of microalgae with cations, followed by electrostatic bridging between the ion and cell leading to mass precipitation of flocs by sweep flocculation (Fig. 2) [12]. These processes mainly involve three stages: In-situ metal ion release, coagulation reaction and separation of liquid-solid phase. Firstly, the metal ion coagulants are dissolved from the anode by oxidation. These ions get hydrolyzed to generate positively charged hydroxides. Secondly, the hydroxides destabilize the suspended algal biomass and aggregate them into flocs. Finally, the metal cations neutralize the negative charges on the microalgal cells [33,50].

The characteristics of floc such as floc size, density and structure depend upon the mechanism by which they are formed. The chemical reactions taking place at the anode and cathode are two independent half-reactions as follows [14].

Electro-oxidation occurs at the anode, releasing metal ions and free electrons (Eq. (1))

$$M \rightarrow M^{n+} + ne^{-} \tag{1}$$

Simultaneous reduction occurs at the cathode receiving free electrons and water molecules to produce hydroxide ions and hydrogen gas is shown in Eq. (2).

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \tag{2}$$

The number of electrons that gets transferred from the cathode is stoichiometrically related to the amount of reactant consumed or product formed. These electrons are measured as the charges that flow in the external circuit. Faraday's law of electrolysis (Eq. (3)) gives the relationship between the charges and the quantity of product generated.

$$m = \frac{i * \ t \ * \ MW}{96485 \ * \ e} \tag{3}$$

where, m is the mass of the product generated in grams, i is the current applied to the electrodes in amperes, t is the time of applied current in seconds, MW is the molecular weight of the element used and e is the number of electrons generated from the half-reaction.

The metal ions then combine with hydroxyl ions to form a metal-hydroxide complex as given in Eq. (4).

$$M^{n+} + nH_2O \rightarrow M(OH)_n + nH^{+} \tag{4}$$

These reactions occur due to the chemical attack of the metal electrode under acidic and alkaline conditions. This can also proceed to the variation in the faradaic yield at the end of each run which depends on the loss of electrode mass. Faradaic yield, also called current efficiency, is a correction factor that accounts for the gap between the theoretical and experimental dissolution of the anode. The faradaic yield value is usually less than 1 but can exceed 1 when the electrochemical and chemical oxidation mechanisms of the metal co-occur. The latter case is frequent in the case of aluminium. It can be found that faradaic yield decreases when current increases [18,21].

The positively charged ions neutralize the negatively charged cell wall of the microalgae to form flocs. This tendency of the flocs to coagulate results from the inter-particle net force, which is determined by the sum of opposing forces between van der Waals force of attraction and electrical double-layer forces of repulsion as defined by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. This aggregation process is termed as destabilization. The mechanisms are as follows [10,28].

- *Double-layer compression*: This is caused by the interaction between the microalgal cell wall and the soluble ionic species generated through the dissolution of the sacrificial anode. It reduces the repulsion between the cells by altering the electrical potential difference between the cell surface and the bulk solution.
- *Charge neutralization*: This occurs by the adsorption of ionic metal species or precipitation of charged hydroxide precipitates onto the surface of negatively charged microalgal cells. This can be indicated by the variations in the zeta potential around the isoelectric point.
- *Sweep flocculation*: It is an enmeshment mechanism in which the hydroxide precipitates entrap the suspended microalgal cells. It

depends on the species of ions formed which further depends on the pH of the medium.

2.1.2. Electrode materials

A number of electrodes have been reported for use in electroflocculation process such as aluminium (Al), iron (Fe), magnesium (Mg), copper (Cu), steel (stainless steel, galvanized steel, mild steel), brass, bronze, titanium and zinc (Zn). Among these Al and Fe are the most commonly used electrodes in electroflocculation. This can be attributed to their abundance on earth, low price and high valency that leads to potent removal of microalgae [28]. Al is generally regarded to be more efficient with respect to microalgal recovery (95.4%) as it increases the separation efficiency by 38% compared to iron (64.7%) [4]. In the case of Al electrodes, the $3OH^-$ ions formed at the cathode are counter-balanced by the Lewis acidity of Al. This induces a buffer effect, leading to a final pH between 7 and 8 that strongly differ from Al salts used in chemical coagulation. The $Al^{3+}$and OH^- ions produced in these reactions can combine to form mononuclear ions or polymeric forms. In practice, Al^{3+} ions prevail when pH is less than 4. At a pH higher than 10, soluble aluminate anions or $Al(OH)_{3(s)}$ predominates. Thus, initially, all the species are in the form of $Al(OH)_{3(s)}$and later gets converted to $Al_n(OH)_{3n(s)}$. $Al(OH)_{3(s)}$, called 'sweep flocs' that have a large surface area and are capable of serving as a reliable and efficient adsorbent. This shows that the formation of different types of ionic species is highly dependent on the pH of the media [25,28].

Bleeke et al. [9] tested four other electrodes (Mg, Cu, Zn, brass) in addition to Al and Fe for harvesting *Scenedesmus acuminatus* and reported that, among the six electrodes, magnesium showed the highest flocculating efficiency. About 90% of the suspension was clarified at 40 V within 9.2 min. The efficiency was found to increase at higher voltage inputs. At lower voltages, a short lag phase was observed due to insufficient ions for flocculation. The highest efficiency depended on the incubation time taken to recover 90% biomass at 40 V and the ranking was followed by Al (9 min), Zn (14.2 min), Cu (14.6 min), Fe (46.9 min) and brass (30.9 min). In this study, the supernatant after harvest was used for the growth of algae. It was observed that the highest cell count of 1.86×107 cells ml^{-1} with Fe after 12 days. The active chlorine molecules present were capable of diminishing the zeta potential and raising the liberation of metal ions for improved harvesting of microalgae.

Electroflocculation was carried out using inert electrodes to reduce the deposition of metal ions. An efficiency of 80–95% was reached in 35 min [16]. However, considerable capital and operational cost were met due to high energy requirements and the use of valuable metals. Jeon et al. [32] developed a de-centralized, self-powered electrocoagulation system for harvesting microalgae up to 90% efficiency. It uses a triboelectric nanogenerator that harvests ambient wind energy to provide the necessary power. Xiong et al. [69] dosed the culture medium with sand to improve the recovery efficiency of *Dunaliella salina* from 95.13% to 98.09% in 4.5 min. During the process, the isoelectric point of the sand particles increased and obtained a positive charge. This change enhanced the flocculation potential and reinforced the destabilization of the microalgal suspension. Cultivation and harvesting of marine microalgae *Scenedesmus obtusiusculus* using electroflocculation seemed more efficient in the view of energy consumption, resulting in revenue return by 8.88% for a recovery efficiency of 88% [17]. Most of the experiments are carried out in a batch mode. Continuous mode of harvesting microalgae *Nannochloris oculata* (KMMCC-16), with electrolysis has also been reported with polarity exchange and improved recovery up to 95.8% [34].

2.1.3. Secondary reactions

In the view of practicality, the efficiency of ions released varies among researches. Some studies indicate that only 50% of the predicted mass of ions is being produced while others have reported contradictory results of 200% of mass being generated. This can be a consequence of secondary reactions that might occur at the electrodes, leading to an increase in the concentration of the dissolved metal ion. The reactions are shown in Eqs. (5) and (6).

$$2Al + 6H^+ \rightarrow 2Al^{3+} + 3H_2 \quad (5)$$

$$2Al + 6H_2O + OH^- \rightarrow 2Al(OH)_4^- + 3H_2 \quad (6)$$

Similar reactions take place with iron electrodes during EF. However, they are more complex than Al as oxidation of Fe anode could lead to the formation of both ferrous and ferric cations. Depending on the pH and ion concentration in the electrolyte, the ferrous and ferric ions hydrolyse to form various monomeric and polymeric species. Recent studies assume that oxidation of anode releases Fe^{2+} as it has been proved that the dissolution rate of Fe^{3+} is negligible [14,28].

In acidic medium, the ferrous ions oxidize very slowly when in contact with dissolved oxygen, while in case of a neutral or alkaline medium, the Fe^{2+} gets immediately transferred to form ferrous hydroxide. The latter is further oxidized by dissolved oxygen to form ferric hydroxide. The iron dissolution follows Faraday's law with faradaic yield varying between 80% and 100%. In acidic media, the faradaic yield is greater than 100%, whereas, in alkaline media, it is the opposite [22,28]. Two reasons as follows can be stated for this variation:

- Firstly, the chemical and pitting corrosion occurring at both the electrodes due to the presence of ionic compounds such as chloride present in the electrolyte. This condition is prevalent at lower pH values.
- Secondly, the decrease in dissolution efficiency can be related to the secondary reactions that occur near the anode, including oxygen evolution. At alkaline pH, oxidation reactions take place leading to the formation of ferric ions. This might decrease the concentration of iron as it required three electrons and hence a higher current is necessary for achieving the required concentration.

2.2. Electroflotation

Electroflotation is a physical flocculation technology. Though the technique is not completely effective compared to electroflocculation, studies have shown better microalgal recovery efficiencies. The process is said to depend on various parameters such as current density, time of applied current, electrode material and arrangement. The mechanism of electroflotation is discussed below and pictorially represented in Fig. 2.

2.2.1. Principles and mechanisms

In electroflotation, the electric field applied hydrolyses the water molecules emanating hydrogen gas molecules. Harvesting by flotation involves the attachment of the microalgal cell to these air or gas bubbles. The microalgal cell surfaces are negatively charged and hence they move towards the anode where they get neutralized and form aggregates or flocs. These bubbles accumulate and carry the flocs to the surface of the media by the flotation effect of hydrogen on the cathode, from where they can be easily collected. Baierle et al., ($year$) [4,15]. The primary process of harvesting involved here is the flotation of flocs which happens by the release of H_2 gas at the cathode and O_2 at the anode to a smaller extent. The electrochemical reactions taking place in electroflotation process are as follows [22,24].

At the cathode (Eqs. (7) and (8)):

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \mathrm{E_o} = -0.83\mathrm{V} \quad (7)$$

$$2H_3O^+_{(aq)} + 2e^- \rightarrow 2H_2O_{(l)} + H_{2(g)} \mathrm{E_o} = 0\mathrm{V} \quad (8)$$

where, E_o is the standard electrode potential at 298 K.

At the anode (Eq. (9)):

$$2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + 4e^- E_o = 1.23V \quad (9)$$

2.2.2. Strategies involving electroflotation

Additional aeration using an air pump also enhances the performance of floc formation and removal efficiency by 102% [3]. The high-power input positively correlated with increased separation of algae. Higher the instability generated between the cells, the higher the success of the flotation rate. However, electroflotation without flocculation will not be able to achieve high harvesting efficiency [2]. In an experiment with titanium electrodes, the maximum efficiency reached was only 36.6% which proves the importance of flocculation [18]. Contrarily, Ghernaout et al. [24] has reported an algal removal efficiency of ~100% using stainless steel electrodes at a current density of 170 A m-^{2}. The electrodes were placed covering the bottom of the vessel so that all the bubbles produced rises to the top. One main advantage of the electroflotation method is that there is no requirement for the added chemicals. But the risk of metal ions deposited with the biomass and those remaining in the supernatant still exist.

Neto et al. [15] used non-consumable electrodes made of steel to harvest mixed microalgae culture by alternating current (AC). The AC generated uniformly varied electromagnetic field for the efficient harvest of algae up to 99% by the generation of hydrogen gas composition of 36.2%. In this system, no metal ions were released into the environment which reduced the process costs. A minimum power of 20.7 W/dm^3 for 20 min was sufficient to acquire an efficiency of 80% and to disrupt the cells to release lipids that were found to accumulate on the floating biomass. Sometimes the process might damage the algal cells causing the release of harmful toxins. Precautionary measures such as low applied voltage and high residence time can reduce cell damage [24].

2.3. Electrocoagulation-flotation (ECF)

In the ECF system, the mechanisms of both electroflocculation and electroflotation are integrated. The electrolysis provides simultaneous flocculation and flotation of microalgae. This system remains to be a promising alternative to traditional harvesting methods with regards to the potential, simplicity and capability of the technique to scale up [36,38]. It can easily recover cells up to 90% with low consumption of power [10]. A bench-scale ECF set-up required power input 5 times less than centrifugation and 9 times less when a settling step was coupled [17].

2.3.1. Principles and mechanisms

ECF uses polyvalent metal anodes and inert cathodes for the simultaneous release of metal ions and gas bubbles. The detailed mechanism of ECF is portrayed in Fig. 3. The series of reactions occurring in this combined system are represented below [18,28].

At the anode:

The metal ion oxidizing to form cations is given in Eq. (10).

$$M_{(s)} \rightarrow M^{n+}_{(aq)} + ne^- \quad (10)$$

where, *M* represents the metal and *n* is the number of electrons transferred per mole of metal. Secondary reactions might occur in case of high anode potential. In such cases, the water molecule gets oxidized and leads to the formation of hydronium cation and oxygen gas (Eq. (11)).

$$2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^- E_o = 1.23V \quad (11)$$

In case of the presence of chlorine anions, Cl$^-$ ions may get oxidized to Cl_2 (Eq. (12)). Cl_2 is a strong oxidizing agent that might contribute to the oxidation of dissolved organic compounds or might lead to the formation of another oxidant, ClOH (Eq. (13)). However, this might be detrimental to a microalgal system [28,38].

$$2Cl^- \rightarrow Cl_2 + 2e^- E_o = 1.36V \quad (12)$$

$$Cl_2 + H_2O \rightarrow ClOH + Cl^- + H^+ \quad (13)$$

At the cathode:

The water molecules get reduced to hydrogen gas and hydroxyl anions. The subsequent reactions are shown in Eqs. (14)–(16).

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)} \quad (14)$$

$$2H_2O_{(l)} + 2e^- \rightarrow 2H_{2(g)} + 2(OH)^- \quad (15)$$

$$3H_2O + 3e^- \rightarrow \frac{3}{2}H_2 + 3OH^- \quad (16)$$

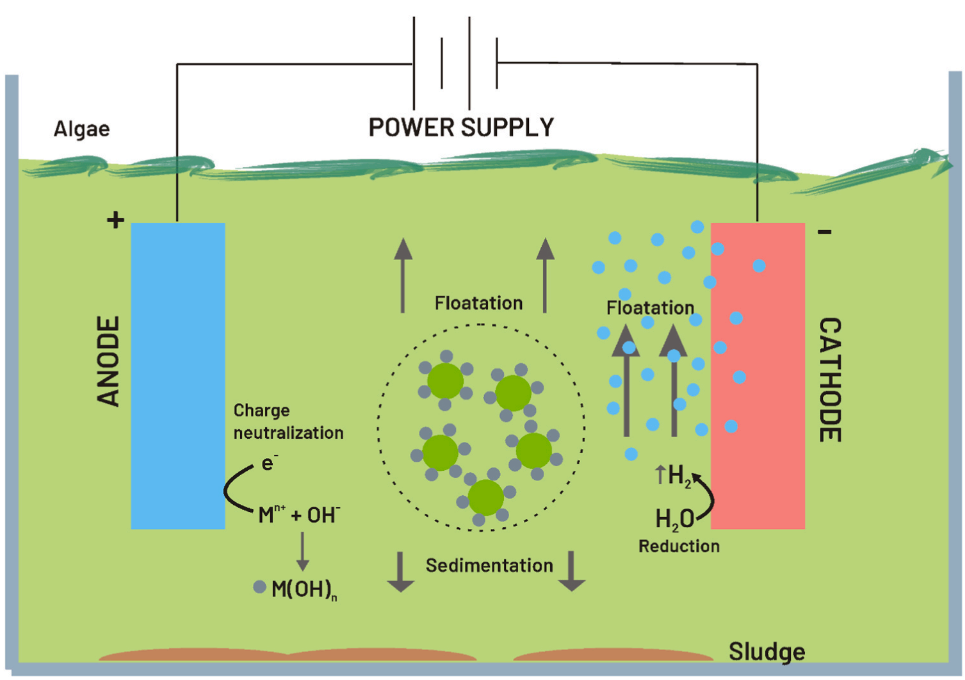

Fig. 3. Schematic representation of the mechanism of electrocoagulation-flotation set-up.

In the electrolyte (Eq. (17)):

$$M^{n+} + nH_2O \rightarrow M(OH)_{n(s)} \downarrow + 3H^{+} \quad (17)$$

The metal anode supplied coagulating ions for flocculation and the cathode produced hydrogen gas bubbles to uplift the flocs to the surface. The microalgae are harvested by complexation and precipitation with metallic hydroxides or by adsorption or by electrostatic attraction of hydroxides on the surface of microalgae. In the case of complexation, the microalgae act as the ligand to which the metal hydroxide ions bind [61, 69].

In case of aluminium electrode [28], the reaction is as follows (Eq. (18)):

$$Microalgae - H_{(aq)} + (OH)(OH)_2Al_{(s)} \rightarrow Microalgae - (OH)_2Al_{(s)} + H_2O \quad (18)$$

For iron electrode, the hydrous iron moiety binds to the microalgae as follows (Eq. (19)):

$$Microalgae - H_{(aq)} + (OH)OFe_{(s)} \rightarrow Microalgae - OFe_{(s)} + H_2O \quad (19)$$

2.3.2. Strategies involving ECF

This combined technique offers an attractive alternative to conventional methods by reducing energy consumption. Though electroflocculation alone was able to harvest 93.6% of *Botryococcus braunii* in 30 min, ECF harvested 98.9% within a time of 14 min [33]. ECF was found to be the most efficient method amongst centrifugation and chemical flocculation, for harvesting a small-sized microalgae *Ankistrodesmus falcatus* by using non-sacrificial carbon electrodes. The energy consumption (1.76 kWh kg^{-1}) was much lower than centrifugation (65.34 kWh kg^{-1}) for obtaining an efficiency of 91.26% in 30 min. In fact, the harvesting efficiency was higher than harvesting larger size microalgae *Scenedesmus obliquus* (67.73%) provided the same experimental conditions. The lipid content was slightly higher for biomass harvested using ECF. This can be attributed to the irreversible pores generated by the electric field, making the intracellular components accessible by solvents [27]. It is said that augmentation of turbulence and diminishing the initial pH can improve the performance of ECF [33]. A high working temperature up to 60 ℃ resulted in high recovery efficiency of 99% and 98% for *Chlorococcum* sp. and *Tetraselmis* sp., respectively. Also, as temperature increased, the kinetic energy of the cells increased, resulting in a higher probability of collision and agglomeration. An increase in temperature also raised the kinetics of anodic dissolution. This suggests the reason for seasonal fluctuations in recovery efficiency from open High Rate Algal Ponds (HRAPs) [64]. In another study, electroflocculation and electroflotation were integrated as a continuous cultivation and harvesting system. The DC electric field was inverted between a sacrificial anode and an inert cathode. The efficiency of the set-up was improved by modifying the polarity of the electrodes [22].

Though non-ideal, a probable indirect reaction that can occur in an ECF system is the Fenton's reaction. An et al. [3] presented an electrocoagulation-fenton process alternating with three convertible electrodes for the efficient removal of cyanobacteria and microcystins. The metal coagulants released formed a protective layer surrounding the algae to aggregate them and to prevent the release of cyanotoxins. Later in the fenton process, the ferrous ions react with hydrogen peroxide to remove the left-out cells. These methods improved efficiency by 30% and reduced energy consumption by up to 92% [21]. In a study by Ryu et al. [56] electroflotation was initially carried out, followed by electrochemical oxidation of boron-doped diamond anode for recovering *Scenedesmus quadricauda*. This method significantly reduced the metal ion contamination but a high electrolysis time for required to obtain high efficiency of 91.8%.

The choice of harvesting technique mainly depends on the size, shape and strength of the microalgal cell of interest, which determines the processing time and efficiency. The conventional methods like gravity separation and centrifugation are only suitable for harvesting cells greater than 70 µm and 30 µm, respectively and are highly cost-intensive [31]. However, microalgal cells are of small hydrodynamic size (1–30 µm) with low density and colloidal stability [27]. In electrochemical perspective, electroflocculation and electroflotation are the predominant techniques used for harvesting microalgae. It is based on the fact that, the microalgal cells possess electronegative potential due to the ionizable functional groups on their surfaces. These techniques are appropriate for recovering a variety of microalgae as they can handle diversity in their size, shape, charge and specific weight. Especially for very small microalgae, electroflotation can be preferred as the bubbles produced can easily lift up the cells to the surface [31]. In general, electroflocculation is more effective than electroflotation, as it involves charge neutralization by dissolving of ions from anode and bigger floc formation. Hence the combined method of electrocoagulation-flotation has been reported to be the most efficient and performs in unison for a variety of microalgae varying in size, shape and motility such as *Haematococcus pluvialis* (spherical, 20–40 µm), *Tetraselmis chuii* (ovoid, 7–15 µm), *Chlorella sorokiniana* (spherical, 2–10 µm), *Dunaliella tertiolecta* (ovoid, 4–7 µm), *Nannochloropsis oceanica* (spherical, 2–3 µm), *Rhodomonas reticulata* (rod, 3–12 µm), *Phaeodactylum tricornutum* (canoe, 3–30 µm), *Pavlova lutheri* (spherical, 3–6 µm), *Dunaliella salina* (ovoid, 5–8 µm) and *Ankistrodesmus falcatus* (spindle, 2–3 µm) [38,63].

Though the choice of harvesting technique depends on various physicochemical parameters of microalgal species, the sole criteria rely on the selection of the most energy and cost-effective method, as harvesting unit alone incurs 20–30% of the total processing cost. Among the electrochemical techniques discussed in this manuscript, electroflocculation is reported to be the most efficient method with high yield rates; however, it is reported to be energy-intensive. On the contrary, electroflotation has less hazardous effect on the residual biomass; yet, renders low recovery efficiency. Hence the selection of technique can be chosen based on the pros and cons of each methods listed in the Table 1.

3. Influential parameters of electrochemical processes

Electrochemical processes depend on various systemic parameters like reactor design, electrode arrangement, material, and inter-electrode distance, operational variables like current density, duration of current supply and stirring speed and physicochemical factors such as pH, temperature, conductivity and surface properties of various microalgal species. Variation in these parameters can have a positive or negative effect on microalgal recovery efficiency. Hence, they can be altered accordingly to improve the yield with reduced power consumption. Those parameters that significantly affect the harvesting process are depicted in Fig. 4 and are briefly discussed.

Table 1
Merits and demerits of electrochemical microalgal harvesting techniques.

	Electroflotation	Electroflocculation	Electrocoagulation-flotation
Merits	Suitable for recovering very small-sized microalgae Low contamination in the residual biomass and supernatant Cost-effective for lab-scale operations	High microalgal recovery efficiency Suitable for almost all microalgal strains Energy-efficient at low current densities	Quick and higher microalgal yield Low cost of raw materials Simple and easy to operate Positive effect on the microalgal pigment and lipid quantity Suitable for diverse microalgal species
Demerits	Low recovery efficiency Might not be effective for large algal cells Foam production	Frequent replacement of sacrificial anode Metal ion contamination	Electrode passivation Need for maintenance

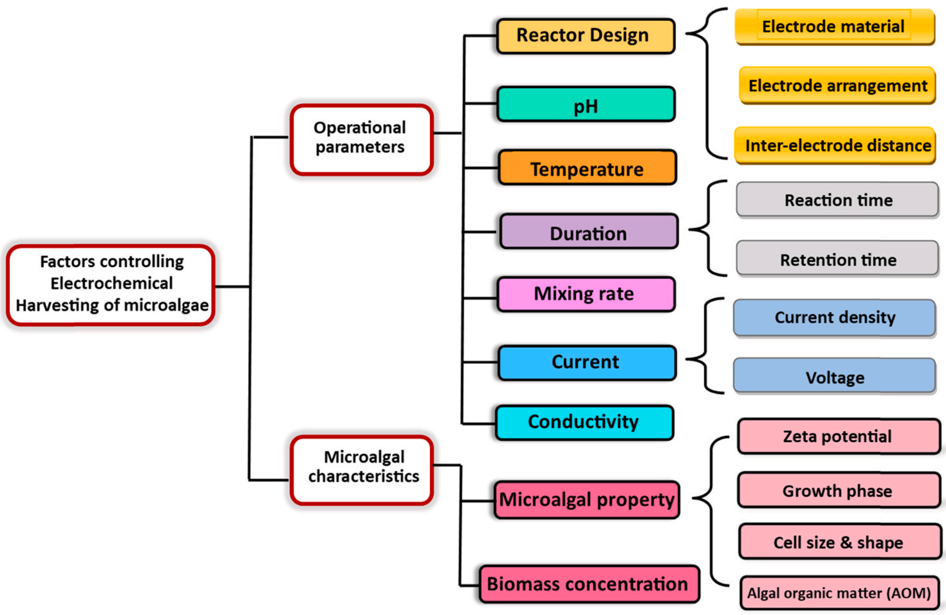

Fig. 4. Systemic and experimental factors that possess significant effect on electrochemical processes of microalgal harvesting.

3.1. Electrode and reactor design

Electrode and reactor design includes the optimization of parameters like arrangement of electrodes in the harvesting reactor, material of electrode that determines the kind of ionic species being released, the distance between the electrodes, size and shape of the electrode and construction of reactor with suitable design for efficient recovery of microalgae.

3.1.1. Electrode arrangement

The arrangement of electrodes tends to affect the functionality of the electrochemical process. The reactor might be set-up with single or multiple cathodes and anodes. The arrangement can be classified as monopolar and bipolar electrodes. Generally, bipolar electrodes necessitate low current and high voltage compared to monopolar electrodes that require low voltage and high power. Both the electrode settlements exhibit similar efficiencies and hence it is not easy to conclude which is better. However, taking into consideration the ratio effectiveness/cost, monopolar electrodes have known to offer high removal efficiencies with lower energy consumptions. Though bipolar electrodes consume high energy, the operational and maintenance cost is less. Hence, the overall operational cost should also be taken into consideration to decide on the mode of electrode configuration [22,28]. The descriptions of monopolar and dipolar electrodes are stated in Table 2.

Table 2
Descriptions of various electrode configurations used in ECF systems [22,28].

Electrode configuration	Description
Monopolar electrodes (Series connection)	• Each pair of electrodes that are internally present is connected with each other, while the outer anode and cathode don't have any interconnections. • The current passing through every electrode is the same. • The total voltage is aggregate of individual voltages in an electrolytic cell.
Monopolar electrodes (Parallel connection)	• In this, the anodes and cathodes are alternatively arranged with the same cathodic or anodic potential, respectively. • The total current is the sum of the current in each electrolytic cell. • The voltage is the same in each pair of electrodes in an electrolytic cell.
Bipolar electrodes (Series connection)	• The outer electrodes are monopolar and are connected to the electric power supply. • The inner sacrificial electrodes are bipolar, fixed between the two external electrodes and are not interconnected. • The opposite side of each bipolar electrode is oppositely charged. • The anodic and cathodic dissolution happens on the positive and negative sides, respectively.

In addition to electrode arrangement various shapes have been incorporated in designing electrodes for enhanced surface area and efficiency. Various geometries of electrodes besides the popular rectangular, circular, cylindrical, are being used. Baierle et al. [4] designed Al and Fe electrodes in a spiral shape for harvesting *Desmodesmum subspicatus*, which was claimed to be advantageous. These electrodes have increased surface area which can improve the flotation efficiency up to 95.4% and dispersion of oxygen bubbles. A reduction in the surface area resulted in a less efficient biomass harvest. In another study, perforated electrodes of Al and Fe were used for yielding *Nannochloris* sp. and *Dunaliella sp*. These perforated plates provided the necessary turbulence for mixing. Similarly, Golzary et al. [25] designed a blade-shaped aluminium electrode to enhance mixing which further improved the algal separation efficiency up to 96.8%. Parmentier et al. [52] developed a novel ECF reactor which has tubular electrodes and a separate flotation unit. This set-up provided enough time for the cells to react with the dosed ion and form flocs. In this case, the recovery efficiency of *Chlorella vulgaris* with Fe (88%) was higher than Al (73%).

Electrodes are also being installed either vertically or horizontally. Horizontal placement of electrodes has been stated to possess high mixing efficiencies [25]. Another important parameter that influences the efficiency of ECF is the size of the electrodes (*i.e.,* medium contact surface). It has been reported that the surface of the electrode exposed determines the number of microbubbles produced. Also, a high current density results in a higher generation of bubbles providing a better harvest [4].

3.1.2. Electrode material

The electrode material plays an important role in terms of cost, type of ions released, removal efficiency, downstream processing of residual biomass and safety when supernatant is reused for microalgal growth. For harvesting microalgae through electrochemical processes, the type of electrode used and its corresponding ionic species is a fundamental indicator in determining the mechanism. The electrodes are chosen based on the ions necessitated for the application. The most used and preferred electrodes are Al and Fe [45,49]. Besides, the choice of electrode should depend on the species of microalgae used as it can reduce the energy input. For example, harvesting *Nannochloris oculata* KMMCC-16 and *P. tricornutum* with Al required an energy input of only 0.3–2 kWh kg^{-1}. Whereas, for harvesting *Chlorococcum sp.* and *Tetraselmis* sp., Fe electrodes were preferred as the energy consumed was 0.31 kWh kg^{-1} and 0.54 kWh kg^{-1}, respectively [63].

Many electrodes had been employed for electrocoagulation so far. These include Cu, Fe, brass and sacrificial anodes such as Al, Mg and Zn. The different types of electrodes used in various electrochemical processes are shown in Table 3. However, in most studies, Al electrodes prove to be more efficient in terms of coagulation and flotation than Fe. This can be due to the higher current generated at the electrode. Experiments with the Al electrode also exhibited minor turbidity. Another reason for the higher efficiency of Al is attributed to pH. The amount of aluminium hydroxide produced at pH 7 is higher than ferrous/ferric ions. This results in an increased destabilization of biomass by hydroxide molecules. In addition, the transport efficiency and faradaic yield of Fe are relatively lesser than Al. Iron has a weaker buffer effect and the destabilization effect is inefficient due to its high solubility. However, iron electrodes are relatively less detrimental to human health due to less toxicity of metal ion residues in the effluent [28]. Also, it is reported that iron electrodes exhibit better conductivity than aluminium. This ability of iron will help maintain currents at lower voltages and hence can compensate for the low harvesting efficiency. Also, though the mass loss of iron electrode is high, flocculation using iron was found to be energy and cost-efficient [4]. The price of aluminium throughout 2012 was averaged to be 2.187 ± 0.12 USD/kg, whereas the price of iron was averaged to be 0.113 ± 0.02 USD/kg, nearly 20 times lesser. Hence, the operational cost for harvesting *Nannochloris* sp. using iron was less than 0.03 USD/L oil with 35% efficiency, while with aluminium, the cost was around 0.75 USD/L oil with 42% efficiency [14]. Moreover, the presence of aluminium in the effluent (>1%) interferes with the downstream processing and affects population health, causing brain disorders such as Alzheimer's and Parkinson's diseases. It is said that extension in the period of use of iron electrodes can increase the yield of biomass [11]. The comparison of various aspects of aluminium and iron along with magnesium is shown in Table 3.

The performance of Fe in an ECF system can be improved by following a few optimization techniques [28].

- Aeration of water to increase the concentration of dissolved oxygen and Fe^{2+} oxidation.
- Increasing the residence time of the medium to achieve complete oxidation of iron.
- Increasing the Fe^{2+} oxidation rate by increasing the pH ≥ 7.5
- Introduction of an alternative oxidant such as chlorine to accelerate the ferrous oxidation rate.

Another metal that proved to be efficient than Al and Fe is Mg. Apart from being highly efficient and economical for microalgae harvesting, it has other advantages like exhibiting less toxicity at high concentrations. In other words, the acceptable limit of Mg in water is much higher than aluminium or iron. The bivalency of magnesium helps in the formation of stable hydrogen bonds in the algal flocs [9].

3.1.3. *Inter-electrode distance*

Distance between the electrodes is an important parameter that affects the efficiency of the electrocoagulation process. The efficiency was found to decrease with an increase in the spacing between the electrodes. Also, the power consumption increased with an increase in distance of the electrodes without changing the degree of separation as only a less voltage was required to maintain the desired current. This is because electric conductance is inversely proportional to electrode distance. Hence it is wise to maintain a short electrode distance [18,53]. For a current density of 103 A m^{-2}, 95% of microalgae were recovered after 5 min with an inter-electrode distance of 1 cm. But only 88% was recovered with a distance of 2 cm. However, as the time increased to about 20 min, the efficiencies in both cases were approximately at the same level [24]. The inter-electrode distances preferred in various electrochemical processes are shown in Table 4.

The reason for low recovery efficiency can be the large ohmic losses taking place at a higher distance. This loss in relation to the cathode and anode over-voltages and mass transfer resistance results in the decline of charge transfer kinetics. Hence lesser cations are released at the anode, leading to more inferior microalgal aggregation [11]. The spiral-shaped electrodes designed by Baierle et al. [4] reduced the distance between the cathode and anode (about 2 mm), resulting in the reduction of

Table 3
Comparison of electrode materials generally preferred for electrocoagulation-flotation of microalgal harvesting.

Characteristics	Aluminium	Iron	Magnesium
Crystal structure	FCC	BCC	HCP
Anodic reaction	$Al \rightarrow Al^{3+} + 3e^-$	$Fe \rightarrow Fe^{2+} + 2e^-$ $Fe \rightarrow Fe^{3+} + 3e^-$	$Mg \rightarrow Mg^{2+} + 2e^-$
Cathodic reaction	$3H_2O + 3e^- \rightarrow 3OH^- + 1.5H_2$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $3H_2O + 3e^- \rightarrow H_2 + 3OH^-$	$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$
Overall reaction	$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$	$Fe^{2+} + 2H_2O \rightarrow H_2 + Fe(OH)_2$ $Fe^{3+} + 2H_2O \rightarrow 1.5H_2 + Fe(OH)_3$	$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$
Monomeric species	$Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_2^{4+}$	$Fe(OH)^{2+}$, $Fe(OH)_2^+ Fe(OH)_2^{4+}$	$Mg(OH)^+$
Polymeric species	$Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, $Al_{13}O_4(OH)_{24}^{7+}$	$Fe(OH)_4^-$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)_2^+$, $Fe(H_2O)_8(OH)_2^{4+}$, $Fe(H_2O)_6(OH)_4^{2+}$	
Standard reduction potential (SHE)	-1.66	-0.447	-2.37
Cost	Mg > Al > Fe		
Advantages	High efficiency due to high current generated at the electrodes Increased aluminium hydroxide production at neutral pH High transport efficiency High faradaic yield	Low toxicity Exhibit high conductivity Maintains current at low voltages Low operating costs	Low toxicity at high dosages Formation of stable algal flocs
Disadvantages	Interferes in downstream processing Detrimental to health even at low dosages (neuro- & nephrotoxic) High capital and operating costs	Highly soluble Comparatively low transport efficiency Lesser faradaic yield Weak buffer effect	High material cost

Table 4
Experimental conditions and harvesting efficiencies of various electrochemical processes.

Method	Electrodes	Microalgae of interest	Current/current density/voltage	Time of current applied (min)	Inter-electrode distance (cm)	Energy input ($kWhkg^{-1)}$)	Efficiency (%)	References
ECF in continuous mode	Fe	*Chlorella vulgaris*	1.2 mA cm^{-2}	1.32	6 mm	2	88	[52]
ECF	Al	*Chlorella vulgaris*	2.9 mA cm^{-2}	60	1	1	100	[18]
Electroflocculation	Mg	*Scenedesmus acuminatus*	40 V	9.2	2.5	–	90	[9]
Electrocoagulation	Al	*Desmodesmus subspicatus*	0.5 A	30	5.5	0.1067	94.75	[11]
Electroflotation by AC	Steel	Mixed microalgae	12 V	20	5 mm	20.7 W/dm^3	80	[15]
ECF	Al	*Chlorella* sp. (PTCC 6010)	1.36 mA cm^{-2}	17.65	1	0.067 kWh m^{-3}	96.8	[25]
Electrocoagulation by AC-Dielectrophoresis	Al	*Tetraselmis sp.*	7.1 mA cm^{-2}	10	1	4.62	90.9	[29]
Electroflotation-oxidation	Boron-doped diamond-Al	*Scenedesmus quadricauda*	30 mA cm^{-2}	60	20 mm	11	98.3	[56]
Discharging electroflocculation	Al (Air electrode, flake)	*Dunaliella salina*	100 mA	20	35 mm	0.11	97	[40]
ECF	Al	*Chlorella vulgaris*	0.42 mA cm^{-2}	20	2	0.61	99.4	[70]
ECF	Al	*Chlorella vulgaris`*	66.7 A cm^{-2}	4	3	3.35×10^{-4} kWh L^{-1}	98	[59]
ECF	Al-IrO_2/TiO_2	*Phaeodactylum tricornutum*	3 mA cm^{-2}	30	4.4	0.4	78	[66]
ECF	Al-Ti/IrO_2	*Chlorella vulgaris*	5.75–8.25 A	30	5 mm spacers	1.25 kWh m^{-3}	99.5	[68]
ECF in continuous flow reactor	Nickel	*Nannochloropsis* sp.	7 V	30	6.35 mm	3 kWh m^{-3}	92	[60]
Continuous flocculant-free electrolytic flotation	Carbon Stainless steel	*Chlorella vulgaris*	3 A	10	4.5 mm	2.73	> 90	[44]
Electrolytic flocculation	Al-Graphite	*Scenedesmus* sp.	3 V	20	5.08	0.88	98.5	[42]
Electrochemical harvesting using non-sacrificial electrodes	Carbon	*Scenedesmus obliquus*	1.5 A	60	6	3.384	83	[47]
Indirect electrocoagulation	Al-Fe	*Dunaliella viridis*	3 V	15	4	1.2 kWh m^{-3}	> 95	[48]

power consumption and an increase in the lifetime of the electrodes. Another reason for increased efficiency at a shorter inter-electrode distance can be explained by faradaic yield. The faradaic yield decreases with an increase in distance between the electrodes. This decreases the amount of metal coagulants released with time [18].

3.2. Surface property of microalgae

Though microalgal cells tend to adapt to the prevailing adverse environmental and culture conditions for growth, the lipid content, yield and growth rates might vary depending upon the type of microalgal species and specific culture conditions. The concentration of biomass at the time of harvesting also plays an important. At low biomass concentrations, the demand of coagulant per unit cell surface area will be high as the probability of contact between the cells to form a floc is low. However, at very high biomass concentrations, the flocs are too large to interact and settle. Hence maintenance of an optimum concentration of biomass for flocculation is necessary, which is suggested to be in the range of 0.5–2.5 g L^{-1} [24,45].

3.2.1. Zeta potential

Zeta potential (ZP) is another aspect of the surface property that influences the harvest of microalgae. It is defined as the potential difference between the surface of the particle and bulk solution. ZP is a physicochemical parameter that has an effect on the electro-kinetic potential of a microalgal system. Its significance is based on the fact that the surface charge of the microalgal cells determines their stability in the medium. ZP measures the electrostatic force between adjacent cells [10]. Accurate knowledge of ZP is necessary to predict and control the stability of the microalgal suspension. When a high positive or negative zeta potential prevails in a system, the dispersion stability of the culture is high. This is because of the electrostatic repulsion between the cells, which prevents them from adhering to one another by van der Waals forces [33]. Cells having a ZP more positive than +30 mV or more negative than −30 mV are considered highly stable. However, cells having low values of zeta potential cannot be prevented from coming together, resulting in instability. The effect of ZP is highly dependent on the pH and ionic strength of the surrounding environment [12,13].

3.2.2. Ionic strength and pH

Ionic strength influences the width of the electric double layer and hence the value of ZP. When the electrolyte concentration increases in the liquid medium, the width of the electric double layer decreases. The high or low ionic strength on the liquid media determines the thickness of the electric layer. Furthermore, it depends on the electrostatic interactions occurring with distance. Thus, the resulting interaction is dependent on the property of the surrounding electrolyte and character of the cell charge. The electrostatic interactions are prominent in low ionic strength solutions and play a considerable role in the surface interaction of cells with the flocculant [10,28].

In another way, it can be related to the pH of the liquid. Depending on the pH of the environment, the COOH & NH_2 groups become protonated or deprotonated. Microalgal cells, in general, possess a net negative charge on their surface at neutral and alkaline pH values. The ZP for green microalgae at pH between 4 and 10, is typically electronegative, ranging between −10 to −36 mV. The isoelectric point for all algal species is generally around pH 3–4. At a pH of about 4–5, the carboxylic acid group dissociates from the cell, possessing a negative charge. Hence a negative charge is observed above pH 4–5. In such cases, there is no charge on the amine groups present. In other words, the value of zeta potential is higher at higher pH and decreases when pH decreases [18,24].

3.2.3. Growth phase of microalgae

The microalgal surface charge is due to the presence of ionisable functional groups such as carboxyl (COOH), hydroxyl (OH) and amine (NH_2). These functional groups present on the surface of carbohydrate-based cell walls determine their charge in the medium. The composition of these groups changes with different life cycle stages of microalgae. At the exponential phase of growth, the zeta potential values were highly negative, causing instability. As the cells grew older, the intercellular repulsion forces were lower in the stationary and death phase and the cell suspension was found to be somewhat unstable. Evidences show that the cells of *Neochloris* sp. and *C. fusiformis*, at the stationary phases, were already clumped [10,12].

3.2.4. Algal organic matter (AOM)

The cell surface components and composition contribute to the hydrophilic or hydrophobic, acid-base nature of the algal cell surface, which can play a crucial role in the interaction between the cell wall and coagulant. The algal organic matter (AOM) present on the surface of microalgae competes and interferes with flocculation for metal ion binding. This is due to the presence of ionisable functional groups attached to the surface of extracellular AOM. Some authors have reported that the amount of flocculant required also depends upon the quantity and composition of AOM. The variations in ZP with respect to the stages of the life cycle can also be associated with the variations in the quantity and composition of AOM on the cell surface [10].

3.3. Current/ current density

ECF can be driven either under galvanostatic or potentiostatic mode. When the process is carried out by controlling or varying the current applied, it is termed to be galvanostatic mode. For potentiostatic mode, the voltage applied is varied as a function of the amount of coagulant required. However, the latter is rarely used in the ECF system and often used for electro-redox reactions where sacrificial electrodes are not used [28]. The current or current density plays a vital role in the electrochemical system. According to Faraday's law of electrolysis, the amount of electrical power input determines the number of ions released at the electrodes. It also determines the rate of anode dissolution and hydrogen gas production at the cathode.

Moreover, the current density is proportional to the speed of ions and gas emanated. Hence the desired number of ions can be obtained through combinations of time and amperages. This will produce a particular charge density based on the surface charge of the electrode. Thus it has a direct effect on the rate of anode dissolution, influencing the performance of the ECF process [13]. Generally, a current density of 10–150 A m^{-2} is said to be desirable for the separation of liquid-solid [24]. Various current or current densities used in electrochemical processes are represented in Table 4. High input of electrical current was shown to provoke high and fast removal efficiency of microalgae. It can increase the removal rate of chlorophyll within a short electrolysis time. Notably, in the case of continuous experiments, the volumetric current intensity is considered as an operating and scale-up factor to maintain a balance between high biomass removal efficiency and minimum release of metal ions [2].

Current density has a significant effect on operational costs. Higher current input, in addition to increasing the efficiency, also increased the overall cost per litre of bio-oil. The rapid process at higher current had less impact on the reduction of algal pigments and can avoid the effect of oxidative agents such as oxygen, pH and light intensity [18,38]. The energy consumed to maintain higher currents for a short period of time was much higher than smaller currents for long durations. Hence from an economic point of view, lower energy inputs or lower current densities with shorter time for lower harvesting efficiencies were recommended. Though charge densities were reported to have less significance on the removal efficiencies within each metal group, its higher charge densities had a significant influence on the energy consumption in the range of 0.5–5.0 mA cm^{-2} [13]. However, high power input tends to increase the temperature and pH of the system and also leads to over-dosage. This problem is overcome in continuous systems where the dilution effects provide an excellent buffering to maintain the pH and temperature. Another theory is that at lower current densities, the destabilization of cells was not sufficient, but the dissolution of metal cations kept increasing. When the concentration of an ion in the liquid was enough to destabilize all the cells present, the metal concentration in the effluent biomass decreased [4,22].

3.4. Time of current provided and sedimentation

Evidence proves that duration is the most effective factor for efficient microalgae separation and operational cost. Long durations resulted in high efficiencies. Likewise, increasing the time of current applied significantly increased the microalgae recovery efficiency [11,15]. In another study, it was concluded that high algal removal efficiency (99.5%) could be reached at a short time of 15 min when a power input of 550 W is used. In addition, it was found that the same efficiency can be achieved with 100 W, provided the time of power applied was 30 min. Similarly, increasing the duration of the reaction from 2.61 min to 14.39 min, increased the algal removal efficiency from 51% to 89.9%. But eventually, the operating cost increased from 0.042 USD to 0.236 USD [25].

Sedimentation time also has a significant effect on recovery efficiency. Valero et al., ($year$) [65] concluded that though the efficiency of 80% can be reached within 15 of current supply and 30 min of sedimentation, a high sedimentation time of 1140 min was required to achieve an efficiency of 95% [11]. This can be explained by the fact that low-density flocs take time to settle. Hence an increase in the settling time increases the harvesting efficiency. In addition, it is reported that the contact between the dissolved metal hydroxides and microalgae cells continues to exist even after sampling. The settling velocity of the floc also plays an important role in designing the sedimentation vessel [10, 18].

3.5. pH & alkalinity

pH remains a crucial factor for ECF processes as it is a measure of hydrogen and hydroxide ions present in the liquid. It determines the speciation of metal hydroxides in the solution. It tends to increase gradually towards alkalinity during the flocculation process due to the hydroxyl formation at the cathode. In other words, the rate of pH increases with an increase in current density. In some cases, the hydroxide ions generated immediately get clung on to the cells, not contributing to the pH increase. At an initial pH of 7, higher current densities accelerated the removal of microalgae. On the contrary, it is reported that if the initial pH of the medium remains in the range of 6–8, the harvesting efficiency will decrease [18,24]. A drop in initial pH is said to improve harvesting efficiency; however, its impact on the operational cost is negligible. As the pH increased in an electrolysis system, the harvesting efficiency decreased. In a study, pH adjustment with CO_2 was tested on the viability of *Microcystis aeruginosa* and *Anabena spiroides*. It was found that pH 5.5–6.5 had a significant inhibitory effect on their growth when acidification was performed during the logarithmic phase. On the contrary, Golzary et al. [25] recommended a natural pH condition of 6 to attain the highest separation efficiency of marine *Chlorella sp.*

Another study showed that the efficiency and recovery time decreased from pH 7–11 and increased at pH 12. This can be due to the lysis of algae and varied speciation of metal ions at different pH. For example, the aluminium hydroxides generated during ECF with aluminium electrodes is dominantly present as $Al(OH)_3$, $Al(OH)_4^-$, $Al_2(OH)_2^{4+}$, $Al(OH)_5^{2-}$ and AlOOH between pH 4–10 on the basis of pourbaix diagram. At pH < 4, the dominant species are $Al(H_2O)_6^{3+}$ In acidic conditions, monomeric hydroxyaluminium cations and polymeric species of aluminium such as $Al_{13}O_4(OH)_{24}^{7+}$ dominate in water, while aluminium hydroxide precipitates. Polymeric species have high tendency to neutralize and adsorb algal cells. Between pH 5.2 and 8.8, the commonly present species is $Al(OH)_{3(s)}$ and at pH above 9, the most dominant species is $Al(OH)_4^-$. $Al(OH)_{3(s)}$ is a strong adsorbent for algal removal, while $Al(OH)_4^-$ is not efficient [28]. Hence, generation of cations at lower pH will facilitate the formation of microalgal aggregates. Contrarily, precipitation of flocs occurs at higher pH values. In case of electrocoagulation, recovery efficiencies are less important at acidic pH than alkaline. The pH increased if the initial pH value was below 7 and decreased if pH value was above 7. In short, ECF tends to adjust the pH to neutrality [21,25].

In addition, pH determines the mechanism responsible for microalgae harvesting at each point in time. It alters the kinetics of microalgae recovery. Charge neutralization is the primary mechanism of harvest at acidic pH 4–6, while mechanisms such as sweep flocculation, adhesion or enmeshment take over at an alkaline pH above 8. However, charge neutralization tends to possess a higher ability to separate microalgae. This concept can be further proved by the change in zeta potential values at acidic and alkaline pH (*i.e.,* a small variation in zeta potential at low pH and large variation at higher pH). Hence lowering the initial pH can improve the efficiency by charge neutralization as the aggregation starts immediately and leading to sweeping flocculation at a longer electrolysis time [13,18].

3.6. Salinity & conductivity

For electrocoagulation to be effective, electrolytes should be present at sufficient levels. Increasing the salinity of the electrolyte increases the conductivity to improve the harvesting efficiency. It induces the compression of the electrical double layer in an algal cell [10]. The salinity level is not an issue for marine or brackish water microalgae. Electrochemical harvesting of marine species utilizes 10 times less energy compared to freshwater microalgae due to high ionic strength and thus the conductivity of seawater. This reduces the power required to release the necessary number of metal ions and bubbles from the electrodes. However, for freshwater microalgae addition of ions to the electrolyte becomes essential. For example, harvesting freshwater microalgae *Nannochloris sp*. required the addition of sodium chloride (NaCl) to increase the salinity to 2 ppt to increase the electrocoagulation efficiency [13]. With an addition of 1.5 g L^{-1}, NaCl to the culture medium, a 100% harvesting efficiency was achieved for *Chlorella sorokiniana* after 50 min with a specific power consumption of 1 kWh kg^{-1} [18]. NaCl is a cheap salt and optimization of its concentration can reduce the electric energy consumption. High saline levels have been reported to be beneficial for avoiding high power consumption. In the case of open ponds, there lies a possibility that the salinity levels increased without any addition of chemicals due to high evaporation rates. But as the salinity increased, the zeta potential of the microalgal suspension decreased. The zeta potential value decreased from −33.6 mV to −13.9 mV when the cells were cultured in 4 ppt solution. In addition, the microalgal growth was also found to decrease with increase in salt concentration [14]. However, the microalgal species which are cultured in high saline levels are more likely to form aggregates, as complete charge neutralization is not necessary to initiate floc formation.

3.7. Stirring rate

Stirring speed or mixing is a crucial process that defines the intensity and number of collisions, enabling aggregation of cells. Escalating the turbulence of the microalgal suspension can improve its harvesting efficiency. Generally, high power input supplied in the system provides natural turbulence for mixing. It creates a temperature difference between the liquid surrounding the electrode and the bulk liquid that provides the necessary turbulence. But in case of low power input, a small degree of external mixing is required. However, very high mixing rates have shown to reduce chlorophyll-a harvesting efficiency. High shear forces can disturb the algal flocs formed and also lead to disruption of cells [10,18].

4. Energy and economical perspectives

Dewatering or dehydration of microalgal suspension for harvesting alone constitutes approximately 20–30% of the total processing cost. The method opted for drying should consider the scale of operation and the application of the intended product. Also, in case of lipid extraction, decision has to be made if algae has to be dried previously [30,44]. Obtaining 1 kg of dry biomass would approximately require an energy supply of 800 kcal and hence the technique chosen should render beneficial in terms of cost and energy standpoints. There are numerous factors that contribute to the functioning of electrochemical processes and their optimization will not only reduce the cost but will render the entire system economically feasible. Also, microalgae has a high market value and hence exploiting multiple product strategies across biorefinery design will aid in making the overall process economically practicable [19].

ECF was found to be a low-cost technology whose capital cost (0.35 USD m^{-3}) was much lower than centrifugation (0.53 USD m^{-3}) and flotation with flocculants (USD 0.47 m^{-3}) [42]. Additionally, it was compared to chemical flocculants with high harvesting efficiency such as chitosan, ferric chloride and potassium ammonium sulphate and was established that for harvesting 1 kg of biomass, the cost acquired was 15.30, 2.30 and 3.01 USD respectively; but only 1.15 USD for ECF. Under optimized conditions of 12 mA cm^{-2} current density, pH 5, electrolysis time of 15 min, the total energy and cost of ECF was assessed to be 2.65 kWh kg^{-1} and 0.29 USD kg^{-1}, respectively that was lower than the conventional techniques used [51]. The only drawback was the hazardous nature of using high concentration of inorganic flocculants [8]. Organic flocculants render to be very effective even at low dosages, still the problem of high market price persists [1]. Liu et al. [42] reported the energy consumed by Al electrodes to be 2.25 kWh m^{-3} which was lower than chemical flocculation using aluminium sulphate. Similarly, Luo et al. [44] stated that an energy consumption of 2.73 kWh kg^{-1} of biomass was obtained for ECF and it was several folds lower than those of centrifugation (16 kWh kg^{-1}) and filtration (3.58 kWh kg^{-1}). The total cost of harvesting including, electrode, energy and capital depreciation summed up to 0.19 USD kg^{-1} of dry *Tetraselmis* sp. [39]. These investigations show that ECF can be considered very economical compared to other conventional methods. The fact that ECF does not require addition of chemical reagents greatly reduces the overall cost of process.

Electroflotation is thought to be an easy operating, cost-effective and highly efficient technique and widely used for wastewater treatment purposes. However, lab-scale units are considered relatively cheap in terms of operating cost. In pilot scale, a rectifier in place of a saturator might be required to maintain the necessary potential difference for bubble generation, which might add-up to the cost. The potential difference might as well be dependent on electrical conductivity of the medium [37]. In case of ECF, application of high current tends to speed-up the metal dissolution process, resulting in quicker and higher algal yield. However, this led to increase in the energy consumption. The energy required to attain 98% harvest efficiency of *Chlorella vulgaris* was 66.7 A m^{-2} (3.35×10^{-4} kWh), which was 1.32 and 3.38 times greater than those at 44.4 and 22.2 A m^{-2} [59]. The presence of residual ions in the supernatant should also be looked into as it might have a negative impact on the environment due to its toxicity. In case of Al electrodes, increasing the charge density increased the residual Al concentration as high as 4.9 mg L^{-1} [36,54]. Also, the heat generated during the process was very high which can be detrimental to the biomass. It was shown that beyond 80% of the efficiency, the energy demand presented a decreasing trend, thereby proving that it is not always required to remove all the biomass in the medium, as the remaining can possibly benefit further flocculation of microalga. The energy usage can be minimized by increasing the conductivity of the medium by using electrolytes with high salt concentration. In fact, electrolyte addition can also enhance the lipid extraction efficiency by 22% [30,59]. Combining this set-up with closely placed electrodes at a low electric current can further reduce the power consumption. Energy consumed by mixing and settling (0.33 MJ m^{-3}) can be minimalized on a large scale by replacing them with baffled hydraulic mixer [39].

The current supplied should also be maintained with an optimum pH at which the biomass recovery efficiency will be maximum. Generally during algal cultivation, the pH is alkaline ($\geq$8.5) and requires supplementation of HCl as acidic pH enhances microalgae recovery. But this might increase the chemical cost of the process. According to the ICIS website, the cost of HCl was estimated to be 0.215 USD kg^{-1}. Thus a balance between current density and pH has to be retained as a higher value of the former will shoot up the energy consumption of the system and a lower value of the latter will increase the cost of the process [42].

The electrode material used in ECF play a major role in terms of cost and energy. Though a number of materials such as Mg, Cu, Zn, brass have been tested, Al and Fe are the ones that widely employed. Al is proven the most efficient metal so far for harvesting microalgae; however, the cost is quite high (2.187 $\pm$ 0.12 USD/kg) [14]. Yet, when used in salt form (aluminium sulphate) the microalgal removal efficiency was only 7.1%. But, when salt addition was carried out after application of graphite electrodes, the efficiency reached 90% for which the cost and energy required were 0.21 USD m^{-3} and 0.3 kW h m^{-3} respectively [42]. In case of graphite electrodes, the energy consumption (1.12 kWh kg^{-1}) was very high compared to Al (0.46 kWh kg^{-1}). However, this was not the case at 0.2 A, where the operational cost of graphite (0.036 USD m^{-3}) was distinctively lower than Al (0.08 USD m^{-3}) [1]. Generally, the cathode materials used in this process are inert which renders them electrochemically non-degradable. This aspect can reduce the electrode replacement costs and pollution issues. In addition, ECF does not significantly affect the microalgal pigments and lipids which makes them superior and preferable than other common techniques [18].

Various trends in ECF have been explored recently whose harvesting efficiencies recorded are higher than the usual method. Energy input was provided in a pulse waveform which not only reduced the cost of electric usage by 32% (0.5 Wh g^{-1}) but increased the recovery efficiency up to 96.4% with residual Al concentration of 7% [35]. Another novel approach is discharging electroflocculation (DEF) technology which uses aluminium-air batteries for discharge of positive aluminium hydroxide hydrates that have high microalgal flocculation potential. The efficiency reached 97% within 20 min and the energy consumed was only 0.11 kWh kg^{-1} [41]. In another study, an asymmetrical electrode configuration was employed to induce dielectrophoretic (DEP) force with alternating current for the harvest of microalgae *Tetraselmis* sp. An efficiency of 90.9% was achieved in 10 min of electrolysis time and the energy consumed was reported to be 4.62 kWh kg^{-1}. The metal contamination in biomass reduced by 52% compared to conventional electrodes [29].

Electrochemical way of harvesting microalgae has been proved suitable for almost all species with additional benefits such as high efficiency, low process time and continuous operation. Also, reuse of the spent media is possible in this method which can reduce the process cost. However, for scaling-up of process, factors like power consumption, electrolysis time, biomass contamination should be carefully considered. In addition, development or choice of electrodes with efficient, less-toxic and non-fouling properties is required for long-term practical application. So far, ECF is being carried out and proved successful only at the laboratory and bench-scale with mechanical stirring. The technique was shown to outperform all the conventional methods in terms of harvesting efficiency (>95%), energy and cost factors. However, for application on an industrial scale, optimization of several operational parameters is required to ensure economic feasibility. For instance, a decrease in the inter-electrode distance and increase in the electrode surface area can benefit the overall performance. Similarly, for large-scale recovery of microalgae, an optimum agitation intensity of 100 rpm for Ruston turbine with Reynold's number 4000–6000 was recommended [43]. This process was installed on a commercial level for treatment of drinking water; yet, was not feasible for further establishment due to capital and electrical energy costs. A proper balance between the experimental factors, cost and processing time can optimize the overall microalgal harvesting efficiency. Indeed, a large reactor infrastructure with application of low current density and long retention time would serve the purpose of large-scale commitment [67]. In addition, a continuous flow reactor system is preferred for integration from a process engineering perspective [20]. Also, addition of salt such as NaCl to improve the conductivity of the medium for economic viability can pose challenges regarding cost, media reuse, disposal and microalgal motility [62]. Thus, with utmost examination and control of these considerations, ECF can be economically viable for scale-up.

5. Challenges and future prospects

Electrochemical processes are considered to be more attractive than chemical coagulation due to their lower power consumption and dosage requirement. It neglects the additional cost required to induce alkalinity as the hydrolysis of water simultaneously supplies it. In an ECF system, the cost of raw materials used is less, considering the same environmental adjustments. It includes the replacement of the sacrificial anode, which is efficient and cost-effective. The equipment is comparatively simple and easy to operate [16]. However, some problems occur during the ECF process that might hinder the process efficiency. The major challenges and highlights of ECF are addressed in Fig. 5. The foam produced during the release of air bubbles seems to grow denser with time and current density, which can influence the efficiency of ECF. One another issue is the rate of chemical corrosion of anode [18]. The two main mechanisms of corrosion include formation of a passive oxide layer on the electrodes and partial destruction of this layer by pitting. The pitting corrosion mainly depends on the current density, initial pH and concentration of the electrolyte in contact. It can affect the overall dissolution of the sacrificial anode [22,28]. Cathode fouling is another issue occurring due to the high total hardness of the medium that causes an increase in cell voltage and energy consumption [24]. This can be overcome by the optimization of current reversal frequency or by the addition of NaCl. Also, changing the polarity of the electrodes at certain intervals might help avoid the cathode passivation [29]. However, the electrodes were still prone to fouling. A solution was put forth by OriginOil Inc. that using electromagnetic pulses to induce flocculation can reduce the effect of fouling [10]. Literary references show that ECF can eliminate smaller flocs more efficiently than conventional methods due to electrophoretic mobility [22]. In these processes, the number of counter ions (*e.g.*, chlorides, sulphates) introduced is comparatively low. The flocs generated are large, stable and contain lesser bound water molecules than chemical flocs. Moreover, it is reported that the ECF did not have any significant effect on the amount of lipid and microalgal pigments. In fact, it had a positive impact on soluble algal products (SAP) such as carbohydrates and proteins [53].

6. Closing remarks and perspectives

Microalgae have proved to be a potential biofuel feedstock with high biomass productivity, and deliver more oil for biodiesel production compared to other plants. For an economically feasible biofuel production in large scale, the paramount challenge factor, harvesting process selected should be cost-effective, scalable and environment-friendly. In this regard, this review paper has given a brief insight of the electrochemical processes such as electroflocculation,

Fig. 5. Challenges and highlights of electrocoagulation process for microalgal harvesting.

electroflotation and electrocoagulation-flotation that offer the potential to be a low cost and energy-efficient microalgal harvesting technique. The electrophoretic mobility accessible by these processes is an add-on for efficient recovery. However, the process controlling parameters have to be optimized to minimize the energy requirements and overcome other challenges such as corrosion and electrode fouling. Though aluminium and iron electrodes are widely used with regard to the availability and cost, other metals and sacrificial anodes such as magnesium and zinc can be explored for chances of improvement of the process. Microalgal species whose characteristics and behaviour might suit the electrochemical harvesting can also be explored. Rigorous efforts to seal the research gap and challenges addressed in this review have to be undertaken. The nutritional quality of the microalgae recovered, energetics and cost are additional pivotal conditions to be taken into consideration. Considering the challenges and highlights addressed, the electrochemical processes for harvesting microalgae still prove to be a promising and sustainable approach for commercial viability. Some of the key takeaways of this review are presented below:

- Electrocoagulation-flotation is the most effective harvesting technique to recover microalgae irrespective of its size, shape, surface charge *etc.*
- With concerns to environment, energy and cost aspects, it is not always necessary to obtained recovery efficiencies $>$ 90%, as the residual cells in the medium can favour flocculation in further batches/cycles.
- Increasing the conductivity of the medium and decreasing the electrode distance can minimize power consumption.
- As the cathode materials used in ECF processes are electrochemically inert and non-degradable, the additional cost of electrode replacement and issues regarding toxicity and pollution can be significantly reduced.
- Electrochemical techniques are exclusively suitable for pigment extraction and biofuel production, as they have a positive effect on the amount of lipids and pigments present in microalgae.

CRediT authorship contribution statement

Nageshwari Krishnamoorthy: Conceptualization, Data curation, Writing - original draft preparation. **Yuwalee Unpaprom**: Visualization, Funding acquisition, Writing - review & editing. **Rameshprabu Ramaraj**: Visualization, Investigation. **Gaanty Pragas Maniam**: Project administration, Funding acquisition, Writing - review & editing. **Natanamurugaraj Govindan**: Project administration, Investigation. **Thirugnanam Arunachalam**: Supervision, Writing - original draft preparation. **Balasubramanian Paramasivan**: Conceptualization, Funding acquisition, Writing - review & editing, Final approval.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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