



## Electrocoagulation–flotation (ECF) for microalgae harvesting – A review

Simone Visigalli<sup>a</sup>, Maria Giulia Barberis<sup>a</sup>, Andrea Turolla<sup>a</sup>, Roberto Canziani<sup>a</sup>,  
Maja Berden Zrimec<sup>b</sup>, Robert Reinhardt<sup>b</sup>, Elena Ficara<sup>a,\*</sup>

<sup>a</sup> Politecnico di Milano, Department of Civil and Environmental Engineering, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

<sup>b</sup> AlgEn -Algal Technology Centre, Brnčičeva 29, 1231 Ljubljana, Slovenia

### ARTICLE INFO

#### Keywords:

Electrocoagulation  
Electroflotation  
Harvesting  
Dewatering  
Microalgae

### ABSTRACT

Harvesting has been recognized as a major bottleneck in any microalgae-based technology, making it a relevant research topic in the field. Among applicable technologies, electrocoagulation-flotation (ECF) has been devoted a lot of attention as an effective alternative to conventional metal salts addition. This paper reports and comments the relevant available literature on ECF, aiming at retrieving and assessing the main parameters affecting process performance by identifying their optimal ranges. After introducing the basic principle of ECF, the paper presents a qualitative analysis of the main factors (electrochemical parameters, microalgae and broth characteristics) and the way they affect the process performance. Then, a quantitative assessment has been performed based on the analysis of a dataset of 190 records from 29 research papers. Metal toxicity and process costs are addressed. Finally, guidelines for future experimentations are discussed in order to support and facilitate the further development of the ECF technology.

### 1. Introduction

In all kinds of microalgal cultivation, harvesting is a challenge as it must perform an efficient solid/liquid separation of small (typically 3–30 μm) microalgal cells from diluted culture suspension. Microalgae are cultivated in a variety of reactors including open ponds, photobioreactors of various shapes, thin-layer and biofilm systems [1,2] and for a variety of purposes, spanning from food, feed, pharmaceutical, cosmetic, to fertilizers and bioremediation [3]. The harvesting density of a typical algal culture depends on the optical path length of the cultivation system: in ponds, the typical cultivation density is below 1 g/L (0.1%), in the short optical path photobioreactors it can be up to 5–20 g/L, while it can reach 50–60 g/L in thin layer systems [4,5] and 100–200 mg/L in heterotrophic fermenters [6]. Except for the densest cultivation methods, it is clear that pre-concentration and separation (harvesting) is an essential step in any microalgae-based technology and it has been recognized as the major bottleneck in achieving the sustainability and cost-efficiency of these technologies [7].

Typically, algae harvesting is performed in the steps shown in Fig. 1. In a primary concentration step, the microalgae biomass is separated from the bulk of the culture in the form of a slurry having 1–3% solid content. In the secondary concentration step, a biomass paste up to 30% solid content can be achieved, eventually followed by a drying step,

based on the requirement of the downstream processing. Using a 2-step approach, dewatering costs are reduced by more than one order of magnitude [8,9].

Options for the primary concentration include various technologies based on the use of metal-salts [10], biopolymers [11], magnetic coagulants [12], ultrasounds [13], bioflocculation [14], electrocoagulation and a number of (patented) processes applying very diverse principles [15]. However, the majority of innovative processes are at a low technology readiness level (TRL). The principle of operation, advantages and disadvantages of those various alternatives have been summarized in recent literature reviews (e.g. [15–17]) to which the reader is referred for more details. While chemical coagulation is considered as the benchmark technology [10], alternative technologies for primary concentration have still to be proven as cost effective.

In the conventional coagulation-flotation process, pH variations and the dosage of polymers or polyvalent metal ions, such as iron (Fe<sup>3+</sup>) or aluminum (Al<sup>3+</sup>), allow charge neutralization of the microalgal particles and aggregation in flocs [18].

Electrocoagulation-flotation (ECF) is also based on the release of cations but via electrochemistry and this makes it easier to control and prevent overdosing. During ECF, aluminum and/or iron ions are released into solution by the anode oxidation and form metal hydroxides, which act as the coagulation/flocculation agents. ECF does not add

\* Corresponding author.

E-mail address: [elena.ficara@polimi.it](mailto:elena.ficara@polimi.it) (E. Ficara).

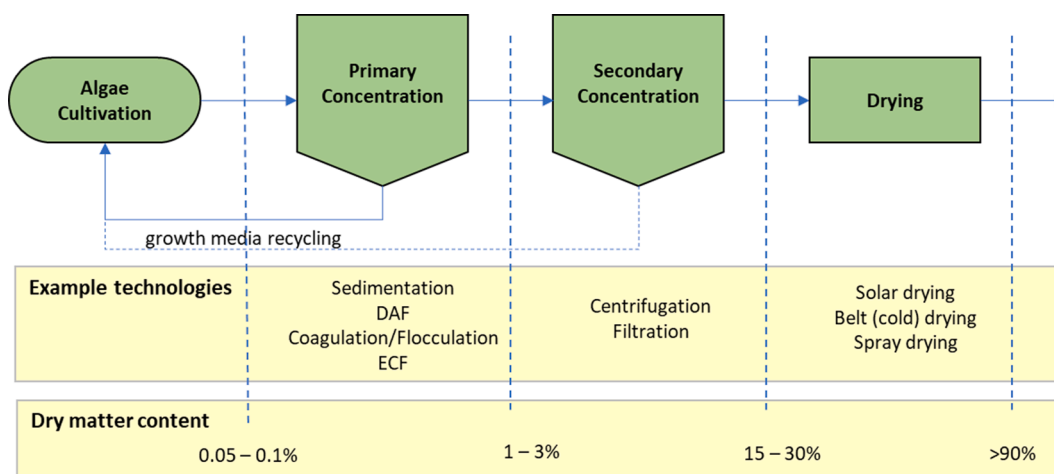


Fig. 1. General framework for microalgae harvesting.

any anion, other than OH<sup>-</sup>, into solution and produces microbubbles that float algal flocs to the surface for easy skimming [19–21]. Using electricity for water treatment was first proposed in UK in 1889, while electrocoagulation with aluminum and iron electrodes was patented in the US in 1909. The electrocoagulation of drinking water was applied on a large scale in the US since 1946 but its application worldwide was found impractical due to the high capital and energy costs [22]. During the past three decades, electrochemical wastewater treatment technologies have regained importance [23]. Electrocoagulation is now a solid alternative to other conventional technologies in different fields, such as metal recoveries, treatment of drinking water, process water, wastewaters from various origins including tannery, electroplating, dairy, textile processing, oil and oil-in-water emulsions [21,22]. This technique seems a promising alternative to the conventional chemical coagulation of microalgae via metal salts addition, but most of the reported results still come from bench-scale tests. Furthermore, relevant operational parameters and their optimal range are still unclear or too wide, making it difficult to perform a sound technical-economic analysis in comparison to the conventional techniques.

Within this framework, this review aims at collecting and organizing the available literature data on operational principle, equipment, protocols, and main parameters affecting the process efficiency in order to support further developments and scale-up of the process. Moreover, comparison with the conventional flocculation is addressed together with a very approximate cost analysis.

## 2. General principles of ECF

### 2.1. Why microalgae harvesting needs coagulation/flocculation

There are three main reasons that make microalgal biomass recovery difficult to achieve: (i) microalgal cells are small (typically within 3–30 μm, though even smaller cells do exist, e.g. 0.8–1.5 μm for *Synechococcus*), (ii) culture broths concentration is typically low (from <0.5 g/L in outdoor open ponds), (iii) like most of biological material, microalgae usually carry a negative surface charge, which provides them with colloidal stability in a suspension [10,24]. The surface charge density is a function of microalgal species, ionic strength of the medium, pH and other environmental conditions [25]. Microalgal cell wall is composed of polysaccharides, proteins and lipids [26] which contain numerous functional groups, such as carboxyl (–COOH), hydroxyl (–OH), phosphate (–PO<sub>3</sub>), amine (–NH<sub>2</sub>) and sulfhydryl (–SH) [27]. Carboxyl and amine groups are especially relevant since they can generate surface charges and consequently surface potential. Indeed, under typical neutral/alkaline pH, these functional groups are deprotonated, resulting in a net negative surface charge, coherent with their negative zeta

potential [28]. Therefore, the behavior of a microalgal suspension is similar to that of colloidal suspensions where the charge-related repulsive forces (increasing with the decrease in the particle size) overcome Van der Waals attractive forces (decreasing with the decrease in the particle size) and microalgae cells remain in a stable dispersed state. To favor algae separation, repulsive forces should be reduced by allowing microalgal cells aggregation and facilitating their separation from water [23].

The electric configuration around microalgal cells can be modelled by the DLVO (Derjaguin, Landau, Verwey, Overbeek) theory [29,30]. In fact, to maintain net electrical neutrality, the negatively charged cells attract cations from the solution, the so-called counter ions, building up a structure called electric double layer. The electric double layer consists of an inner region (Stern layer), where oppositely charged ions are tightly bound to the surface of colloidal particles and an outer layer, where the ions move freely due to diffusion (ion diffusion layer or slipping plane). The interface between the inner and outer layers is known as the shear plane that defines the outer limit of the Stern layer (Fig. A1 in appendix). The maximum (negative) potential occurs at the surface of colloidal particle and is known as the Nernst potential, where it decreases in absolute value across the Stern layer due to the presence of oppositely charged particles resulting in what is defined as Zeta potential (Z) [23]. Zeta potential is easily measurable and it is a useful indicator of the degree of the suspension stability. When it is high ( $|Z| > 25$  mV) the repulsion is strong, and the suspension is stable. The more it gets closer to zero, the more the particles tend to aggregate thus forming flocs. Therefore, the role of coagulants, either added as chemicals or as ions from electrocoagulation, is to destabilize the colloidal particles by reducing the repulsive forces that prevent particles aggregation thus allowing attractive forces to prevail [10,23,31]. Moreover, when metal salts are used as coagulants, insoluble metal hydrates are also formed that precipitate and settle easily. These precipitates eventually entrap colloidal particles during and after precipitation, favoring particle separation, this mechanism being known as *sweep coagulation* [23,32]. Indeed, under typical ECF conditions, the coagulation/flocculation of microalgal cells is mostly due to the sweeping coagulation/flocculation by insoluble hydroxides [33,34]. According to the solubility diagram (see Figure 9–11 in [35]) for Fe, optimal conditions for an effective sweep coagulation are achieved by a metal dosage of 10<sup>-3</sup>–10<sup>-5</sup> M and at pH of 6–10. Similarly, for Al sweep coagulation occurs with a dosage of 3x10<sup>-4</sup>–3x10<sup>-5</sup> M and at pH of 6–9.

### 2.2. Fundamentals of electrocoagulation-flocculation

In the ECF process, electrodes are usually made of metals, while the non-metal electrodes or mixed solutions of metal and non-metal

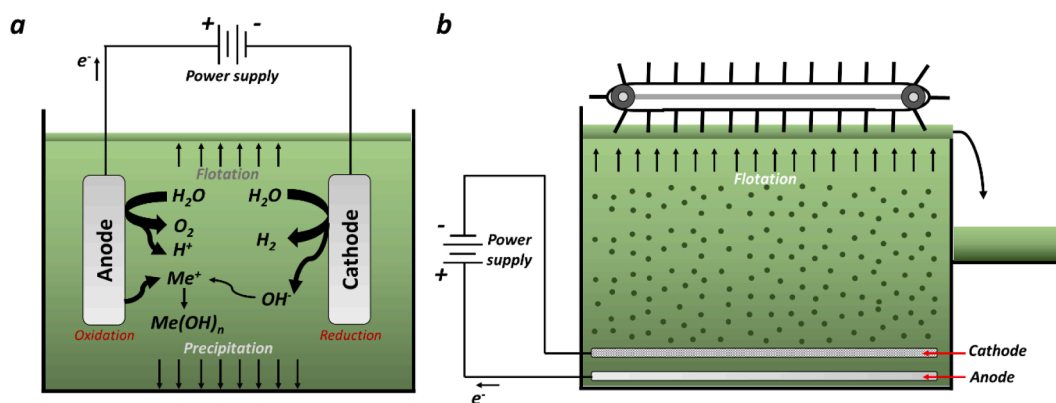


Fig. 2. Schematics of (a) electrocoagulation and (b) electroflotation processes for microalgae harvesting.

electrodes are less frequently used [36]. These alternatives are discussed in the following sections.

### 2.2.1. Sacrificial metal electrodes

In the most conventional configuration, ECF is performed by using metal electrodes submerged in the aqueous suspension that has to be treated (Fig. 2). The electrodes are usually made of aluminum or iron, which are effective, cheap and readily available [20,37], although other materials were tested, such as stainless steel.

During electrocoagulation with the metal electrodes, two main phenomena occur (Fig. 2a): (i) the electrolysis of water that produces microbubbles causing floc flotation (electroflotation), (ii) the oxidation of the anode to the metal cations which are released into the microalgal suspension and induces the destabilization of the algae cells and their coagulation/flocculation (electrocoagulation). Integrating electrocoagulation and electroflotation in a combined process allows the destabilization of microalgae suspension and their aggregation in flocs, which are then floated by microbubbles [18]. The combination of these two effects, which are later discussed in more details, justifies the name given to the technology (i.e. electrocoagulation-flotation, ECF).

The electrolysis of pure water produces oxygen gas at the anode (Eq. (1)) and hydrogen gas at the cathode (Eq. (2)) ( $E^0$  is the standard electrode potential):



Microbubbles ( $\text{O}_2$  and  $\text{H}_2$ ), released at the electrode surface, adhere to the microalgal cells or flocs and cause flotation by carrying them to the liquid surface and forming a floc-foam layer [37,38]. Floated flocs can be easily skimmed off (as illustrated in Fig. 2b). Compared to sedimentation, flotation is a fast process requiring a few minutes [25]. Since water hydrolysis involves the release of  $\text{H}^+$  or  $\text{OH}^-$ , the process is affected by pH: alkaline conditions favoring anodic reaction (Eq. (1)), while acidic pH supporting cathodic reaction (Eq. (2)). Because of water electrolysis, pH rises at the cathode, and it is reduced at the anode. Beside water electrolysis, metal dissolution occurs at the anode in ECF. The anode oxidation reactions depend on the electrode material.

The expected metal forms from electrocoagulation in aqueous systems can be predicted by the Pourbaix diagram. This diagram reports, in a graphical form, the thermodynamic equilibria under various pH and ORP conditions and under defined concentrations of solubilized metals (relevant equilibria for Fe and Al are reported in Table A1, in appendix [39]). According to this diagram, at a temperature of 25 °C and at a concentration of soluble metals of 1 M (which is definitely too high under typical application conditions),  $\text{Fe}^{2+}_{(aq)}$  dominates at a  $E_0$  below 0.77 V. However,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  precipitate as  $\text{Fe}(\text{OH})_{2(s)}$  at  $\text{pH} > 6$  and

$\text{FeO}(\text{OH})_{(s)}$  at  $\text{pH} > 1.3$ , respectively. In the presence of lower soluble Fe species, the predominance of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  increases, while the pH above which precipitates prevail also increases [40]. Final speciation of Fe is also affected by concomitant chemical transformations, such as the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by molecular oxygen which develops at the anode level.

As for aluminum,  $\text{Al}(\text{OH})_{3(s)}$  is the prevailing form for pH ranging from 3.4 to 12.4, while this pH range shifts toward higher values with the decrease in the soluble forms concentration.

The practical use of the Pourbaix diagram is however complicated by the fact that chelation with organics which are typically present in microalgae suspensions may interfere with the final speciation as predicted by the Pourbaix diagram. Moreover, pH and redox potential at the anode are rarely measured during experimental electrocoagulation trials. Finally, it has to be stressed that the Pourbaix diagram refers to the thermodynamic equilibrium, which is rarely attained during experimental tests, thus suggesting that complex dynamic models are needed for a reliable prediction of ECF performances [41].

The number of electrons released from the electrode during the ECF process is stoichiometrically related to the amount of metal released by the anode oxidation, as quantified by the Faraday's law (Eq. (3)):

$$m = \frac{I \times t_s \times M_{\text{Me}}}{z \times F} \quad (3)$$

where  $m$  is the mass of anode dissolved,  $I$  is the applied current,  $t_s$  is the treatment time,  $M_{\text{Me}}$  is the molar mass of the electrode material ( $M_{\text{Al}} = 26.98 \text{ g/mol}$ ,  $M_{\text{Fe}} = 55.85 \text{ g/mol}$ ),  $z$  is the valence of ions of the electrode material ( $z_{\text{Al}} = 3$ ,  $z_{\text{Fe}} = 2$ ),  $F$  is the Faraday's constant (i.e. the charge of a mole of electrons, 96,485 C/mol) [23,37,42].

Many other factors may lead to a dissolution yield different from the theoretical one, computed from Eq. (3). It has been found that the theoretical amount of anodic dissolution is often exceeded in real ECF applications and the experimental values of metal dissolution can be as high as 190% of the theoretically expected value. The cause of this mismatch, known as superfaradaic efficiency, may be the chemical (rather than electrochemical) dissolution of the electrode surface [43,44]. Chemical dissolution is favored by the evolution of oxygen at the anode that in turn is favored at alkaline pH and sufficiently high anodic potential [21,44,45]. Because of water electrolysis, pH rises at the cathode and it is reduced at the anode, thus chemical dissolution is promoted for aluminum at higher pH (cathode) and for iron at lower pH (anode) [43]. Moreover, pitting corrosion can also take place, especially in the presence of chlorine ions [22,37].

Once electrochemically or chemically solubilized, metal cations react spontaneously in solution, forming various monomeric hydroxides such as:





Other species are formed in solution. Ferric ions may form monomeric ions, ferric hydroxo-complexes with  $\text{OH}^{-}$  ions, and polymeric species such as  $\text{Fe}(\text{OH})_2^{2+}$ ,  $\text{Fe}(\text{OH})_2^{+}$ ,  $\text{Fe}(\text{OH})_2^{4+}$ ,  $\text{Fe}(\text{OH})_4^{-}$ ,  $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ ,  $\text{Fe}(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$  and  $\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4^{2+}$ , which further react to form  $\text{Fe}(\text{OH})_3$  [21,37]. For aluminum, monomeric species include  $\text{Al}(\text{OH})_2^{2+}$ ,  $\text{Al}_2(\text{OH})_2^{4+}$  and  $\text{Al}(\text{OH})_4^{-}$ . Polymeric species are also produced such as  $\text{Al}_6(\text{OH})_{15}^{3+}$ ,  $\text{Al}_7(\text{OH})_{17}^{4+}$ ,  $\text{Al}_6(\text{OH})_{15}^{3+}$ ,  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{4+}$  and  $\text{Al}_{13}(\text{OH})_{34}^{5++}$ , which finally transform into  $\text{Al}(\text{OH})_3$  according to complex precipitation kinetics [21,34,37,46-48]. The presence and relevance of the above listed hydroxides depends on the total metal cation concentration, the pH, potential, and the type and concentration of other species present in the solution [49].

Further phenomena are involved in ECF, including the electrophoresis, i.e. the migration of negatively charged particles towards the anode. Moreover, the above-mentioned sweep flocculation mechanism allows the entrapment of microalgal cells in the amorphous hydroxide precipitates [38].

Several factors, such as pH and electrode material, have an impact on the relevance of charge neutralization and sweep flocculation as addressed by solubility diagrams, such as those reported by Crittenden et al. [35]. Nonetheless, as solubility diagrams only consider mono-nuclear species, empirical observations are also important, especially when dealing with complex liquid media for microalgae culturing. As an example, above pH 9, negatively charged hydroxides ( $\text{Al}(\text{OH})_4^{-}$  and  $\text{Fe}(\text{OH})_4^{-}$ ) are the dominant species [37] which do not react with the negatively charged microalgal cells. Under alkaline conditions, the coagulation/flocculation of microalgal cells is probably due mostly to the sweeping coagulation/flocculation by insoluble hydroxides [33,34]. Conversely, under acidic conditions, positively charged monomeric and polymeric hydroxides are formed that react with the negatively charged surface of the microalgal cells and destabilize the microalgal suspension by charge neutralization. In general, larger amounts of aluminum hydroxide are formed than ferric/ferrous hydroxide [7,11,44] leading to better performances in neutral suspensions.

The performance of the ECF process depends on various factors, the main being:

- The metal dissolution per unit of electric energy applied (dissolution efficiency). This efficiency is affected by the overall electrical resistance of the cell elements (electrodes and solution) which influences the efficiency of the electrolytic processes, but also by the concomitant chemical dissolution. The higher this efficiency the lower the cost of releasing active metal ions in solution;
- The efficiency of the coagulation/flocculation process, that depends, in turn, on many factors, mainly related to the chemical characteristics of the suspension (ionic composition, salinity, pH, and temperature), the nature of particles (size, zeta potential) and the hydrodynamics (including mixing, electrophoresis, and bubble formation).

In practice, the ECF performance is typically quantified in terms of:

- the dissolution efficiency,  $Ed$  ( $\text{kg}_{\text{Me}}/\text{kWh}$  or  $\text{mol}_{\text{Me}}/\text{kWh}$ , as its quantification allows for a fair comparison among performances of different metals);
- the applied metal dosage in terms of metal dissolved per unit of mass of microalgae recovered,  $sMD$  ( $\text{kg}_{\text{Me}}/\text{kg}$ );
- the electric energy consumption per unit of volume of the treated suspension,  $vEEC$  ( $\text{kWh}/\text{m}^3$ ), or per unit of mass of microalgae recovered,  $sEEC$  ( $\text{kWh}/\text{kg}$ );

- the recovery efficiency,  $Er$ , i.e. the fraction of algae biomass separated by the ECF process.

### 2.2.2. Non-sacrificial electrodes

When non-sacrificial electrodes are used [51,52], the negatively charged algal cells move towards the anode by electrophoresis, where they lose their negative charge through neutralization, and flocculate [53]. Carbon electrodes, usually in graphite, are inert and safe, but the harvesting efficiency is lower than that achieved with sacrificial anodes since metal cations enhancing the coagulation/flocculation are absent, thus resulting in higher power consumption [31,32,40]. The lower efficiency of carbon electrodes is a cost to pay in the case ECF is used for harvesting microalgae for the food industry, since sacrificial anodes are unacceptable due to the contamination by metal ions of the harvested biomass [33,55]. Moreover, flotation is induced by gas bubbles from water electrolysis, which favor cells separation. However, no convincing evidence is available allowing distinguishing between electric field-induced and mixing-induced cell trajectories, which would allow highlighting the relative importance of these concurrent phenomena.

### 2.2.3. Hybrid systems

There is no guarantee that a simple ECF system would provide just enough metal ions for coagulation/flocculation and hydrogen bubbles for flotation. To independently control these processes, hybrid solutions have been suggested. One option is to add external organic polymers (such as chitosan) to amplify the coagulation/flocculation effects of the electrically-assisted metal release, as suggested by Zhou et al. [55]. Alternatively, metal salts addition was suggested to enhance the efficiency of systems based on the non-sacrificial electrodes [36]. Integrated approaches can also include extra air-bubbling in a conventional sacrificial electrodes system [56,57]. However, limited experience is available to assess the efficiency and cost effectiveness of these alternatives.

An interesting hybrid approach consists in mixing the sacrificial metal electrodes for electrocoagulation and non-sacrificial electrodes for the electroflotation. This combined ECF process was declared to have two significant advantages: a shorter retention time and more efficient harvesting [58]. Kim et al. [36] studied the ECF process on *Nannochloris oculata* by applying polarity reversal between Al and a non-sacrificial electrode (dimensionally stable anode, DSA®, Ti-RbO<sub>2</sub>) allowing to vary the ratio between the Al dissolution and bubbles formation. They found that an increase in the duration of the phase in which DSA operated as anode and Al as cathode (thus leading mainly to water electrolysis) appeared to reduce the electricity consumption by 30% and the accumulation of aluminum in the harvested microalgae of 57%, with an unchanged cells viability.

## 3. Experience in the application of ECF to microalgae

Due to the multitude of reactions occurring simultaneously, the process modelling and harvesting efficiency predictions are extremely complicated. Consequently, in the view of scaling-up, a systematic approach to assess performance still needs to be established [38]. Relevant information can be obtained by analyzing the literature on the application of ECF to microalgae that is summarized in Table A2.

There are three most important factors affecting harvesting efficiency:

- (i) ECF parameters: type and arrangement of the electrodes, current density and process time, hydrodynamics, reactor setup [17,37,59].
- (ii) Microalgae characteristics: cell morphology, motility, extracellular organic matter composition and concentration, surface charge [19].
- (iii) Broth characteristics: temperature, pH, salinity, chloride concentration [37,59].

Moreover, in electroflotation, the size and quantity of bubbles and their collision and particle adhesion are key factors influencing the harvesting efficiency [59]. All these factors of influence are discussed in more details in the following paragraphs.

### 3.1. ECF parameters

#### 3.1.1. Type and arrangement of the electrodes

Various experiments were performed to compare the efficiency of aluminum and iron electrodes using different microalgae. Gao et al. [60] worked with *Microcystis aeruginosa*, Vandamme et al. [33] and Fayad et al. [50] with *Chlorella vulgaris*, Dassey and Theegala [42] with *Nannochloris* sp. and *Dunaliella salina*. Experimental results have shown higher recovery efficiency (*Er*) of Al compared to Fe. This better performance was explained by the higher performance of aluminum-based coagulation/flocculation under neutral/alkaline pH [7,11,44]. However, this advantage can be off-set by the better conductivity of Fe leading to higher values of *Ed* and the Fe lower cost. In the case of stainless steel anodes, iron ions are expected to be electrically generated. However, the anodic behavior of stainless steel is similar to that of carbon steel (due to the same anodic consumption), but at higher cost [61]. Moreover, when ECF is used in biotechnological applications such as microalgae harvesting, other aspects are to be considered mainly related to the toxicity and biomass contamination. These aspects are analyzed later on in Section 4.

Although less common, other metals were also tested. Shuman et al. [62] applied ECF for the harvesting of *Nannochloropsis* sp. and found that nickel electrodes were more efficient than aluminum ones. Rahmani et al. [63] developed an ECF system for harvesting of *Chlorella pyrenoidosa* with different electrode materials, namely aluminum, iron, zinc, copper, and carbon. They reported that the aluminum electrodes exhibited the highest harvesting efficiency (95.8%), and best *sEEC* (0.28 kWh/kg) followed by copper, zinc, carbon and iron. Poelman et al. [64] carried out ECF tests with anodes and cathodes made of aluminum and lead, respectively. They found that the cathodes were covered with a non-stable film reducing current intensity by 5–10% due to the increased resistance, thus leading to increased ohmic losses. Issues related to the toxicity and costs were not considered in that work.

Beside the electrode material, their geometry also affects the ECF efficiency. Valero et al. [65] studied ECF on a mixture of *Scenedesmus* sp. (24%), *Kirchneriella* sp. (1%) and *Microcystis* sp. (75%) with iron electrodes at different distances. They found that the highest efficiency occurred with a shorter electrode distance (5.5 cm), which was slightly (2.6% and 3.1%) more effective than with separation of 7 and 11 cm, respectively [65]. Wong et al. [66] studied different configurations of aluminum electrodes for harvesting of *Chlorella vulgaris* and observed that the highest efficiency was achieved with two cathodes and one anode (CAC), rather than two anodes and one cathode (ACA), or configurations with two (AC) or four electrodes (AACC). Regarding the shape of electrodes, Luo et al. [59] reported that algae cells accumulate more easily on the surface of stainless steel anodes in a grid shape, rather than on plate or bars, and are harder to be cleaned. In fact, plate electrodes were commonly used in electrochemical harvesting methods [59,67]. Baierle et al. [67] studied iron and aluminum electrodes in a spiral shape for harvesting of *Desmodemus suspicatus*. According to the authors, spiral shaped electrodes allow an improvement in the ECF efficiency due to the increase of the surface area, the formation of small and fast-dispersing bubbles of oxygen, the reduction of power consumption of the process and an increase in the electrode lifetime. It is worth noting that it is difficult to draw definitive conclusions on the optimal shape, since limited data are available in the literature and the hydrodynamic properties of ECF cell could also affect the final ECF results.

#### 3.1.2. Current and process time

Current is another important factor that affects both harvesting

efficiency and energy consumption [53]. In most of the literature works, current is normalized to the electrode area and therefore reported in terms of *current density*. Typical values for the current density used during batch tests is of few mA/cm<sup>2</sup>, with the majority of values ranging within 2 and 20 mA/cm<sup>2</sup>. The amount of metal that dissolves from the anode increases with the current (and also with current density when working with the same experimental set-up) and process time, according to the Faraday's law (Eq. (3)), which in turn promotes algal aggregation and floc formation. Various experiments tested the effect of the current/current density, observing that:

- higher current density causes an increase in the specific electric energy consumption [60,67];
- increasing the current (and current density) reduces the process time by speeding up the electrochemical dissolution [68];
- increasing current density improves the generation of bubbles. At low current density bubbles tend to stick to the cathode affecting the media conductivity [13,39,40]. Increased current density also tends to decrease the size of bubbles (they detach sooner) which improves their effectiveness in the flotation process [27,44];

A proper balance should be maintained between process time and energy cost in order to optimize the overall process efficiency [53]. Indeed, since the use of a low current density requires relatively long retention times, larger reactor size would be required at the industrial scale. In addition, since the algal biomass harvesting time may affect its final quality and viability, process time may be constrained [33].

#### 3.1.3. Hydrodynamics

As for conventional coagulation/flocculation processes, stirring speed has a relevant effect on the ECF efficiency, so that mixing should be optimized since it plays the following opposite effects:

- On the one hand it improves the microalgae harvesting by enhancing contact between the coagulants and the cells [21]. Vandamme et al. [33] showed that for an increase in stirring speed from 0 to 60 and 150 rpm, the time required to achieve destabilization of the microalgal suspension decreased by almost a factor of two;
- On the other hand, mixing at higher stirring speeds causes high shear forces, which may break-up microalgal flocs and reduce ECF efficiency [33,69].

It is worth noting that most of the literature reports stirring conditions in terms of stirrer RPM, while it is known that the effectiveness of mixing also depends on the velocity gradient and the geometry of the tank. Better reporting parameters would be the specific power input ( $W m^{-3}$ ) or velocity gradient ( $G, s^{-1}$ ). The adoption of unified parameters would facilitate the comparison among different experiments, also with respect to other coagulation techniques.

When considering electroflotation, the liquid depth is relevant. Luo et al. [59] reported that higher values result in higher efficiency as a consequence of the increased distance for hydrogen bubbles to travel to the surface of the liquid and, thus, of the higher contact time for collisions between hydrogen bubbles and algal cells. However, at higher liquid depth, the hydrogen bubbles separation from the cathode surface can be hindered because of the higher liquid pressure, which results in a higher energy consumption [59]. Contrary to what is reported above, Valero et al. [65] reported that different liquid depths (2.7, 5.2 and 6.4 cm), resulted in statistically equivalent recovery efficiencies.

Most of experimental data in literature were obtained in batch reactors, only few of them were continuously operated. In continuous systems, flow velocity determines the residence time and, consequently, the ECF process time. A fast flowrate may promote the detachment of bubbles from the cathode surface, although high velocities can result in bubble dragging to the reactor outlet, instead of letting them rise up to the liquid surface [59].

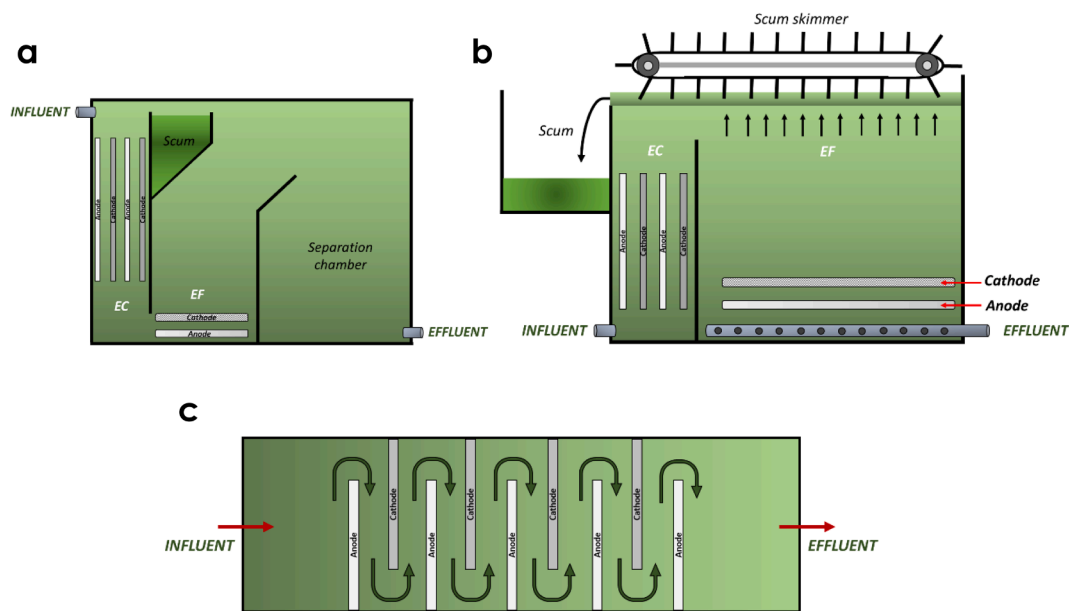


Fig. 3. Typical designs of ECF continuous reactors: (a, b) EC and EF in separated chambers (adapted from [58]) and (c) baffled reactor (adapted from [70]).

Xu *et al.* [57] tested the ECF process integrated with dispersed air flotation and found that the aggregate size of microalgae was bigger and increased more quickly in the integrated process than in the ECF process. On the other hand, the overall maximum efficiency in the integrated process was lower, since the shear stress and turbulence caused by the continuously dispersed air broke the up-floated flocs which resuspended in the algal culture broth [57].

### 3.1.4. Reactor setup

Among the available configurations for ECF reactors, batch and continuous systems can be found. Batch reactors typically operate with a fixed volume of algal suspension treated in cycles, whose characteristics may change over time. On the other hand, continuous reactors work with a continuous feed and under (pseudo) steady-state conditions. The large majority of published results were obtained in batch configurations, that were used to assess the influence of relevant parameters on the process efficiency and to identify optimal operating conditions. Nevertheless, a continuously flowing process is usually preferred (and targeted) from a process engineering perspective, since it can be more easily integrated into large scale cultivation systems.

Typical designs of ECF continuous reactors are shown in Fig. 3, including configurations in which EC and EF are performed in separate chambers and baffled reactors. In the latter case, in which EC is carried out by forcing the microalgal suspension to flow in zigzag path between the electrodes, the active surface is maximized as well as the residence time of the suspension in the reactor [70].

Some relevant applications of continuous reactors are reported hereafter. Shuman *et al.* [62] tested a small electrocoagulation reactor using electrodes in aluminum or nickel, positioned at 6.35 mm distance and designed to prevent recirculation zones. A separated settling beaker was used for microalgae separation. The reported energy input was 0.08 kWh/m<sup>3</sup> when treating 3.9 L/min of a *Nannochloropsis* sp. suspension. Short EC times were required (0.8–7.5 s), followed by a 30-min downstream separation time [62]. Zhou *et al.* [55] tested a bench-scale electroflotation reactor with a nominal capacity of 1.5 m<sup>3</sup>/h and geometry similar to Fig. 3b, except for the horizontal positioning of electrodes in

the inlet zone. Non-sacrificial electrodes were used to induce flotation while chitosan was added to favor flocculation [55]. Luo *et al.* [59] tested an 80-L electroflotation reactor with an *sEEC* of 2.73 kWh/kg. More recently, an innovative setup was proposed by Parmentier *et al.* [71] consisting in an electrolytic cell made of a pair of vertical concentric tubular electrodes (inner stainless steel cathode and outer metal anode), and a flocculation tower installed on top of the electrolytic cell for flotation of the coagulated cells. When treating *Chlorella vulgaris* at neutral pH, a 100 or higher concentration factor was achieved with an *sEEC* of 2 kWh/kg for iron electrodes and 1.1 kWh/kg for aluminum electrodes [71]. Although promising, these results are still insufficient to draw any robust conclusion on reactor design, so that the TRL level of this technology is currently set to 3–4.

### 3.2. Microalgae characteristics

As stated before, microalgae cells are negatively charged [72] due to the presence of ionizable functional groups on the cell wall or of extracellular organic matter (EOM) attached to the cell surface [73,74]. EOM has been pinpointed as the major source of electronegative charge for four algae species (*C. vulgaris*, *Microcystis aeruginosa*, *Asterionella formosa* and *Melosira* sp.), showing hydrophilicity with negative Zeta potential values for pH between 2 and 10 [74]. Zeta potential measurements on the green microalgae confirmed that algal cells are typically electronegative for pH between 4 and 10, ranging around -10 to -36 mV [74]. Algal surface charge has been shown to be species dependent; the cell surface of *Microcystis aeruginosa* has a lower hydrophobic character and a more negative surface charge over a larger pH range than *Chlorella vulgaris*, with the stage of life cycle influencing Zeta potential due to the variations in quantity and composition of the EOM [74]. The value of the Zeta potential was not correlated with the tendency of microalgae to grow in colonies of biofilms, but was markedly larger for marine species [28]. The negative surface charge is the main reason for the need of metal cations to allow for cell coagulation.

Cells surface properties are expected to influence the flotation process which is based on the generation of up-rising gas bubbles that bind

to algal cells and induce their flotation to the liquid surface [16]. An efficient flotation relies on successful collision and attachment of bubbles and particles, and works best when algal cells are hydrophobic [75]. Though hydrophobicity is more common, it varies greatly depending on the species of algae. Gonçalves *et al.* (2015) showed that *Chlorella vulgaris*, *Pseudokirchneriella subcapitata* and *Microcystis aeruginosa* presented a hydrophilic surface, while *Synechocystis salina* and co-culture with *S. salina* showed hydrophobic properties. Ozkan and Berberoglu (2013) measured the free energy of cohesion to assess the hydrophobicity character of microalgae surface. Seven out of 12 strains showed an hydrophobic surface; moreover, the authors acknowledge that the hydrophilic character of the remaining strains could be turned to hydrophobic in the presence of multivalent cations, which are normally available in cultivation media and released in solution during ECF or upon addition of coagulants [77].

As shown in Table A2, the species studied for ECF harvesting were selected based on the popularity of their cultivation for various products. Green algae are known for their high applicability and ease of cultivation, especially the species from the genus *Chlorella*. The most popular species, *Chlorella vulgaris*, is known for its wide utilization, from production of biofuels (biodiesel, biomethane and biohydrogen), to high-value products in cosmetics (skin care), nutraceuticals (polyunsaturated fatty acids), and pigments (carotenoids and chlorophyll). They are commonly used also in wastewater treatments (reduction of nutrient and organic matter content) [78–80]. Different species of the genus *Scenedesmus* are cultured for the wastewater bioremediation, antioxidant properties, polyunsaturated fatty acid (PUFA) production, and utilization for the animal feed (high protein content, fatty acids), cosmetics (pigments), sunscreen, biofuel, and biofertilizers [79,81]. Many species have been recognized as a perspective source of biofuel due to their high lipid content, i.e. species from genera *Kirchneriella*, *Chlorococcum*, *Tetraselmis*, *Nannochloris*, *Nannochloropsis* (Chlorophyta), *Phaeodactylum* and *Ankistrodesmus* (Bacillariophyceae/diatoms) [79,81–83]. *Botryococcus braunii* is used in the biofuel industry, in bioremediation, as an alternative source of carotenoids for the human health applications, as well as in cosmetics [82,84]. *Dunaliella salina* is one of the most popular beta-carotene producers featured in numerous studies about this pigment [84]. Cyanobacteria *Spirulina/Arthrospira* has been consumed for ages due to its high nutritional value (proteins, essential amino acids, vitamins, essential fatty acids and microelements, antioxidant potential), and it is frequently utilized in the production of pigment phycocyanin, protein meal or feed additive in diets of poultry, fish and domestic animals, and products in cosmetics [83].

It is worth noting that the majority of literature data refer to monospecies laboratory cultures, while the outdoor open-pond cultivations are usually characterized by the multispecies communities with one or more dominant species that may change over seasons. Gonçalves *et al.* (2015) demonstrated that species interactions have significant impact on flocculation and sedimentation characteristics of mixed cultures, mainly due to a decrease of the free energy of hydrophobic interaction, resulting in a more hydrophobic surface [76]. Extensive data on the mixed cultures are still missing and further investigations should be carried out to identify the efficient harvesting solutions in bioremediation.

### 3.3. Broth characteristics

#### 3.3.1. Temperature

The increase of temperature favors the ECF process by increasing the kinetic energy of the cells and the electrical conductivity, and by decreasing the viscosity, thus favoring particle transport [19,60].

Uduman *et al.* [19] found that the ECF harvesting efficiency of two marine algae, namely *Chlorococcum* sp. and *Tetraselmis* sp., were as low as 5% and 68%, respectively, at a temperature of 5 °C, but when the operating temperature was increased up to 60 °C, the efficiencies significantly increased to 96% and 94%, respectively.

#### 3.3.2. pH

As already described in the Section 2, pH plays an important role in the ECF process, since it affects water electrolysis, metal solubility and, especially, determines speciation of aluminum and iron hydroxides in the microalgal suspension. Some authors suggested that the neutralization mechanism is more effective for the destabilization and separation of microalgae than the sweeping mechanism [34,60] and neutral pH should be properly considered for the effective operation of the ECF process [53].

However, conflicting results are reported in the literature. Misra *et al.* [54], when treating *Scenedesmus obliquus* with aluminum electrodes, showed that an initial pH of 5 was optimal and that efficiency decreased at higher values. Uduman *et al.* [19], working with *Tetraselmis* sp. and stainless steel electrodes, could not observe any clear effect of pH (tested pH interval 4–9) on harvesting efficiency. Similarly, Golzary *et al.* [34] reported that initial pH had a smaller effect on *Chlorella* sp. separation with aluminum electrodes, if compared to time and current density. Xu *et al.* [69] reported that the time needed for *Botryococcus braunii* harvesting with the aluminum electrodes decreased with increasing pH from 7 to 11, while algal lysis occurred when pH was increased up to 12.

Experimental evidence indicated that pH is influenced by the ECF process itself by the concurrent release of hydroxyl ions at the cathode and hydroxyl removal by hydroxide precipitation, whose extent is in turn affected by pH. Misra *et al.* [54] showed that the initial pH of 5 was gradually increased due to the formation of hydroxyl ions at the cathode, while a slight decrease was observed when working at an initial pH 9, due to the consumption of hydroxyl ions. Gao *et al.* [60] reported that the pH increased with increasing of current density and electrolysis time. This effect was attributed to the continuous production of hydroxyl ions at the cathode with the generation of  $Al^{3+}$  at the anode, in a molar ratio ( $Al^{3+}/OH^-$ ) of 3 or lower. On the other hand, when the initial pH was increased to 9–10, pH slightly decreased at the beginning, probably due to the consumption of hydroxyl ions as a consequence of the formation of  $Al(OH)_4^-$ , while it remained constant afterward, probably due to the buffer effect of  $Al(OH)_3/Al(OH)_4^-$  [60].

Contrasting experimental data can be explained by the fact that the effect of pH mostly depends on the different parameters of the ECF process as well as on differences of the medium chemistry (alkalinity and ionic composition), which are frequently not characterized thus preventing a deeper understanding of the underlying mechanisms.

#### 3.3.3. Salinity and chloride presence

The medium salinity affects the electrical conductivity of the microalgal suspension, as an increase in the salt content increases conductivity and may lead to a decreasing power demand in the ECF process. Also, salinity promotes the compression of the electrical double layer [19].

A special beneficial role is played by chloride ions. They were proved to be able to promote the breakdown of the alumina ( $Al_2O_3$ ) film, which usually reduces electron transfer through pitting corrosion [85]. Oxidation of chloride ions may lead to the formation of active chlorine species (e.g. hypochlorous acid, hypochlorite ion) on the electrodes surface and in the bulk solution. Chloride ions can be oxidized at the anode to form chlorine gas that may dissolve in the solution to form hypochlorite ions, which act as oxidant [86,87]. Moreover, if organic chemicals are present in the microalgae suspension, the generated

**Table 1**

Descriptive statistics for: (a) main ECF operating parameters and microalgae suspension characteristics and (b) process KPIs: minimum, maximum, median, first and third quartiles (Q1 and Q3). The number of data used for descriptive statistics estimation (# data) and the number of data recognized as outlier by the software (# outliers) are reported.

		Minimum	Q1	Median	Q3	Maximum	# data	# outliers
(a)	Applied current density (mA/cm <sup>2</sup> )	0.36	2.72	6.70	15.0	33.3	161	20
	Applied potential (V)	0.66	1.80	6.46	10.5	20.0	92	15
	Process time (min)	0.5	6.0	15.0	45.0	75.0	174	4
	Electrode distance (mm)	5	10	10	20	30	61	11
	pH (-)	6.0	7.0	7.2	8.0	9.2	63	9
	TSS (mg/L)	16	300	500	1000	1600	157	30
(b)	Er (%)	49	76	90	96	100	190	19
	sEEC for freshwater (kWh/kg)	0.09	1.05	2.18	5.40	10.47	36	3
	sEEC for marine (kWh/kg)	0.06	0.10	0.65	3.42	7.05	53	5
	sMD for iron (kg/kg)	0.007	0.085	0.394	1.157	1.611	18	1
	sMD for aluminum (kg/kg)	0.002	0.019	0.055	0.243	0.443	106	10

chlorine gas would react with them producing chlorine derivatives. These chlorinated organic compounds are harmful to health and many of them are carcinogens [61]. Chlorine gas from ECF was not considered to be hazardous to the general public or site personnel under open air conditions since ECF did not produce detectable levels of chlorine emissions [88]. However, the production of chlorinated by-products is to be considered carefully and would deserve an in-depth analysis.

Active chlorine species can be beneficial to the ECF process by favoring metal oxidation. Indeed, in the presence of chloride, the ratio of Al<sup>3+</sup> concentrations over the theoretical value (calculated from Faraday's law) can be up to 200% [85].

As a consequence, significant difference in ECF harvesting efficiency between fresh and marine algal species has been reported. Vandamme et al. [33] reported that the minimum sEEC for harvesting of the freshwater alga *Chlorella vulgaris* was 2.1 kWh/kg, while it reduced to 0.2 kWh/kg under salty conditions in case of the marine alga *Phaeodactylum tricornutum*. Similar conclusions were reported by Matos et al. [89] comparing the efficiencies and electric consumption of *Nannochloropsis* sp. and *Chlorella vulgaris*. By using carbon electrodes, ECF harvesting efficiency of *Chlorella sorokiniana* and *Scenedesmus obliquus* increased by increasing the NaCl concentration in the medium up to 6 g/L [32,39]. Similar results were achieved by Fayad et al. [50] on *Chlorella vulgaris* with sacrificial electrodes.

The external supplementation of NaCl to improve ECF efficiency should be properly considered for large-scale applications as it may imply some drawbacks. The addition of salts increases costs and poses some issues related to the return of the growth media to the culture, the disposal of saline waters, as well as the biological effect of NaCl, such as the reduced motility of flagellated microalgae [19].

Salinity plays also a role also in the bubble/cell adhesion. Under high ionic strength, gas bubbles were reported to be larger and with tendency to rupture more easily, suggesting that a lower flotation efficiency can be expected on marine species [53].

### 3.4. Literature data synthesis

Literature data synthesis was carried out in the attempt to summarize information by means of Minitab software (ver. 19.2020.1) based on data reported in Table A2. A total of 190 records were processed, limiting the assessment to research works testing iron or aluminum sacrificial electrodes, for which a relevant number of observations is available in literature. From available published information, the main ECF operating parameters were considered as well as process key performance indicators (KPIs). As for the KPIs, Er, sEEC, and sMD were analyzed. When not declared by the authors, those parameters were computed from the published original data. To this purpose, metal

**Table 2**

Descriptive statistics (Median [minimum–maximum]) for main ECF operating parameters (a) leading to optimal process KPIs (b). The number of data after data-set reduction for each group (freshwater and marine microalgae) is reported. The analysis for Fe was prevented by the limited data-set for freshwater microalgae (N/A = not available).

	Freshwater		Marine	
	Aluminum	Iron	Aluminum	Iron
(a) # data	20	3	18	9
Applied current density (mA/cm <sup>2</sup> )	1.15 [0.44–6.82]	N/A	2.46 [0.61–12.30]	2.05 [0.55–5.26]
Applied potential (V)	9.2 [1.2–20.0]	N/A	1.0 [0.7–5.3]	3.0 [1.8–10.0]
Process time (min)	9 [1–60]	N/A	8.5 [0.5–12]	6 [1–15]
(b) Er (%)	96 [45–99]	N/A	84 [47–95]	67.5 [55–98]
sEEC (kWh/kg)	1.07 [0.09–3.37]	N/A	0.12 [0.06–0.4]	0.34 [0.18–1.79]
sMD (kg/kg)	0.01 [0.002–0.24]	N/A	0.05 [0.02–0.08]	0.07 [0.06–0.19]

dissolution was quantified from the electrochemical process parameters via the Faraday's law. It is worth noticing that the data reported in the literature are often incomplete, making the estimation of KPIs inapplicable.

Descriptive statistics were determined to aggregate literature data for main ECF operating parameters (applied current density and potential, process time and distance between anode and cathode) and microalgae suspension characteristics (pH and TSS), as reported in Table 1. The software identified outliers (i.e. observations that are at least 1.5 times the interquartile range above the upper interquartile value or below the lower interquartile value) for various ECF operating parameters and microalgae suspension characteristics, which were excluded from estimation of descriptive statistics, as detailed in Table 1. Though outliers were automatically detected, they were associated with experimental setups or experimental conditions that were very much different from those applied in the majority of the trials, making them hardly comparable to the remaining data in the dataset.

Data processing evidenced that in most cases current density values from 0.36 to 33 mA/cm<sup>2</sup> were applied, with a median value of about 6.7 mA/cm<sup>2</sup>, while applied potential values varied from 0.66 to 20 V, with a median value of about 6.5 V. Process time was limited to 75 min, with a median duration of about 15 min. Maximum distance between electrodes was 30 mm, being about 10 mm the median value for this



operating parameter. The pH average value was 7.2, with quartile values indicating that most of tests were carried out over a limited pH range (7–8). Conversely, TSS concentration was widely dispersed from 16 to 1,600 mg/L. In general, ECF operating parameters and microalgae suspension characteristics varied within very large ranges spanning among 2–3 orders of magnitudes.

Considering KPIs, a significant fraction of literature works reported *Er* values higher than 75%, with a median of about 90%. Although these results indicate the promising nature of ECF, they must be considered in combination with other KPIs, in the view of assessing process sustainability. As for electric energy consumption, values of *sEEC* were differentiated between freshwater and marine microalgae, since descriptive statistics showed significantly different figures. *sEEC* varied in the ranges 0.09–10.0 kWh/kg and 0.06–7.0 kWh/kg for freshwater and marine microalgae, respectively. A different behavior emerged also for *sMD* depending on metal coagulant, so experimental data were processed separately. A relevant variability is evident also for the coagulant dosage, which in most cases had to be computed from data declared by authors by applying the Faraday's law (from 0.007 to 1.6 kg/kg and from 0.002 to 0.4 kg/kg, respectively for iron and aluminum), with median value much higher for iron than for aluminum, as shown in Table 1. However, it is worth mentioning that the number of data for iron dosage is small (18), as a consequence of the limited number of works in which experimental conditions are detailed, so that results from literature data analysis are questionable. Moreover, observed variabilities in energy consumption and metal dosage indicate that previous research works were mostly carried out for assessing process suitability, often applying completely unrealistic process conditions. So, it is clear that further research works aimed at promoting process application under applicable conditions are still needed, particularly with the aim of assessing influencing ECF operating parameters.

In the view of identifying some ranges for optimal ECF operating parameters, the database has been further cleaned up by two following steps: (i) records referring to extreme conditions for operating parameters and microalgae suspension characteristics (outliers as previously stated) were removed, (ii) data-set was reduced so as to maintain only records belonging to the top 50% results for *sEEC* and *sMD*, thus optimizing energy consumption and coagulant dosage. Descriptive statistics on ECF operating parameters for this selected data-set are summarized in Table 2, except for ECF process performed by iron electrodes on freshwater microalgae, for which the analysis was prevented by the limited number of data. Although these ranges remain quite large, they are still much narrower than the initial ranges.

Descriptive statistics in Table 2 provide an indication on optimal operating parameters, suggesting that highest performance for *sEEC* and *sMD* were obtained for values of applied current density and process time belonging to the lowest part of the range reported in literature for these operating conditions. In addition, the significant difference between freshwater and marine microalgae was confirmed for aluminum electrodes, with the marine microalgae characterized by lower values for applied potential at similar applied current density, possibly as a consequence of the higher medium conductivity. Such difference is responsible for lower energy consumption values. No indications could be identified for electrode distance, due to the lack of sufficiently informative data in literature. It is important to point out that ranges reported in Table 2 should be considered as a coarse reference for process design, while a detailed cost analysis should be carried out to assess process sustainability, as discussed later. Finally, since predictors for process efficiency based on microalgae suspension characteristics could not be identified from literature data, case-specific pilot-testing activities appear as a fundamental preliminary phase when approaching microalgae harvesting via the ECF process.

## 4. Metal contamination

### 4.1. Metal concentration in biomass and residual water

When using ECF, the aluminum concentration in algal biomass and processed water should be kept as low as possible due to its harmful effects to the human health and environment. Aluminum release depends on the current density and ECF time according to the Faraday's law. Aluminum content found in the literature for *Chlorella* spp. biomass ranged from 0.56 to 3.2% depending on the ECF parameters: for example 0.56% and 1.4% after 10 min ECF at 3.3 and 8.3 mA/cm<sup>2</sup>, respectively [8], 0.9±0.1% after 30 min of 6.7 mA/cm<sup>2</sup> at pH 4 [50]. Vandamme et al. [33] found that the aluminum content in algal biomass can approximately double in the case of prolonged ECF: in *Chlorella vulgaris*, treated at 1.5 and 3 mA/cm<sup>2</sup>, the content of 0.6% and 1.4% after 10 min rose to 1.4% and 3.2% after 30 min. Similar results were observed with the marine microalga *Phaeodactylum tricornutum*, where, at 0.6 and 1.5 mA/cm<sup>2</sup>, Al-content of 0.75% and 1.2% after 10 min rose to 1.2% and 2% after 30 min [33]. In *Desmodesmus subspicatus*, the aluminum content varied in the range 9.9–17.56 mg/g of biomass depending on different combinations of the current (1–3 A) and exposure time (10–20 min) [67].

In the liquid phase of *Chlorella vulgaris* culture, the same trend was observed at 1.5 and 3 mA/cm<sup>2</sup>: the aluminum content was 0.6 and 1.3 mg/L after 10 min, and 2.1 and 2.7 mg/L after 30 min [33]. In *P. tricornutum* liquid phase, the time-related difference was not as pronounced. Fayad et al. [50] found that aluminum content in the liquid phase was 1.2 mg/L after 30 min at 6.7 mA/cm<sup>2</sup> and pH 4. In Baierle et al. tests with *D. subspicatus*, the aluminum content in the liquid phase varied between 2.85 and 16.24 mg/L depending on the current and exposure time combinations [67].

Although rarely measured in ECF tests, the accumulation of iron was analyzed in the *D. subspicatus* biomass in Baierle et al. study [67]. The iron concentration (14–46 mg/g of biomass) in the biomass was found to be higher than with the aluminum electrodes (10–18 mg/g of biomass) at the same ECF conditions. In contrast, the content of iron in the liquid phase was lower: 0.15–4.9 mg/L for iron vs. 2.85–16.24 mg/L for aluminum [67].

Although some important studies have already been performed, it has to be noted that the available data are yet insufficient to properly address factors affecting the apportioning of metal released from the electrodes between the liquid and solid phase.

As pointed out by the calculation of the metal dosage according to the Faraday's law (*sMD*), a number of literature works have been conducted by applying unrealistically high metal dosages (as high as 1.61 and 0.443 kg of metal per kg of harvested biomass for Fe and Al, respectively, see Section 3.4) which would result in unacceptable process costs, metal contamination of the harvested biomass, and metal toxicity (see following Section 4.2). Therefore, in the ECF operation *sMD* should be maintained within reasonable values since effective separation can be achieved with *sMD* < 0.096 kgFe/kg and < 0.131 kgAl/kg for freshwater algae, and *sMD* < 0.063 kgFe/kg and < 0.052 kgAl/kg for marine microalgae (as discussed in Section 3.4).

### 4.2. Metal toxicity

Metal content in the aggregated algal biomass and remaining liquid can potentially cause health and environmental problems.

Aluminum and iron are already naturally present in the soil and can become toxic at higher concentrations, especially in the acidic environment. If improperly used, the ECF-obtained algal biomass and residual liquid for the soil fertilization and irrigation could thus result in

the toxic effects. Aluminum is widely recognized as one of the most important limiting factors to crop production in the soils with a pH below 5.5 [90]. The aluminum in soil reduces the crop growth and root cell expansion, thus reducing the water and nutrient uptake [90-92]. It also irreversibly binds with phosphorus in the soil or in cells, making it unavailable for the plants growth and development [90]. This causes a huge problem in the phosphate-deprived and acidic soils. The most toxic forms are typically the monomeric and hydrolyzed forms [90]. Toxicity of aluminum in the soil is strongly related to the soil parameters and crop sensitivity, so generalization of the limiting concentration is not easily assessable. Aluminum concentration in the fertilizers is also not set by the new EC regulative for fertilizing products [93]. Limits exist for the irrigation water though, namely 5 mg/l for the long-term use and 20 mg/l for the short-term use [94]. Most of the remaining water from the ECF studies in Section 4.1 complies with the Food and Agricultural Organization (FAO) limits for the long-term irrigation and all for the short-term.

Iron is a microelement essential for the plant growth, but it is needed only in very low concentrations. Although iron deficiency is the usual concern in the crop production, iron can become toxic in the acidic environment as it reduces the availability of phosphorus and manganese. The maximum allowable limits of heavy metals in soils and vegetables have been established by the standard regulatory bodies such as World Health Organization (WHO) and FAO, indicating the limits for iron concentration in the irrigation water as 5 mg/l for the long-term use and 20 mg/l for the short-term use [94], although in some regulations can be even as low as 0.50 mg/L, 50 mg per gram of soil and 425 µg/g in vegetables [95]. Baierle *et al.* [67] reported that the iron content in final biomass and the broth was considered harmless to humans or animals, and indeed it didn't exceed the limit for irrigation set by FAO (2003), although the iron concentration in algal biomass is higher than the limitation for vegetables [95]. The iron in the broth may cause the formation of a brown-colored iron-algae slurry [53], making the valorization of algae problematic. The colored water also reduces light penetration and affects the microalgae photosynthetic activity, and consequently severely limits the use of iron electrodes if the remaining water is planned to be re-used for the algal cultivation [59].

Aluminum effects on the algae are difficult to generalize due to the various sensitivity. As in the crops, aluminum may bind with the phosphorus and reduce its availability also in water [90]. It can decrease the photosynthetic rates of algae [90] and probably induce the deficiency of magnesium, which is the central element of chlorophyll [91]. Aluminum concentrations as low as 52 µg/l can result in the total growth inhibition of microalgae (genus *Chlorella* and *Scenedesmus*) [96], so based on the Al-concentrations in the liquid phase after ECF [12,38,55], the remaining liquid could be reused for algal cultivation only if severely diluted.

For the aquatic animals, aluminum has been identified as a possible cause of reduced survivorship or impaired reproduction of the invertebrates, amphibians and fish, for example mucification and inflammation of the fish gill tissues which block the diffusion of O<sub>2</sub> and CO<sub>2</sub> through the gills [90]. Great care should thus be taken if the residual water is reused in the aquaculture [90]. Chronic harmful effects of the exposure to aluminum in the freshwater environment can be observed already at concentrations of 0.63–3,200 µg/L (depending on the water chemistry conditions [97]), indicating that the water remaining from ECF could not be used in undiluted form.

If ECF harvested algal biomass is utilized for the animal feed, care should be taken as metals can accumulate in the animal tissues. Concentrations of aluminum in the plant tissues are also of concern because of the plant based diets of many farm animals [90]. The principal effects

of aluminum on mammals include the reduced food intake, decreased weight gain in the young animals or weight loss in the adults, depressed serum magnesium and phosphorus, and increased aluminum concentrations in some tissues. In humans, the elevated aluminum body content has been correlated with serious health conditions like the Alzheimer's disease, encephalopathy, renal osteodystrophy, Parkinson's disease and other nerve and brain disorders [50,67]. The FAO limiting values for the provisional tolerable weekly intake were set to 2 mg/kg body weight for all aluminum compounds in food, including additives, and the provisional maximum tolerable daily intake of 0.8 mg/kg body weight for iron [98]. This means only few grams of ECF harvested algae could be eaten per week.

Vandamme *et al.* [33] states that the maximum limit of aluminum content should be < 1% in the biomass and 2 mg/L in the remaining water. According to his proposal, this has already been achieved in several ECF studies with the high microalgae recovery efficiency [8,33,50,67].

## 5. Costs of ECF

The objective of this section is to provide some general assessment of ECF costs and compare them to reference technology such as conventional flocculation and DAF process.

Since no direct comparison among parallel real installations treating similar algal suspensions is available, cost information has been deduced based on the previously discussed literature data. Costs disclosed in published papers are not easy to compare since the assumptions used in the evaluations are often lacking, and consumptions of electric energy and of metals are case-specific. In addition to this, the cost comparison is affected by the level of integration, location, branding margin, maturity of technology, place of manufacture, etc. The objective of this section is therefore limited to calculate the order-of-magnitude cost information to compare it with similar conventional processes, being aware that the published cost information of the conventional processes suffers from the same problems.

First, equipment complexity can be compared by considering the main components of each technology:

- DAF: flocculant preparation, pH adjustment (optional), flocculation mixer, DAF vessel, skimmer, compressor and air drum;
- ECF: pH adjustment (optional), mixer (optional, depending on the fluid-dynamics, mixer may be not required), ECF vessel, skimmer, electrodes and power supply.

The above list of basic components suggest that system complexity is quite similar for both technologies. Moreover, footprint and size are typically in favor of ECF [99]. This shows that there is no fundamental difference in the equipment cost; any commercial difference is caused by branding, market positioning, integration, technology transfer, fashion.

Therefore, operational costs (OPEX) more than construction costs are to be compared to evaluate the economic viability of ECF.

OPEX can be evaluated by adapting the approach suggested by Golzary *et al.* [34]. The applied model uses the specific electric and metal consumptions as follows:

$$OPEX = sEEC \times C_E + sMD \times C_m \quad (7)$$

where C<sub>E</sub> and C<sub>m</sub> are the unit price of electricity and metal, respectively.

To quantify the OPEX according to Eq. (7), *sEEC* and *sMD* values were retrieved from the median values reported in Table 2, separately computed for Fe and Al and for fresh and marine microalgae (with the

exception of Fe on freshwater for which not enough data were available). As for cost items, the following values were used:

- $C_E$ : 0.119 €/kWh weighted EU27 average using the most recent national data for the quantity of consumption by non-household consumers, with non-recoverable taxes and levies included but VAT excluded (Eurostat, 2019 [100]);
- $C_m$ : metal costs were assessed from EU market values, as 0.58 €/kg for iron (MEPS, 2020 [101]) and 1.55 €/kg for aluminum (Forbes, 2020 [102]). These values were multiplied by a factor 2.5 which considers more realistic retail costs. Note that these costs are higher than those recently assumed by Parmentier et al. [71] (0.079 €/kg for iron and 3.51 €/kg for aluminum).

According to the above-mentioned assumptions, the final OPEX values were:

- freshwater microalgae: 0.166 €/kg for aluminum.
- marine microalgae: 0.14 €/kg and 0.22 €/kg as for iron and aluminum, respectively.

According to Golzary et al. [34], CAPEX costs account for the 13% of the overall costs, and, by assuming a similar proportion of CAPEX over total costs, our estimates would finally result in 0.19 and 0.25 €/kg for marine and freshwater microalgae, respectively, using Al, and in 0.16 €/kg for marine microalgae using Fe. Although the *sEEC* is lower for marine than for freshwater microalgae, the larger metal dissolution (as *sMD* and corresponding metal cost) compensates for the energy saving, eventually leading to a slightly higher overall cost.

These values are comparable with those of other technologies used in microalgae primary concentration (from 0.18 to 0.48 AUD/m<sup>3</sup> [75]). It is worth noting that the values of *sEEC* and *sMD* refer to tests performed under very wide operational conditions. A significant reduction is expected from the optimization of the ECF process.

In conclusion, the above reported cost assessment shows that the order-of magnitude costs are comparable between processes, which means that proper optimization in best-fit applications can potentially render ECF harvesting as the most cost-effective process.

## 6. Comparison with conventional coagulation/flocculation

Compared with conventional coagulation/flocculation processes, ECF allows many advantages: (i) no anions such as sulfate and chloride, which are always coupled with traditional coagulants, are introduced in the microalgal biomass; (ii) a lower dosage of coagulant is required; (iii) pH adjustment is unnecessary since ECF performs well at broad pH range [11,15,103]; (iv) alkalinity consumption by hydroxides formation is compensated by OH<sup>-</sup> ions generation at the cathode; (v) microbubbles are produced at the electrodes that contribute to the harvesting through flotation [60]. Moreover, the flocs produced in ECF have less water, are larger and more stable [34], thus reducing the volume of the harvested solids. In addition, economic advantages are also claimed, including relatively low investment, maintenance and operational costs. Furthermore, ease of automation and compact size of ECF system makes it adequate in small scale systems [37].

On the other hand, drawbacks have been recognized. The sacrificial anodes are dissolved as a result of oxidation and need to be periodically replaced and an impermeable oxide film may be formed on the cathode, leading to loss of efficiency. Electric costs are the major operational costs which make ECF more competitive in highly conductive suspensions,

although, in some cases pre-treatments (pH adjustment, equalization, ...) may be required [38].

A dated assessment was carried out by Aragón et al. [104], that compared the efficiency of coagulation/flocculation with aluminum sulfate [Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 18H<sub>2</sub>O] and ECF with aluminum electrodes for the harvesting of microalgae (80% *Scenedesmus acutus* and 20% *Chlorella vulgaris*) grown on wastewater. Their results showed that ECF was more effective than flocculation, due to a faster harvesting time, a lower probability of contamination of recovered microalgae with metallic hydroxides and a lower total cost.

More recently, Vandamme et al. [33] compared the dosage of aluminum through ECF with some data reported in the literature about conventional coagulation/flocculation. In their ECF experiments, the aluminum dosages for harvesting *Chlorella vulgaris* and *Phaeodactylum tricornutum* were 3.5 mg/L and 1.7 mg/L, respectively [33]. These data have been compared to the results achieved by flocculation with Al, where the corresponding aluminum dosages were 7.2–23 mg/L [25] and 120 mg/L [105]. It was concluded that ECF is more efficient in terms of aluminum consumption than coagulation/flocculation with alum.

Golzary et al. [34] observed that conventional coagulation/flocculation was highly sensitive to pH variations, so that if the pH of the medium was not in the narrow interval of 4.5–5, flocs would not form satisfactorily, and effective separation would not be achieved. Instead, ECF was less sensitive to pH changes and had a good performance in the natural pH of algae medium, with no need of pH adjustment. They showed that in coagulation, the cost of coagulant was around 1.5 USD/m<sup>3</sup>, without considering the cost of providing alkalinity. On the other hand, the operational costs of ECF were estimated in 0.024 USD/m<sup>3</sup>, with no need of alkalinity supplementation due to water hydrolysis [34].

Lately, Guldhe et al. [52] reported that ECF of *A. falcatus* achieved a higher *Er* compared to conventional coagulation/flocculation with chitosan and alum. In detail, 91% separation was achieved by ECF in 30 min instead of 55% and 86% obtained respectively by chitosan and alum over 60 min process time. It is worth noting that alum could hamper the downstream processing of biomass for extraction and conversion of lipid and could also deteriorate the quality of harvested biomass, while chitosan flocculation is reported to be pH dependent and needs a pH adjustment. In terms of recovery efficiency and process time, centrifugation was found to be the best harvesting method. In the same work, ECF was compared with centrifugation. Although similar recovery efficiencies were obtained, the energy consumption for centrifugation was 65.3 kWh/kg, while ECF consumed 1.8 kWh/kg [52].

## 7. Electro-dewatering of microalgae

In the view of a two-step approach for microalgae dewatering, filtration and centrifugation are usually considered as the best options to follow the ECF process. Conventional dewatering technologies can hardly get dry matter contents higher than 15–30% [75,106]. An emerging alternative consists in the application of an electric field for the dewatering of the recovered microalgae paste, which still contains a considerable amount of water. Electro-dewatering (EDW) is a recent technology that allows increasing the water removal efficiency with respect to the conventional dewatering devices. It is based on the application of an electric field, which favors the migration of the negatively charged particles towards the anode by electrophoresis, while water is transported through the suspension towards the cathode by electro-osmosis, where it can be easily removed [107,108].

In typical EDW tests, the applied voltages are in the range of few volts to several tens of volts [108]. Similarly to ECF, electrochemical reactions

are produced at the anode and the cathode, as those reported before (water electrolysis as in Eqs. (1) and (2), and metal dissolution as in Table A1).

Differently from ECF, the oxidation of the anode is an undesired side-effect since it reduces the process efficiency and increases the operating costs [108]. Raats et al. [109], Saveyn et al. [110] and Zhang et al. [111] reported that the corrosion of the anode can be suppressed by using titanium coated with mixed metal oxides plates or meshes, such as Ir<sub>2</sub>O<sub>3</sub>-coated titanium.

So far, electro-dewatering has been mainly investigated on sludge [112-115] and soil [116-118] and it has been demonstrated that high dewatering efficiencies can be achieved, depending on the suspension characteristics and the operating conditions. As for sludge, EDW may be considered also as an alternative to thermal drying due to its lower energy consumption. In fact, literature reported that EDW process can decrease the energy consumption up to 25% to achieve a sludge dryness up to 60% [107,113,119].

Though this is a new technology in the field of microalgae, lately, Cao et al. [120] studied the influence of operating conditions, namely voltage, ionic strength and mechanical pressure, on the electro-dewatering performance of *Microcystis aeruginosa* and on extracellular organic matter (EOM) regionalization. They found that the efficiency of electro-dewatering increased with voltage and ionic strength, but decreased when ionic strength was >0.006 gNaCl/gTSS. Moreover, the content of dissolved organic matter in the filtrate increased with voltage and ionic strength, suggesting that a large amount of EOM was dissolved during EDW [120].

In order to be economically sustainable, electro-dewatering should be preceded by pressure dewatering [107] since the application of the electric field at the beginning of the process does not show any beneficial effect to the water removal. This may be related to the fact that flocculated particles are too large to be transported by electrophoresis [108] and high electrical conductivity of the suspension increases the electrical energy consumption with no significant effect on the final dry matter.

In summary, electro-dewatering may be coupled to ECF as a second step for dewatering, in place of conventional centrifugation and filtration, but also as a further step, to increase the dry matter content at lower energy consumptions than thermal drying processes.

## 8. Summary and further research needs

Although available literature supports the interest towards the application of ECF to microalgae harvesting, conflicting data are reported about the optimal values of the operational parameters to adopt as well as about how relevant factors affect the process efficiency. Indeed, by considering the whole data-set of published experimental trials, process parameters (current density, potential, process time, electrode distance, pH, TSS) varied within a quite large range (up to two orders of magnitude). Nonetheless, by considering only those experiments performed under efficient operational conditions in terms of specific electric consumption and specific metal dosage, this range could be narrowed, as reported in Table 2. KPIs values were distinguished according to the anode metal (Al and Fe) and to the microalgae (marine or freshwater). Al was found to be more efficient than Fe as for all KPIs (*Er*, *sEEC*, *sMD*). Moreover, for Al anodes, *sEEC* was found to be one order of magnitude lower when ECF is applied to marine microalgae since the applied voltage required to maintain the current density is significantly lower. Insufficient data were available to confirm this

finding for Fe anodes. A preliminary cost analysis shows that ECF costs (ranging from 0.16 to 0.25 € per kg of separated biomass) are comparable with those of other technologies used in microalgae primary concentration.

For a more effective comparison among literature data, the use of unified parameters when describing experimental activities would greatly help, facilitating data interpretation. We suggest to provide the following data:

- To assess process performance: biomass recovery efficiency (separated microalgal biomass/total microalgal biomass), dry matter in the recovered algal paste (gDM/100 g), metal content in the recovered algal paste (gMe/kgDM), specific energy consumption (kWh/kgDM), specific metal consumption (gMe/kgDM).
- To address operational conditions: set-up geometry (especially electrode area and electrode distance), type of electrodes (material, shape), electric energy application (AC, DC, fixed voltage/current, current density applied A/cm<sup>2</sup>, voltage/current values, power consumption), metal dissolution compared to Faraday efficiency, fluid velocity and its gradient.
- To assess parameters affecting the ECF process: initial and final pH, alkalinity, main ionic profile and conductivity, temperature, zeta potential of the algal biomass suspension, isoelectric point of the algal biomass.
- To assess the microalgae type: strain when available, culturing medium, marine/freshwater, shape and motility.
- Other information that could be relevant such as: residual metal in the liquid phase, preservation of relevant algal biomass characteristics (e.g. vitality, pigments or lipid content), comparison with other coagulation alternatives.

A comprehensive design of experiment that takes into consideration the above listed parameters of interest would allow drawing more robust conclusions on optimal operational intervals, reporting them as a function of the algae suspension characteristics and expected final valorization of the algal biomass.

There are still many research areas to be explored and future work to be done before we can claim maturity of the technology. We can name but a few that deserve addressing:

- Deepen the understanding of ECF with Mg electrodes (non-toxic) and MgAl alloys;
- Design of continuous ECF reactors: hydrodynamic issues, zones with higher fluid velocity (e.g. over electrodes) and zones of lower fluid velocity (e.g. for flotation);
- Electrode cleaning issue by developing optimized reactor geometries, as well optimized frequencies/modalities of the cleaning procedures;
- Process modelling, including flotation process modelling (multi-phase CFD);
- Process control/feedback mechanisms to optimize performance and minimize metal use/release into biomass and/or water, excessive foaming;
- Explore the use of hybrid systems: sacrificial and non-sacrificial electrodes, augmentation with chemical flocculants/polymers, augmentation with dissolved air, sedimentation and flotation (flocculation and flotation are essentially independent processes and there is no guarantee that they are both running at optimal rate by

just ECF, one of the augmentations may improve the process that is suboptimal);

- Explore the use of micro ECF chambers where flow is mostly laminar emphasizing the electrophoretic effects);
- Reduce the overall costs by studying the re-use of the evolved gasses;
- Integrated ultrasonic that may help in electrode cleaning and contribute to smaller bubble size;

Upon process optimization, ECF may become an effective alternative in microalgae harvesting, with reduced process costs and improved quality of the harvested algal biomass.

## Funding

This work has received funding from:

Fondazione Cariplo: projects Polo delle Microalghie and Wast4bio-plast (2018-0992).

## CRediT authorship contribution statement

**Simone Visigalli:** Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data curation, Writing, original draft, Visualization, Supervision, Project administration. **Maria Giulia Barberis:** Investigation, Resources, Data curation, Writing, original draft. **Andrea Turolla:** Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data curation, Writing, original draft,

Visualization, Supervision, Project administration. **Roberto Canziani:** Investigation, Resources, Writing, review & editing. **Maja Berden Zrimec:** Investigation, Resources, Data curation, Writing, original draft. **Robert Reinhardt:** Conceptualization, Methodology, Formal analysis, Investigation, Resources, Writing, original draft, Visualization, Supervision, Project administration. **Elena Ficara:** Conceptualization, Methodology, Formal analysis, Investigation, Resources, Writing, original draft, Visualization, Supervision, Project administration, Funding acquisition.

## 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.

## Acknowledgements

Authors sincerely thank Mr. Michael Greco for his help.

We thank Prof. Luigi Falciola for his valuable suggestions and proof-reading.

## Appendix

See Fig. A1 and Tables A1 and A2.

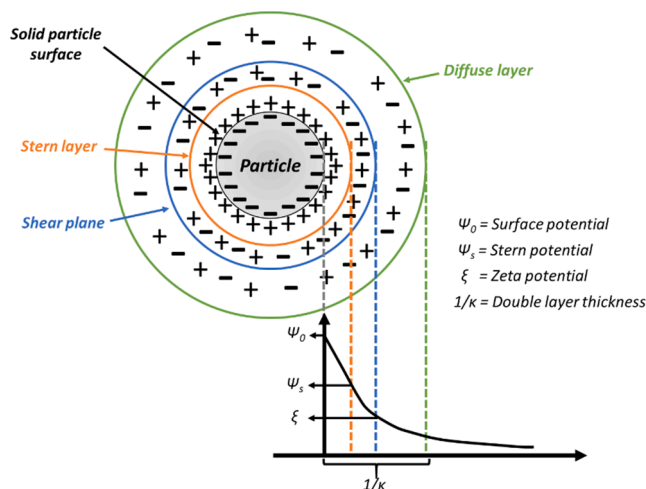


Fig. A1. Structure of the electric double layer, with the corresponding potential distribution with distance from the particle wall.

Table A1

Chemical equilibria at Fe and Al anodes.

Couple	Chemical reaction	Algebraic equation (concentrations in M, E in V)
$\text{Fe}^{2+}/\text{Fe}^{3+}$	$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	$E = 0.77$
$\text{Fe}^{2+}/\text{Fe}$	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	$E = -0.45 + 0.030\log[\text{Fe}^{2+}]$
$\text{FeO(OH)}/\text{Fe}^{2+}$	$\text{FeO(OH)} + \text{e}^- + 3\text{H}^+ \rightarrow \text{Fe}^{2+} + 1\text{HOH}$	$E = 1.00 - 0.177\text{pH} - 0.059\log[\text{Fe}^{2+}]$
$\text{FeO(OH)}/\text{Fe(OH)}_2$	$\text{FeO(OH)} + \text{e}^- + \text{H}^+ \rightarrow \text{Fe(OH)}_2$	$E = 0.30 - 0.059\text{pH}$
$\text{Fe(OH)}_2/\text{Fe}$	$\text{Fe(OH)}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{Fe} + 2\text{HOH}$	$E = -0.10 - 0.059\text{pH}$
$\text{FeO(OH)}/\text{Fe}^{3+}$	$\text{FeO(OH)} + 3\text{H}^+ \rightarrow \text{Fe}^{3+} + 2\text{HOH}$	$3\text{pH} = 3.9 - \log[\text{Fe}^{3+}]$
$\text{Al}^{3+}/\text{Al}$	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	$E = -1.68 + 0.020\log[\text{Al}^{3+}]$
$\text{Al(OH)}_3/\text{Al}$	$\text{Al(OH)}_3 + 3\text{e}^- + 3\text{H}^+ \rightarrow \text{Al} + 3\text{HOH}$	$E = -1.47 - 0.059\text{pH}$
$\text{Al(OH)}_4^-/\text{Al}$	$\text{Al(OH)}_4^- + 3\text{e}^- + 4\text{H}^+ \rightarrow \text{Al} + 4\text{HOH}$	$E = -1.23 - 0.079\text{pH} + 0.020\log[\text{Al(OH)}_4^-]$
$\text{Al(OH)}_3/\text{Al}^{3+}$	$\text{Al(OH)}_3 + 3\text{H}^+ \rightarrow \text{Al}^{3+} + 3\text{HOH}$	$3\text{pH} = 10.2 - \log[\text{Al}^{3+}]$
$\text{Al(OH)}_4^-/\text{Al(OH)}_3$	$\text{Al(OH)}_4^- + \text{H}^+ \rightarrow \text{Al(OH)}_3 + \text{HOH}$	$\text{pH} = 12.4 + \log[\text{Al(OH)}_4^-]$

**Table A2**  
Comparison among results of EC, EF and ECF tests performed on microalgae reported in literature.

Microalgae	Test conditions	Electrodes	Recovery efficiency	Electric energy consumption	Main results	Ref.
Coelosphaerium sp. Aphanizomenon sp. Closterium sp. Pediastrum sp. Cryptomonas sp. Staurastrum sp. Asterionella sp. Cyclotella sp. Melosira sp.	<b>REACTOR:</b> Batch ECF <b>CV MODE:</b> 18-85 V (0.9-4 A) <b>ECF TIME:</b> 0-75 min <b>A/C DISTANCE:</b> 185-265 mm	<b>ANODE:</b> Al (2-4) <b>CATHODE:</b> Pb (4-8)	<b>4 anodes, 8 cathodes</b> <b>DISTANCE: 185 mm</b> • 95.5% (t=35 min, 85 V) • 88.7% (t=35 min, 52 V) • 81.1% (t=35 min, 38 V) • 52.2% (t=45 min, 18 V) <b>3 anodes, 6 cathodes</b> <b>DISTANCE: 265 mm</b> • 97.4% (t=45 min, 85 V) • 97.4% (t=45 min, 57 V) • 96.3% (t=75 min, 26.5 V) <b>2 anodes, 4 cathodes</b> <b>DISTANCE: 265 mm</b> • 94.9% (t=45 min, 85 V) • 95.9% (t=45 min, 57 V) • 85.8% (t=75 min, 26.5 V)	<b>4 anodes, 8 cathodes</b> <b>DISTANCE: 185 mm</b> • 1.983 kWh/m <sup>3</sup> • 0.919 kWh/m <sup>3</sup> • 0.443 kWh/m <sup>3</sup> • 0.135 kWh/m <sup>3</sup> <b>4 anodes, 8 cathodes</b> <b>DISTANCE: 185 mm</b> • 1.913 kWh/m <sup>3</sup> • 0.855 kWh/m <sup>3</sup> • 0.331 kWh/m <sup>3</sup> <b>4 anodes, 8 cathodes</b> <b>DISTANCE: 185 mm</b> • 1.721 kWh/m <sup>3</sup> • 0.770 kWh/m <sup>3</sup> • 0.289 kWh/m <sup>3</sup>	<ul style="list-style-type: none"> <li>Decreasing voltage leads to a slower recovery but consumes less energy</li> <li>Decreasing the total surface area of the electrodes (by using less cathodes and anodes) and increasing the A/C distance leads to lower energy consumption</li> <li>Fouling of the cathodes causes a decrease in the current intensity of 5-10%</li> <li>ECF is less expensive than other separation processes</li> </ul>	(Poesman et al., 1997)
Microcystis aeruginosa	<b>REACTOR:</b> Batch ECF <b>CC MODE:</b> 0.5-5 mA/cm <sup>2</sup> <b>ECF TIME:</b> 15-75 min <b>A/C DISTANCE:</b> 10 mm <b>MIXING:</b> 200 rpm <b>pH:</b> 7-10 <b>T:</b> 18-36 °C	<b>ANODE:</b> Fe <b>CATHODE:</b> Fe  <b>ANODE:</b> Al <b>CATHODE:</b> Al	<b>1 mA/cm<sup>2</sup></b> • 78.9% at pH = 7  <b>1 mA/cm<sup>2</sup></b> • 87.2% at pH=10 • 90.0% at pH=9 • 99.0% at pH=8 • 100.0% at pH=7  <b>1 mA/cm<sup>2</sup>, pH=7, 15 min</b> • 46% at T = 18 °C • 86% at T = 27 °C • 98% at T = 36 °C	• 0.2 kWh/m <sup>3</sup> (pH=7, i=0.5 mA/cm <sup>2</sup> ) • 2.3 kWh/m <sup>3</sup> (pH=7, i=5 mA/cm <sup>2</sup> )  <b>1 mA/cm<sup>2</sup>, pH=7, 15 min</b> • 0.36 kWh/m <sup>3</sup> (18 °C) • 0.24 kWh/m <sup>3</sup> (27 °C) • 0.16 kWh/m <sup>3</sup> (36 °C)	<ul style="list-style-type: none"> <li>Current density affects recovery efficiency</li> <li>Al more efficient than Fe</li> <li>Acidic pH improves recovery efficiency due to charge neutralization</li> <li>T favors recovery efficiency</li> </ul>	(Gao et al., 2010b)
Microcystis aeruginosa	<b>REACTOR:</b> Batch ECF <b>CC MODE:</b> 0.5-5 mA/cm <sup>2</sup> <b>ECF TIME:</b> 45-75 min <b>A/C DISTANCE:</b> 10 mm <b>MIXING:</b> 200 rpm <b>[Cl<sup>-</sup>]:</b> 0-8 mM	<b>ANODE:</b> Al <b>CATHODE:</b> Al	<b>2 mA/cm<sup>2</sup>, pH=7, 60 min</b> • 80.3% [Cl <sup>-</sup> ]=0 mM • 94.5% [Cl <sup>-</sup> ]=1 mM • 99.5% [Cl <sup>-</sup> ]=3 mM • 100% [Cl <sup>-</sup> ]=5 mM  • 90.0% [Cl <sup>-</sup> ]= 8 mM		<ul style="list-style-type: none"> <li>Recovery efficiency increases with [Cl<sup>-</sup>] (higher conductivity, reduction of anode passivation, pitting corrosion)</li> </ul>	(Gao et al., 2010a)
Botryococcus braunii	<b>REACTOR:</b> Batch ECF + AIR DIFFUSER <b>CV MODE:</b> 15-60 V <b>ECF TIME:</b> 0-30 min <b>A/C DISTANCE:</b> 100 mm <b>AIR FLOW RT:</b> 0-60 mL/min <b>pH:</b> 7-12	<b>ANODE:</b> Al <b>CATHODE:</b> Al	<b>60 V, t=30 min</b> • 93.6% at 0 mL/min <b>60 V, t<sub>0AF</sub>=12 min</b> • 95.4% at 15 mL/min <b>60 V, t<sub>0AF</sub>=10 min</b> • 98.6% at 30 mL/min <b>60 V, t<sub>0AF</sub>=8 min</b> • 93.6% at 60 mL/min		<ul style="list-style-type: none"> <li>Increasing the voltage improves recovery efficiency and shortens ECF time</li> <li>The floc size of microalgae is bigger and it increases quicker by integrating dispersed air flotation to ECF</li> <li>The maximum recovery efficiency in the integrated process is lower due to the high shear stress and turbulence</li> <li>The recovery time decreases increasing the pH from 7 to 11</li> <li>The recovery efficiency decreases at a pH=12 because of algal lysis</li> </ul>	(Xu et al., 2010)
Chlorella sp.	<b>REACTOR:</b> Continuous ECF <b>CC MODE:</b> 0.5-1.0-1.5-2.0 A <b>ECF TIME:</b> 60 min <b>A/C DISTANCE:</b> 5 mm <b>FLOW RATE:</b> 1-5 mL/s	<b>ANODE:</b> Al <b>CATHODE:</b> Al	• 80% (I=1 A, t=5 min) • 100% (I=1 A, t=20 min)  • 22% (I=0.5 A, t=120 min) • 50% (I=1.0 A, t=120 min) • 67% (I=1.5 A, t=120 min) • 77% (I=2.0 A, t=120 min)		<ul style="list-style-type: none"> <li>Harvesting rate of the mixture of Cyanobacteria and Chlorella is slower, and a higher current is required to maximize recovery</li> <li>ECF leaves residual metals in the concentrated microalgae</li> </ul>	(Pearshall et al., 2011)
Chlorococcus sp. (saline)	<b>REACTOR:</b> Batch ECF <b>CV MODE:</b> 3-10 V <b>ECF TIME:</b> 3-15 min <b>A/C DISTANCE:</b> 5 mm <b>pH:</b> 4-9	<b>ANODE:</b> Stainless steel <b>CATHODE:</b> Stainless steel	<b>10 V, t=15 min</b> • 98% <b>10 V, t=15 min</b> • 99% <b>10 V, t=15 min</b> • 95.2% at pH=4 • 95.3% at pH=5	<b>3-5-10 V, t=3-15 min</b> • 0.12-9.16 kWh/kg <b>3-5-10 V, t=3-15 min</b> • 0.15-4.44 kWh/kg	<ul style="list-style-type: none"> <li>ZP = -8.7 mV / -10.5 mV</li> <li>T favours recovery efficiency (higher conductivity)</li> <li>Salinity favours recovery efficiency (higher conductivity)</li> </ul>	(Uduman et al., 2011)

(continued on next page)

Table A2 (continued)

			<ul style="list-style-type: none"> <li>95.6% at pH=7</li> <li>96.2% at pH=8.3</li> <li>94.8% at pH=9</li> </ul>		<ul style="list-style-type: none"> <li>No difference between pH 4 and 9</li> </ul>	
<i>Chlorella vulgaris</i> (freshwater)	<b>REACTOR:</b> Batch ECF <b>CC MODE:</b> 1.5–12 mA/cm <sup>2</sup>	<b>ANODE:</b> Al, Fe <b>CATHODE:</b> DSA (TiO <sub>2</sub> /TiO <sub>2</sub> )	<b>Al, 3 mA/cm<sup>2</sup>, pH = 8</b> <ul style="list-style-type: none"> <li>16–92%</li> </ul>	<b>Al, 1.5–12 mA/cm<sup>2</sup>, pH=8</b> <ul style="list-style-type: none"> <li>1.3 – 34.3 kWh/kg</li> </ul>	<ul style="list-style-type: none"> <li>Al more efficient than Fe</li> <li>Recovery efficiency increases by reducing the initial pH</li> <li>Stirring improves ECF efficiency</li> <li>0.5–2 mg/L of Al remains in solution</li> </ul>	[Vandamme et al., 2011]
<i>Phaeodactylum tricornutum</i> (marine)	0.6–3 mA/cm <sup>2</sup> <b>ECF TIME:</b> 10–30 min <b>SETTLING TIME:</b> 0–30 min <b>MIXING:</b> 0–200 rpm		<b>Al, 3 mA/cm<sup>2</sup>, pH=8</b> <ul style="list-style-type: none"> <li>36–78%</li> </ul>	<b>Al, 0.6–3 mA/cm<sup>2</sup>, pH=8</b> <ul style="list-style-type: none"> <li>0.2 – 1.7 kWh/kg</li> </ul>		
<i>Nannochloris oculata</i>	<b>REACTOR:</b> Continuous ECF <b>CC MODE:</b> 0.25 A <b>POLARITY EXCHANGE</b> <b>ECF TIME:</b> 2.5–20 min <b>A/C DISTANCE:</b> 10 mm <b>MIXING:</b> 150 rpm <b>FLOW RATE:</b> 10 mL/min <b>pH:</b> 8.3	<b>POLARITY EXCHANGE</b> <b>ANODE:</b> Al <b>CATHODE:</b> DSA (Ti/RbO <sub>2</sub> )	<b>t=15 min</b> <ul style="list-style-type: none"> <li>99%</li> </ul>	<b>t=15 min</b> <ul style="list-style-type: none"> <li>1.23 kWh/kg</li> </ul>	<ul style="list-style-type: none"> <li>No significant difference in the efficiency with Al–Pt and Al–DSA</li> <li>Al–Pt consumes an average of 0.06 kWh/kg less than Al–DSA</li> <li>Polarity exchange in ECF is a cost-competitive technology</li> <li>No significant difference in total residual Al for Al–Pt and Al–DSA electrodes</li> <li>Cell viability decreases with ECF time (accumulation of Al and/or reactive chlorine species)</li> <li>Al–DSA has a dehydrogenase activity 8% higher than Al–Pt</li> <li>Microalgal cells can live longer and healthier with Al–DSA</li> <li>Increasing duration of P2 has no negative effect on flotation</li> </ul>	[Kim et al., 2012]
		<b>POLARITY EXCHANGE</b> <b>ANODE:</b> Al <b>CATHODE:</b> Pt	<b>t=5 min</b> <ul style="list-style-type: none"> <li>95.6% (P1:P2=1.0:1.5)</li> </ul>	<b>t=5 min</b> <ul style="list-style-type: none"> <li>0.68 kWh/kg (P1:P2=1.0:1.5)</li> </ul>		
			<b>t=10 min</b> <ul style="list-style-type: none"> <li>95.9% (P1:P2=1.0:1.0)</li> <li>99.9% (P1:P2=1.0:1.2)</li> </ul>	<b>t=10 min</b> <ul style="list-style-type: none"> <li>0.98 kWh/kg (P1:P2=1.0:1.0)</li> <li>1.01 kWh/kg (P1:P2=1.0:1.2)</li> </ul>		
			<b>t=15 min</b> <ul style="list-style-type: none"> <li>99.9% (P1:P2=1.0:1.5)</li> </ul>	<b>t=15 min</b> <ul style="list-style-type: none"> <li>1.23 kWh/kg (P1:P2=1.0:1.5)</li> </ul>		
			<b>t=15 min</b> <ul style="list-style-type: none"> <li>99%</li> </ul>	<b>t=15 min</b> <ul style="list-style-type: none"> <li>1.19 kWh/kg</li> </ul>		
					<ul style="list-style-type: none"> <li>Performance of ECF is substantially enhanced by increasing the duration of P2</li> </ul>	
<i>Tetraselmis</i> sp.	<b>REACTOR:</b> Batch EC <b>CV MODE:</b> 10 V (5 A) <b>ECF TIME:</b> 0.5–1 min <b>MIXING TIME:</b> 15 min <b>SETTLING TIME:</b> 30 min <b>MIXING:</b> 191 rpm <b>pH:</b> 8.4	<b>ANODE:</b> Al <b>CATHODE:</b> Al	<b>Supernatant after settling</b> <ul style="list-style-type: none"> <li>85% (5.0 V, t=60 s)</li> </ul> <b>From raceway pond</b> <ul style="list-style-type: none"> <li>95% (5.2 V, t=60 s)</li> </ul> <b>From raceway pond</b> <ul style="list-style-type: none"> <li>92% (5.3 V, t=30 s)</li> </ul>	<b>Supernatant after settling</b> <ul style="list-style-type: none"> <li>0.173 kWh/m<sup>3</sup> (t=60 s)</li> </ul> <b>From raceway pond</b> <ul style="list-style-type: none"> <li>0.181 kWh/m<sup>3</sup> (t=60 s)</li> </ul> <b>From raceway pond</b> <ul style="list-style-type: none"> <li>0.091 kWh/m<sup>3</sup> (t=30 s)</li> </ul>	<ul style="list-style-type: none"> <li>EC integrated with EF needs less time to achieve a higher concentration with respect to EC integrated with mixing and settling (smaller footprint area)</li> <li>EC integrated with EF consumes 1.7 times more energy than by using ECF integrated with mixing + settling</li> <li>ECF may be an economical harvesting technique</li> </ul>	[Lee et al., 2013]
	<b>REACTOR:</b> Batch ECF <b>CC MODE:</b> 10 mA/cm <sup>2</sup> <b>ECF TIME:</b> 2.8–9.2 min <b>A/C DISTANCE:</b> 50–300 mm <b>pH:</b> 8.4		<ul style="list-style-type: none"> <li>87% (150 mm)</li> </ul>	<ul style="list-style-type: none"> <li>0.155 kWh/m<sup>3</sup> (150 mm)</li> </ul>		
<i>Nannochloropsis</i> sp.	<b>REACTOR:</b> Batch ECF <b>CC MODE:</b> 0.8–16.7 mA/cm <sup>2</sup> <b>ECF TIME:</b> 1–15 min <b>SETTLING TIME:</b> 30 min – 24 h <b>A/C DISTANCE:</b> 10 mm <b>MIXING:</b> 150 rpm	<b>ANODE:</b> Al <b>CATHODE:</b> Al	<b>8.3 mA/cm<sup>2</sup>, t<sub>settle</sub>=30 min</b> <ul style="list-style-type: none"> <li>97% t=10 min</li> </ul> <b>3.3 mA/cm<sup>2</sup>, t<sub>settle</sub>=30 min</b> <ul style="list-style-type: none"> <li>91.8% - 30 cm<sup>2</sup>/L</li> <li>93.7% - 60 cm<sup>2</sup>/L</li> <li>97.4% - 90 cm<sup>2</sup>/L</li> <li>98.5% - 120 cm<sup>2</sup>/L</li> <li>98.9% - 180 cm<sup>2</sup>/L</li> </ul>	<ul style="list-style-type: none"> <li>&gt; 0.06 kWh/m<sup>3</sup> (RE&gt;95%)</li> </ul>	<ul style="list-style-type: none"> <li>Current density and EC duration affect recovery efficiency</li> <li>8.2 mA/cm<sup>2</sup> for 10 min is the optimal condition</li> <li>Recovery efficiency increases with the electrode area</li> <li>Recovery efficiency decreases when TSS is too high (3.9 g/L)</li> <li>No significant change in the oil content and composition</li> <li>Slight decrease of total pigment amount after ECF</li> </ul>	[Mafios et al., 2013a]

(continued on next page)

Table A2 (continued)

					<ul style="list-style-type: none"> <li>EC before centrifugation decreases drastically the harvesting energy demand</li> </ul>	
<i>Nannochloropsis</i> sp.	<p>REACTOR: Batch ECF CC MODE: 3.3-33.3 mA/cm<sup>2</sup> ECF TIME: 5-50 min SETTLING TIME: 30 min – 24 h A/C DISTANCE: 10 mm MIXING: 150 rpm</p>	<p>ANODE: Al CATHODE: Al</p>	<p><b>3.3 mA/cm<sup>2</sup>, t=10 min</b>  <ul style="list-style-type: none"> <li>70.9% - t<sub>settle</sub>=30 min</li> <li>98.4% - t<sub>settle</sub>=24 h</li> </ul> <b>8.33 mA/cm<sup>2</sup>, t=5 min</b>  <ul style="list-style-type: none"> <li>77.4% - t<sub>settle</sub>=30 min</li> <li>96.7% - t<sub>settle</sub>=24 h</li> </ul> <b>8.33 mA/cm<sup>2</sup>, t=10 min</b>  <ul style="list-style-type: none"> <li>93.1% - t<sub>settle</sub>=30 min</li> <li>99.7% - t<sub>settle</sub>=24 h</li> </ul> <b>8.33 mA/cm<sup>2</sup>, t=15 min</b>  <ul style="list-style-type: none"> <li>97.2% - t<sub>settle</sub>=30 min</li> <li>99.9% - t<sub>settle</sub>=24 h</li> </ul> <b>16.67 mA/cm<sup>2</sup>, t=10 min</b>  <ul style="list-style-type: none"> <li>97.5% - t<sub>settle</sub>=30 min</li> <li>99.2% - t<sub>settle</sub>=24 h</li> </ul> </p>	<ul style="list-style-type: none"> <li>0.03 kWh/m<sup>3</sup> (RE=80%)</li> </ul>	<ul style="list-style-type: none"> <li>More energy is required to achieve recovery efficiencies of <i>Chlorella vulgaris</i> similar to those achieved for <i>Nannochloropsis</i> sp. (lower conductivity)</li> </ul>	(Matos et al., 2013b)
<i>Chlorella vulgaris</i>			<p><b>8.33 mA/cm<sup>2</sup>, t=15 min</b>  <ul style="list-style-type: none"> <li>52.8% - t<sub>settle</sub>=30 min</li> <li>87.6% - t<sub>settle</sub>=24 h</li> </ul> <b>8.33 mA/cm<sup>2</sup>, t=20 min</b>  <ul style="list-style-type: none"> <li>65.2% - t<sub>settle</sub>=30 min</li> <li>85.6% - t<sub>settle</sub>=24 h</li> </ul> <b>8.33 mA/cm<sup>2</sup>, t=30 min</b>  <ul style="list-style-type: none"> <li>78.1% - t<sub>settle</sub>=30 min</li> <li>90.9% - t<sub>settle</sub>=24 h</li> </ul> <b>8.33 mA/cm<sup>2</sup>, t=50 min</b>  <ul style="list-style-type: none"> <li>81.5% - t<sub>settle</sub>=30 min</li> <li>91.8% - t<sub>settle</sub>=24 h</li> </ul> <b>16.67 mA/cm<sup>2</sup>, t=30 min</b>  <ul style="list-style-type: none"> <li>87.3% - t<sub>settle</sub>=30 min</li> <li>94.7% - t<sub>settle</sub>=24 h</li> </ul> <b>33.33 mA/cm<sup>2</sup>, t=30 min</b>  <ul style="list-style-type: none"> <li>88.7% - t<sub>settle</sub>=30 min</li> <li>94.9% - t<sub>settle</sub>=24 h</li> </ul> </p>	<ul style="list-style-type: none"> <li>1.00 kWh/m<sup>3</sup> (RE=80%)</li> </ul>		
<i>Nannochloris</i> sp.	<p>REACTOR: Batch ECF CC MODE: 0.05–1.0 A ECF TIME: 1-2 min SETTLING TIME: 30 min A/C DISTANCE: 13 mm [NaCl]: 1-2-4-14 g/L</p>	<p>Monopolar-parallel 4 electrodes: ANODE: Fe (2) CATHODE: Fe (2)</p>	<p><b>0.2 A, t=1 min</b>  <ul style="list-style-type: none"> <li>55%</li> </ul> <b>0.1 A, t=2 min</b>  <ul style="list-style-type: none"> <li>55%</li> </ul> </p>	<p>t=1 min  <ul style="list-style-type: none"> <li>&lt;0.010 kWh/m<sup>3</sup></li> </ul> t=2 min  <ul style="list-style-type: none"> <li>&lt;0.010 kWh/m<sup>3</sup></li> </ul> </p>	<ul style="list-style-type: none"> <li>Addition of NaCl reduces the energy consumption</li> <li>Al is more efficient at harvesting</li> <li>Fe has better conductivity than Al and consumes less energy</li> </ul>	(Dosev and Theegala, 2014)
<i>Chlorella sorokiniana</i>	<p>REACTOR: Batch ECF CC MODE: 0.5–1.0–1.5 A ECF TIME: 60 min A/C DISTANCE: 30 mm [NaCl]: 2-6 g/L</p>	<p>3 electrodes: ANODE: C (2) CATHODE: C (1)</p>	<p>t=60 min  <ul style="list-style-type: none"> <li>59.6% at I=0.5 A</li> <li>66.0% at I=1.0 A</li> <li>79.2% at I=1.5 A</li> </ul> <b>I = 1 A</b>  <ul style="list-style-type: none"> <li>68.4% [NaCl]=2 g/L</li> <li>92.3% [NaCl]=4 g/L</li> <li>94.5% [NaCl]=6 g/L</li> </ul> </p>	<p>t=60 min  <ul style="list-style-type: none"> <li>1.8 kWh/kg at I=0.5 A</li> <li>4.0 kWh/kg at I=1.0 A</li> <li>6.0 kWh/kg at I=1.5 A</li> </ul> <b>I = 1 A</b>  <ul style="list-style-type: none"> <li>2.7 kWh/kg [NaCl]=2 g/L</li> <li>1.7 kWh/kg [NaCl]=4 g/L</li> <li>1.6 kWh/kg [NaCl]=6 g/L</li> </ul> </p>	<ul style="list-style-type: none"> <li>Current density and EC duration affect recovery efficiency</li> <li>Variation in microalgal cell size and culture density affects recovery efficiency</li> <li>Addition of NaCl (0-6 g/L) increases recovery efficiency</li> <li>ECF is a cost competitive technology</li> <li>No change in biomass composition</li> </ul>	(Mira et al., 2014)
<i>Scenedesmus obliquus</i>			<p>t=60 min  <ul style="list-style-type: none"> <li>49.2% at I=0.5 A</li> <li>52.4% at I=1.0 A</li> <li>57.1% at I=1.5 A</li> </ul> </p>	<p>t=60 min  <ul style="list-style-type: none"> <li>7.5 kWh/kg at I=0.5 A</li> <li>19.6 kWh/kg at I=1.0 A</li> <li>33.0 kWh/kg at I=1.5 A</li> </ul> </p>		
<i>Dunaliella salina</i>	<p>REACTOR: Batch EC CC MODE: 0.3-1 A ECF TIME: 5-20 min A/C DISTANCE: 10-20-30 mm MIXING: 0-400 rpm</p>	<p>ANODE: Fe CATHODE: Fe</p>	<p><b>200 rpm, 10 mm, 5 min</b>  <ul style="list-style-type: none"> <li>33% at I=0.3 A</li> <li>75% at I=1.0 A</li> </ul> <b>200 rpm, 10 mm, 20 min</b>  <ul style="list-style-type: none"> <li>70% at I=0.3 A</li> <li>86% at I=1.0 A</li> </ul> </p>		<ul style="list-style-type: none"> <li>Al more efficient than Fe</li> <li>Current density and EC duration affect recovery efficiency</li> <li>A higher distance between the electrodes causes an increase in the electrical resistance</li> <li>Stirring speed improves the ECF process up to values of 200 rpm, but higher speeds make the recovery</li> </ul>	(Maleki et al., 2014)
		<p>ANODE: Al CATHODE: Al</p>	<p><b>200 rpm, 10 mm, 5 min</b>  <ul style="list-style-type: none"> <li>55% at I=0.3 A</li> <li>86% at I=1.0 A</li> </ul> <b>200 rpm, 10 mm, 20 min</b>  <ul style="list-style-type: none"> <li>91% at I=0.3 A</li> <li>97% at I=1.0 A</li> </ul> </p>			

(continued on next page)



Table A2 (continued)

			<ul style="list-style-type: none"> <li>• <b>I=0.3 A, 200 rpm, 20 min</b></li> <li>• 89% with 20 mm</li> <li>• 79% with 30 mm</li> <li>• <b>I=1.0 A, 200 rpm, 20 min</b></li> <li>• 95% with 20 mm</li> <li>• 85% with 30 mm</li> <li>• <b>I=0.3 A, 10 mm, 5 min</b></li> <li>• 49% at 0 rpm</li> <li>• 55% at 200 rpm</li> <li>• 52% at 400 rpm</li> <li>• <b>I=1.0 A, 10 mm, 20 min</b></li> <li>• 91% at 0 rpm</li> <li>• 97% at 200 rpm</li> <li>• 94% at 400 rpm</li> </ul>		<ul style="list-style-type: none"> <li>• efficiency to decrease (breakage of the flocs)</li> </ul>	
Desmodemus suspicatus	<p>REACTOR: Batch EC  <b>CC MODE:</b> 1-2-3 A                      (1.9-3.7-5.6 mA/cm<sup>2</sup>)  <b>ECF TIME:</b> 10-15-20-30 min  <b>A/C DISTANCE:</b> 2 mm</p>	<p>SPIRAL  <b>ANODE:</b> Al  <b>CATHODE:</b> Al</p>	<ul style="list-style-type: none"> <li>• <b>I=5.6 mA/cm<sup>2</sup></b></li> <li>• 95.4% t=20 min</li> </ul>		<ul style="list-style-type: none"> <li>• Current density and EC duration affect biomass yield</li> <li>• Al more efficient than Fe</li> <li>• pH and conductivity variations were similar between tests for both Al and Fe</li> <li>• ECF with Al results in a lower turbidity of the suspension with respect to Fe</li> <li>• Concentration of Fe in the final effluent is lower than that of Al</li> </ul>	(Boerle et al., 2015)
Chlorella sp. (marine)	<p>REACTOR: Batch ECF  <b>CC MODE:</b> 6.6-23.4 mA/cm<sup>2</sup>  <b>ECF TIME:</b> 2.6-14.4 min  <b>SETTLING TIME:</b> 30 min  <b>A/C DISTANCE:</b> 10 mm</p>	<p>Monopolar-parallel                      4 electrodes:  <b>ANODE:</b> Al (2)  <b>CATHODE:</b> Al (2)</p>	<ul style="list-style-type: none"> <li>• 46.7 – 95.0%</li> </ul>	<ul style="list-style-type: none"> <li>• 0.02 – 0.13 kWh/m<sup>3</sup></li> </ul>	<ul style="list-style-type: none"> <li>• Costs of 0.04 – 0.26 US\$/m<sup>3</sup></li> <li>• Current density and EC duration affect recovery efficiency</li> <li>• Initial pH has a smaller effect on recovery efficiency</li> </ul>	(Goltzav et al., 2015)
Scenedesmus obliquus	<p>REACTOR: Batch ECF  <b>CC MODE:</b> 0.5-1.0-1.5 A  <b>ECF TIME:</b> 60 min  <b>A/C DISTANCE:</b> 30 mm  <b>[NaCl]:</b> 2-6 g/L  <b>pH:</b> 5-7-9</p>	<p>3 electrodes:  <b>ANODE:</b> C (2)  <b>CATHODE:</b> C (1)</p>	<p><b>t=30 min, pH=9</b></p> <ul style="list-style-type: none"> <li>• 41.2% at I=0.5 A</li> <li>• 50.8% at I=1.0 A</li> <li>• 55.4% at I=1.5 A</li> </ul> <p><b>t=60 min, pH=9</b></p> <ul style="list-style-type: none"> <li>• 54.2% at I=0.5 A</li> <li>• 61.7% at I=1.0 A</li> <li>• 65.7% at I=1.5 A</li> </ul>	<p><b>t=60 min, pH=9</b></p> <ul style="list-style-type: none"> <li>• 2.1 kWh/kg at I=0.5 A</li> <li>• 5.4 kWh/kg at I=1.0 A</li> <li>• 8.9 kWh/kg at I=1.5 A</li> </ul>	<ul style="list-style-type: none"> <li>• Current density and EC duration affect recovery efficiency</li> <li>• Addition of NaCl (0-6 g/L) increases recovery efficiency and decreases energy consumption</li> <li>• At acidic pH positively charged ions are formed and recovery efficiency increases</li> <li>• ECF has no adverse effect on lipid extraction and it's improved by electrolyte addition</li> </ul>	(Mira et al., 2015)
Scenedesmus sp. (24%) Kirchneriella sp. (1%) Microcystis sp. (75%)	<p>REACTOR: Batch ECF (3 reactors)  <b>CV MODE:</b> 10-15-20 V  <b>ECF TIME:</b> 1-3 min  <b>SETTLING TIME:</b> 0-24 h  <b>A/C DISTANCE:</b> 5.5-7-11 mm  <b>HEIGHT:</b> 2.7-4-5.2-6.4 cm</p>	<p><b>ANODE:</b> Fe  <b>CATHODE:</b> Fe</p>	<p><b>10 V, t=1 min, H=4 cm</b></p> <ul style="list-style-type: none"> <li>• 95.6% at A/C=5.5 cm</li> <li>• 93.0% at A/C=7 cm</li> <li>• 92.5% at A/C=11 cm</li> </ul> <p><b>10 V, t=1 min, A/C=5.5 cm</b></p> <ul style="list-style-type: none"> <li>• 94.6% at H=2.7 cm</li> <li>• 92.1% at H=5.2 cm</li> <li>• 92.0% at H=6.4 cm</li> </ul> <p><b>t=1 min, H=4 cm, A/C=5.5 cm</b></p> <ul style="list-style-type: none"> <li>• 95.6% at 10 V</li> <li>• 94.6% at 15 V</li> <li>• 94.4% at 20 V</li> </ul> <p><b>10 V, H=4 cm, A/C=5.5 cm</b></p> <ul style="list-style-type: none"> <li>• 95.6% t=1 min</li> <li>• 94.6% t=2 min</li> </ul>		<ul style="list-style-type: none"> <li>• The highest recovery efficiency (95%) occurs with a smaller electrode separation (5.5 cm)</li> <li>• The highest recovery efficiency corresponds to the lower height of the culture (2.7 cm)</li> <li>• ECF time is shortened significantly when the voltage is increased</li> <li>• ECF durations of 1 and 3 min shows a 0.007% difference in recovery efficiency</li> </ul>	(Valerio et al., 2015)

(continued on next page)

Table A2 (continued)

			<ul style="list-style-type: none"> <li>94.4% t=3 min</li> </ul>			
Ankistrodesmus falcatus	<b>REACTOR:</b> Batch ECF <b>CC MODE:</b> 0.5–1.0–1.5 A <b>ECF TIME:</b> 30–45 min <b>A/C DISTANCE:</b> 30 mm	3 electrodes: <b>ANODE:</b> C (2) <b>CATHODE:</b> C (1)	<b>t=30 min</b> <ul style="list-style-type: none"> <li>69.7% at I=0.5 A</li> <li>91.3% at I=1.0 A</li> <li>91.7% at I=1.5 A</li> </ul> <b>t=45 min</b> <ul style="list-style-type: none"> <li>82.9% at I=0.5 A</li> <li>91.6% at I=1.0 A</li> <li>92.2% at I=1.5 A</li> </ul>	<b>t=30 min</b> <ul style="list-style-type: none"> <li>0.84 kWh/kg at I=0.5 A</li> <li>1.76 kWh/kg at I=1.0 A</li> <li>3.62 kWh/kg at I=1.5 A</li> </ul>	<ul style="list-style-type: none"> <li>Lower particles size enhances flotation</li> <li>Comparison with centrifugation and chemical coagulation with alum and chitosan</li> <li>No change in biomass composition</li> </ul>	(Gulthe et al., 2016)
Scenedesmus obliquus			<b>t=30 min</b> <ul style="list-style-type: none"> <li>67.7% at I=1.0 A</li> </ul>			
Nannochloropsis sp.	<b>REACTOR:</b> Continuous ECF (on saltwater) <b>CV MODE:</b> 4–20 V <b>SETTLING TIME:</b> 30–120 min <b>A/C DISTANCE:</b> 6.35 mm <b>FLOW RATE (saltwater):</b> 0.4–3.9 L/min	<b>ANODE:</b> Ni <b>CATHODE:</b> Ni  <b>ANODE:</b> Al <b>CATHODE:</b> Al  <b>ELECTRODE LENGTH:</b> 12.7–30.5 cm	<b>0.4 L/min</b> <ul style="list-style-type: none"> <li>90% at 7 V</li> <li>1.3 L/min</li> <li>90% at 13 V</li> </ul> <b>0.4 L/min</b> <ul style="list-style-type: none"> <li>90% at 7 V</li> <li>1.3 L/min</li> <li>90% at 17 V</li> </ul> <b>12.7 cm, 0.4 L/min, t<sub>seth</sub>=2 h</b> <ul style="list-style-type: none"> <li>31% at 4 V</li> <li>70% at 6 V</li> </ul> <b>30.5 cm, 0.4 L/min, t<sub>seth</sub>=2 h</b> <ul style="list-style-type: none"> <li>41% at 4 V</li> <li>47% at 6 V</li> </ul> <b>12.7 cm, 1.7 L/min, t<sub>seth</sub>=2 h</b> <ul style="list-style-type: none"> <li>52% at 12 V</li> </ul> <b>30.5 cm, 1.7 L/min, t<sub>seth</sub>=2 h</b> <ul style="list-style-type: none"> <li>21% at 6 V</li> <li>47% at 12 V</li> </ul> <b>6 V, 3.9 L/min, t<sub>seth</sub>=2 h</b>	<ul style="list-style-type: none"> <li>0.08–7 kWh/m<sup>3</sup></li> <li>0.08–7 kWh/m<sup>3</sup></li> <li>12.7 cm, 0.4 L/min, t<sub>seth</sub>=2 h</li> <li>0.7 kWh/m<sup>3</sup> at 4 V</li> <li>2.0 kWh/m<sup>3</sup> at 6 V</li> <li>30.5 cm, 0.4 L/min, t<sub>seth</sub>=2 h</li> <li>0.4 kWh/m<sup>3</sup> at 4 V</li> <li>3.0 kWh/m<sup>3</sup> at 6 V</li> <li>12.7 cm, 1.7 L/min, t<sub>seth</sub>=2 h</li> <li>2.5 kWh/m<sup>3</sup> at 12 V</li> <li>30.5 cm, 1.7 L/min, t<sub>seth</sub>=2 h</li> <li>0.7 kWh/m<sup>3</sup> at 6 V</li> <li>3.6 kWh/m<sup>3</sup> at 12 V</li> <li>6 V, 3.9 L/min, t<sub>seth</sub>=2 h</li> </ul>	<ul style="list-style-type: none"> <li>Higher voltages allow higher recovery efficiencies</li> <li>ECF efficiency rapidly increases in the first 30 min after treated saltwater is mixed with algae suspension</li> <li>Recovery efficiency with Ni reaches 80% only at low flow rate (0.4 L/min)</li> <li>Increasing the flow rate does not necessarily process more biomass</li> <li>Ni is more efficient than Al</li> <li>Recovery efficiency of longer electrodes is higher immediately after ECF, but after 2 h is lower than for shorter electrodes</li> <li>Increased input voltage and slower flow rate reduce algal cell viability</li> <li>After ECF, Al and Ni contents significantly</li> </ul>	(Shuman et al., 2016)
			<ul style="list-style-type: none"> <li>30% - 12.7 cm</li> <li>23% - 30.5 cm</li> </ul>	<ul style="list-style-type: none"> <li>0.1 kWh/m<sup>3</sup> - 12.7 cm</li> <li>0.3 kWh/m<sup>3</sup> - 30.5 cm</li> </ul>	<ul style="list-style-type: none"> <li>increase in both the supernatant and the biomass</li> </ul>	
Chlorella vulgaris	<b>REACTOR:</b> Batch ECF <b>CC MODE:</b> 5–50 mA/cm <sup>2</sup> <b>SETTLING TIME:</b> 30 min <b>pH:</b> 9	<b>ANODE:</b> Al <b>CATHODE:</b> Al  <b>ANODE:</b> Fe <b>CATHODE:</b> Fe	<ul style="list-style-type: none"> <li>100%</li> <li>98%</li> </ul>	<ul style="list-style-type: none"> <li>&lt; 0.1 kWh/m<sup>3</sup></li> </ul>	<ul style="list-style-type: none"> <li>Higher current density allows shorter harvesting time</li> <li>Al more efficient than Fe</li> </ul>	(Souza et al., 2016)
Chlorella sp.	<b>REACTOR:</b> Batch ECF <b>CV MODE:</b> 3–3.5–4.5–6 V <b>A/C DISTANCE:</b> 1–2–5–10 mm <b>pH:</b> 6 <b>CHITOSAN DOSE:</b> 10 mg/L <b>MIXING:</b> 30 rpm (180 s)  <b>REACTOR:</b> Continuous ECF <b>CV MODE:</b> 4 V (5.9A) <b>A/C DISTANCE:</b> 1 mm <b>FLOW RATE:</b> 1000 L/h <b>pH:</b> 6 <b>CHITOSAN DOSE:</b> 15 mg/L <b>MIXING:</b> 30 rpm (180 s)	<b>ANODE:</b> graphite <b>CATHODE:</b> graphite	<b>A/C=1 mm</b> <ul style="list-style-type: none"> <li>&gt; 96% - V&gt;4 V, t=4 min</li> <li>90.2% - V&gt;3 V, t=16 min</li> </ul> <b>4 V</b> <ul style="list-style-type: none"> <li>95%-A/C=10 mm, t=25 min</li> <li>95%-A/C=5 mm, t=8 min</li> <li>95%-A/C=2 mm, t=5 min</li> <li>95%-A/C=1 mm, t=2 min</li> </ul>	<b>A/C=1 mm</b> <ul style="list-style-type: none"> <li>0.03 kWh/kg at 4 V</li> </ul> <b>4 V</b> <ul style="list-style-type: none"> <li>2.2 kWh/kg (4 V-A/C=10 mm)</li> <li>0.17 kWh/kg (4 V-A/C=1 mm)</li> </ul>	<ul style="list-style-type: none"> <li>Higher voltage improves the flotation and reduce the flotation time</li> <li>A reduction in the A/C distance reduces the harvesting time</li> <li>Without dosage of chitosan electroflotation is not efficient (recovery efficiency &lt; 5%)</li> </ul>	(Zhou et al., 2014)
Chlorella vulgaris	<b>REACTOR:</b> Batch ECF <b>CC MODE:</b> 2.9–6.7 mA/cm <sup>2</sup>	<b>ANODE:</b> Al <b>CATHODE:</b> Al	<b>6.7 mA/cm<sup>2</sup>, A/C=10 mm, pH=8</b> <ul style="list-style-type: none"> <li>96% 100 rpm</li> </ul>	<b>A/C=10 mm, pH=4, 250 rpm, t<sub>seth</sub>=45 min</b>	<ul style="list-style-type: none"> <li>Increasing stirring speed improves contact between</li> </ul>	(Fayad et al., 2017)

(continued on next page)

Table A2 (continued)

	<p><b>ECF TIME:</b> 60 min  <b>SETTLING TIME:</b> 0-45min  <b>A/C DISTANCE:</b> 10-15-20 mm  <b>MIXING:</b> 100-250-400 rpm  <b>pH:</b> 4-6-8  <b>[NaCl]:</b> 0.5-1.0-1.5 g/L</p>		<ul style="list-style-type: none"> <li>99% 250 rpm</li> <li>93% 400 rpm</li> <li><b>6.7 mA/cm<sup>2</sup>, A/C=10 mm, pH=8, 250 rpm,</b></li> <li>81% - <math>t_{settle}=0</math> min</li> <li>92% - <math>t_{settle}=15</math> min</li> <li>96% - <math>t_{settle}=30</math> min</li> <li>99% - <math>t_{settle}=45</math> min</li> <li><b>A/C=10 mm, pH=8, 250 rpm, <math>t_{settle}=45</math> min</b></li> <li>40% at <math>i=2.9</math> mA/cm<sup>2</sup></li> <li>72% at <math>i=2.9</math> mA/cm<sup>2</sup></li> <li>99% at <math>i=2.9</math> mA/cm<sup>2</sup></li> <li><b>A/C=10 mm pH=8, 250 rpm</b></li> <li>87% at pH=4 - <math>t=20</math> min</li> <li>45% at pH=6 - <math>t=20</math> min</li> <li>22% at pH=8 - <math>t=20</math> min</li> <li><b>6.7 mA/cm<sup>2</sup>, A/C=10 mm, pH=4, 250 rpm</b></li> <li>100% - A/C=10 mm</li> <li>95% - A/C=15 mm</li> <li>90% - A/C=20 mm</li> </ul>	<ul style="list-style-type: none"> <li>5.3 kWh/kg-2.9 mA/cm<sup>2</sup></li> <li>9.4 kWh/kg-6.7 mA/cm<sup>2</sup></li> <li><b>2.9 mA/cm<sup>2</sup>, pH=4, 250 rpm, <math>t_{settle}=45</math> min</b></li> <li>5.3 kWh/kg - A/C=10 mm</li> <li>8.1 kWh/kg - A/C=20 mm</li> <li><b>2.9 mA/cm<sup>2</sup>, A/C=10 mm, pH=4, 250 rpm</b></li> <li>2.8 kWh/kg [NaCl]=0.5 g/L</li> <li>1.7 kWh/kg [NaCl]=1.0 g/L</li> <li>1.0 kWh/kg [NaCl]=1.5 g/L</li> <li><b>4.8 mA/cm<sup>2</sup>, A/C=10 mm, pH=4, 250 rpm</b></li> <li>4.9 kWh/kg [NaCl]=0.5 g/L</li> <li>2.6 kWh/kg [NaCl]=1.0 g/L</li> <li>1.5 kWh/kg [NaCl]=1.5 g/L</li> <li><b>6.7 mA/cm<sup>2</sup>, A/C=10 mm, pH=4, 250 rpm</b></li> <li>5.7 kWh/kg [NaCl]=0.5 g/L</li> <li>2.9 kWh/kg [NaCl]=1.0 g/L</li> <li>1.6 kWh/kg [NaCl]=1.5 g/L</li> </ul>	<p>coagulants and microalgae and increases recovery efficiency but higher stirring speed causes break-up of flocs due to the high shear forces</p> <ul style="list-style-type: none"> <li>Al more efficient than Fe</li> <li>A longer settling time increases recovery efficiency</li> <li>Higher current densities allow higher recovery efficiencies</li> <li>Acidic pH increases recovery efficiency</li> <li>Initial pH changes the kinetics of microalgae recovery</li> <li>Zeta potential is more electronegative at higher pH values and increases with the proceeding of ECF</li> <li>A higher NaCl concentration allows a decrease in the energy consumption</li> <li>ECF has no significant effect on the lipid content</li> <li>ECF has no significant effect on the total pigment content</li> </ul>	
		<p><b>ANODE:</b> Fe  <b>CATHODE:</b> Fe</p>	<ul style="list-style-type: none"> <li>6.7 mA/cm<sup>2</sup>, pH=8, 250 rpm</li> <li>45% - <math>t_{settle}=0</math> min</li> <li>53% - <math>t_{settle}=15</math> min</li> </ul>			
			<ul style="list-style-type: none"> <li>59% - <math>t_{settle}=30</math> min</li> <li>64% - <math>t_{settle}=45</math> min</li> </ul>			
<i>Dunaliella salina</i>	<p><b>REACTOR:</b> Batch ECF  <b>CC MODE:</b> 0.02-0.1 A  <b>ECF TIME:</b> 0-35 min  <b>A/C DISTANCE:</b> 35 mm  <b>pH:</b> 7.4</p>	<p><b>ANODE:</b> Al  <b>CATHODE:</b> 43.8% MnO<sub>2</sub> + 38.7% C + 17.5% PTFE</p>	<ul style="list-style-type: none"> <li>97% at 0.02 A - <math>t=34</math> min</li> <li>97% at 0.05 A - <math>t=28</math> min</li> <li>97% at 0.06 A - <math>t=25</math> min</li> <li>97% at 0.10 A - <math>t=20</math> min</li> </ul>	<ul style="list-style-type: none"> <li>Energy is produced by discharging EF mode</li> </ul>	<ul style="list-style-type: none"> <li>Higher current densities reduce harvesting times</li> <li>The discharging electroflotation mode is a process of energy production (0.098-0.11 kWh/kg produced)</li> </ul>	[Liu et al., 2017]
<i>Chlorella vulgaris</i>	<p><b>REACTOR:</b> Batch ECF  <b>CC MODE:</b> 1-3 A  <b>ECF TIME:</b> 30-60 min  <b>A/C DISTANCE:</b> 3 mm</p>	<p><b>ANODE:</b>  <ul style="list-style-type: none"> <li>Stainless steel</li> <li>C</li> <li>C/Fe</li> </ul> <b>CATHODE:</b>                      Stainless steel</p>	<p><b>Stainless steel, <math>t=60</math> min</b>                      81.61% at <math>I=1</math> A  <b>Carbon, <math>t=60</math> min</b>                      52.21% at <math>I=3</math> A  <b>Carbon/Iron, <math>t=30</math> min</b>                      92.13% at <math>I=1</math> A</p>	<p><b>Stainless steel</b>                      4.4-4.9 kWh/kg at <math>I=1</math> A                      5.9-6.8 kWh/kg at <math>I=2</math> A                      7.8-8.9 kWh/kg at <math>I=3</math> A</p>	<ul style="list-style-type: none"> <li>Higher electric current allows shorter harvesting time</li> <li>Lower cathode's openings size allows shorter harvesting time (higher H<sub>2</sub> bubble nucleation rate and smaller size)</li> <li>Carbon anode less efficient than stainless steel anode</li> <li>Higher liquid depth increases the final concentration</li> </ul>	[Luo et al., 2017]
	<p><b>REACTOR:</b> Continuous ECF  <b>CC MODE:</b> 10 mA/cm<sup>2</sup>  <b>A/C DISTANCE:</b> 4.5 mm</p>	<p><b>ANODE:</b> C  <b>CATHODE:</b> Stainless steel</p>	<ul style="list-style-type: none"> <li>23.72 g/h</li> <li>255 g/(h·m<sup>2</sup>)</li> <li>Conc. factor: 52.78</li> </ul>	<ul style="list-style-type: none"> <li>2.73 kWh/kg</li> </ul>		
<i>Chlorella pyrenoidosa</i>	<p><b>REACTOR:</b> Batch ECF  <b>CV MODE:</b> 5 V (10 mA/cm<sup>2</sup>)  <b>ECF TIME:</b> 5 min  <b>A/C DISTANCE:</b> 30 mm</p>	<p>3 electrodes:  <b>ANODE:</b> Al (1)  <b>CATHODE:</b> Al (2)</p>	<ul style="list-style-type: none"> <li>95.8%</li> </ul>	<ul style="list-style-type: none"> <li>0.28 kWh/kg</li> </ul>	<ul style="list-style-type: none"> <li>ECF with Al achieves the highest recovery efficiency but cost is 30% higher than Fe</li> <li>Color change of the suspension, with the formation of insoluble metal hydroxides (Al: white-milky, Fe: brown, Cu: green-bleu, Zn: white)</li> <li>Weight loss and H<sub>2</sub> rate production increase with increasing current density and ECF time</li> </ul>	[Rahmani et al., 2017]
		<p>3 electrodes:  <b>ANODE:</b> C (1)  <b>CATHODE:</b> C (2)</p>	<ul style="list-style-type: none"> <li>79.2%</li> </ul>	<ul style="list-style-type: none"> <li>0.34 kWh/kg</li> </ul>		
		<p>3 electrodes:  <b>ANODE:</b> Cu (1)  <b>CATHODE:</b> Cu (2)</p>	<ul style="list-style-type: none"> <li>93.7%</li> </ul>	<ul style="list-style-type: none"> <li>0.32 kWh/kg</li> </ul>		
		<p>3 electrodes:  <b>ANODE:</b> Zn (1)  <b>CATHODE:</b> Zn (2)</p>	<ul style="list-style-type: none"> <li>83.3%</li> </ul>	<ul style="list-style-type: none"> <li>0.28 kWh/kg</li> </ul>		
		<p>3 electrodes:  <b>ANODE:</b> Fe (1)  <b>CATHODE:</b> Fe (2)</p>	<ul style="list-style-type: none"> <li>70.8%</li> </ul>	<ul style="list-style-type: none"> <li>0.37 kWh/kg</li> </ul>		

(continued on next page)

Table A2 (continued)

					<ul style="list-style-type: none"> <li>C hinders contamination of the suspension and avoid periodic electrode replacement</li> </ul>	
<i>Chlorella vulgaris</i>	<b>REACTOR:</b> Batch ECF <b>CC MODE:</b> 2.2-4.4-6.7 mA/cm <sup>2</sup> <b>ECF TIME:</b> 8 min <b>A/C DISTANCE:</b> 30 mm <b>MIXING:</b> 200 rpm <b>pH:</b> 8.6	<b>ANODE:</b> Al <b>CATHODE:</b> Al	<b>2.2 mA/cm<sup>2</sup></b> <ul style="list-style-type: none"> <li>98% - t=7 min</li> </ul> <b>4.4 mA/cm<sup>2</sup></b> <ul style="list-style-type: none"> <li>98% - t=6 min</li> </ul> <b>6.7 mA/cm<sup>2</sup></b> <ul style="list-style-type: none"> <li>98% - t=4 min</li> </ul>	<b>2.2 mA/cm<sup>2</sup></b> <ul style="list-style-type: none"> <li>0.087 kWh/kg</li> </ul> <b>4.4 mA/cm<sup>2</sup></b> <ul style="list-style-type: none"> <li>0.222 kWh/kg</li> </ul> <b>6.7 mA/cm<sup>2</sup></b> <ul style="list-style-type: none"> <li>0.294 kWh/kg</li> </ul>	<ul style="list-style-type: none"> <li>The higher current density, the shorter harvesting time</li> <li>No significant changes in the medium temperature and pH after ECF</li> <li>Phosphate decreases and ammonium increases after ECF</li> </ul>	[Shi et al., 2017]
<i>Scenedesmus obliquus</i>	<b>REACTOR:</b> Batch ECF <b>CC MODE:</b> 0.25-0.50-0.75 A <b>ECF TIME:</b> 20 min <b>MIXING:</b> 350 rpm	<b>ANODE:</b> Al <b>CATHODE:</b> DSA (IrO <sub>2</sub> /TiO <sub>2</sub> )	<b>Control (no seawater)</b> <ul style="list-style-type: none"> <li>60%</li> </ul>		<ul style="list-style-type: none"> <li>Higher the salinity, higher is the recovery efficiency: salinity may increase the production of EPS, which can lead to auto-flocculation</li> <li>Salinity reduces energy consumption</li> <li>Higher electric current allows higher recovery efficiency</li> </ul>	[Shin et al., 2017]
	<b>REACTOR:</b> Batch EF <b>CC MODE:</b> 0.25-0.50-0.75 A <b>ECF TIME:</b> 20 min <b>MIXING:</b> 350 rpm	<b>ANODE:</b> DSA (IrO <sub>2</sub> /TiO <sub>2</sub> ) <b>CATHODE:</b> DSA (IrO <sub>2</sub> /TiO <sub>2</sub> )	<b>Control (no seawater)</b> <ul style="list-style-type: none"> <li>90%</li> </ul> <b>S1 (10% seawater)</b> <ul style="list-style-type: none"> <li>95%</li> </ul> <b>S2 (20% seawater)</b> <ul style="list-style-type: none"> <li>95%</li> </ul> <b>S1-S2</b> <ul style="list-style-type: none"> <li>80% at 0.25 A</li> <li>95% at 0.50 A</li> <li>95% at 0.75 A</li> </ul>	<b>S1</b> <ul style="list-style-type: none"> <li>0.834 kWh/kg at 0.50 A</li> <li>1.516 kWh/kg at 0.75 A</li> </ul> <b>S2</b> <ul style="list-style-type: none"> <li>0.985 kWh/kg at 0.50 A</li> <li>1.736 kWh/kg at 0.75 A</li> </ul>		
<i>Chlorella vulgaris</i>	<b>REACTOR:</b> Batch ECF <b>CC MODE:</b> 1.5 A <b>ECF TIME:</b> 60 min <b>A/C DISTANCE:</b> 30 mm	<b>ANODE:</b> Fe <b>CATHODE:</b> Fe <b>ANODE:</b> C <b>CATHODE:</b> C	<ul style="list-style-type: none"> <li>0% - t=45 min</li> </ul>		<ul style="list-style-type: none"> <li>Al more efficient than Fe and C</li> <li>A higher NaCl concentration allows an</li> </ul>	[Wong et al., 2017]
	<b>MIXING:</b> 750 rpm <b>pH:</b> 4-5-6-7-8-9-10 <b>[NaCl]:</b> 0-2-4-6-8 g/L	<b>2 electrodes (AC)</b> <b>ANODE:</b> Al <b>CATHODE:</b> Al <b>3 electrodes (ACA)</b> <b>ANODE:</b> Al (2) <b>CATHODE:</b> Al (1) <b>3 electrodes (CAC)</b> <b>ANODE:</b> Al (1) <b>CATHODE:</b> Al (2) <b>4 electrodes (AACC)</b> <b>ANODE:</b> Al (2) <b>CATHODE:</b> Al (2)	<b>2 electrodes</b> <ul style="list-style-type: none"> <li>11.9% - t=60 min</li> </ul> <b>3 electrodes (CAC)</b> <ul style="list-style-type: none"> <li>14.7% - t=60 min</li> </ul> <b>[NaCl]=8 g/L</b> <ul style="list-style-type: none"> <li>18.55%</li> </ul> <b>pH=4</b> <ul style="list-style-type: none"> <li>23.8% - t=60 min</li> </ul> <b>Optimized conditions</b> <ul style="list-style-type: none"> <li>24.43%</li> </ul>		<ul style="list-style-type: none"> <li>increase in the recovery efficiency</li> <li>Recovery efficiency decreases with an increase of the initial pH</li> </ul>	
<i>Tetraselmis</i> sp.	<b>REACTOR:</b> Continuous <b>CV MODE:</b> 2 V (1 A)	<b>ANODE:</b> Al <b>CATHODE:</b> Al	<ul style="list-style-type: none"> <li>89.2% (2 V, 1 A)</li> </ul>	<ul style="list-style-type: none"> <li>0.250 kWh/m<sup>3</sup></li> <li>0.412 kWh/kg</li> </ul>	<ul style="list-style-type: none"> <li>ECF allows to reach a better quality and biocrude yield</li> </ul>	[Das et al., 2019]
<i>Chlorella vulgaris</i>	<b>REACTOR:</b> Continuous <b>CV MODE:</b> 1.1-1.3 V (0.3 A) <b>ECF TIME:</b> 0.88 min <b>A/C DISTANCE:</b> 6 mm	<b>ANODE:</b> Al <b>CATHODE:</b> Stainless steel	<ul style="list-style-type: none"> <li>72.4% (t=0.88 min, 1.2 V, 0.3 A)</li> </ul>	<ul style="list-style-type: none"> <li>0.242 kWh/m<sup>3</sup></li> <li>1.519 kWh/kg</li> </ul>	<ul style="list-style-type: none"> <li>Recycling the microalgae suspension two times for Fe electrodes and one time for Al electrodes allows a good microalgae removal and a reduction in the treatment time</li> </ul>	[Parmentier et al., 2020]
	<b>REACTOR:</b> Continuous <b>CV MODE:</b> 0.8 V (0.8 A) <b>ECF TIME:</b> 1.32 min <b>A/C DISTANCE:</b> 6 mm	<b>ANODE:</b> Fe <b>CATHODE:</b> Stainless steel	<ul style="list-style-type: none"> <li>87.8% (t=1.32 min, 0.8 V, 0.8 A)</li> </ul>	<ul style="list-style-type: none"> <li>0.440 kWh/m<sup>3</sup></li> <li>2.278 kWh/kg</li> </ul>		

## References

- [1] R.A. Andersen, M. Kawachi, Traditional Microalgae Isolation Techniques, in: *Algal Cult. Tech.*, Elsevier (2005) 83–100, <https://doi.org/10.1016/B978-012088426-1/50007-X>.
- [2] M.A. Borowitzka, N.R. Moheimani (Eds.), *Algae for Biofuels and Energy*, Springer, Netherlands, Dordrecht, 2013, <https://doi.org/10.1007/978-94-007-5479-9>.
- [3] M. Rizwan, G. Mujtaba, S.A. Memon, K. Lee, N. Rashid, Exploring the potential of microalgae for new biotechnology applications and beyond: A review, *Renew. Sustain. Energy Rev.* 92 (2018) 394–404, <https://doi.org/10.1016/j.rser.2018.04.034>.
- [4] A.C. Apel, C.E. Pfaffinger, N. Basedahl, N. Mittwollen, J. Göbel, J. Sauter, T. Brück, D. Weuster-Botz, Open thin-layer cascade reactors for saline microalgae production evaluated in a physically simulated Mediterranean summer climate, *Algal Res.* 25 (2017) 381–390, <https://doi.org/10.1016/j.algal.2017.06.004>.
- [5] J. Doucha, K. Lívanský, Outdoor open thin-layer microalgal photobioreactor: potential productivity, *J. Appl. Phycol.* 21 (2009) 111–117, <https://doi.org/10.1007/s10811-008-9336-2>.
- [6] F. Bumbak, S. Cook, V. Zachleder, S. Hauser, K. Kovar, Best practices in heterotrophic high-cell-density microalgal processes: achievements, potential and possible limitations, *Appl. Microbiol. Biotechnol.* 91 (2011) 31–46, <https://doi.org/10.1007/s00253-011-3311-6>.
- [7] N. Uduman, Y. Qi, M.K. Danquah, G.M. Forde, A. Hoadley, Dewatering of microalgal cultures: A major bottleneck to algae-based fuels, *J. Renew. Sustain. Energy.* 2 (2010), 012701, <https://doi.org/10.1063/1.3294480>.
- [8] C.T. Matos, M. Santos, B.P. Nobre, L. Gouveia, Nannochloropsis sp. biomass recovery by Electro-Coagulation for biodiesel and pigment production, *Bioresour. Technol.* 134 (2013) 219–226, <https://doi.org/10.1016/j.biortech.2013.02.034>.
- [9] M.R. Granados, F.G. Acien Fernández, C. Gómez, J.M. Fernández-Sevilla, E. Molina Grima, Evaluation of flocculants for the recovery of freshwater microalgae, *Bioresour. Technol.* 118 (2012) 102–110, <https://doi.org/10.1016/j.biortech.2012.05.018>.
- [10] D. Vandamme, I. Foubert, K. Muylaert, Flocculation as a low-cost method for harvesting microalgae for bulk biomass production, *Trends Biotechnol.* 31 (2013) 233–239, <https://doi.org/10.1016/j.tibtech.2012.12.005>.
- [11] F. Roselet, J. Burkert, P.C. Abreu, Flocculation of Nannochloropsis oculata using a tannin-based polymer: Bench scale optimization and pilot scale reproducibility, *Biomass and Bioenergy.* 87 (2016) 55–60, <https://doi.org/10.1016/j.biombioe.2016.02.015>.
- [12] G. Prochazkova, I. Safarik, T. Branyik, Harvesting microalgae with microwave synthesized magnetic microparticles, *Bioresour. Technol.* 130 (2013) 472–477, <https://doi.org/10.1016/j.biortech.2012.12.060>.
- [13] J.E. Coons, D.M. Kalb, T. Dale, B.L. Marrone, Getting to low-cost algal biofuels: A monograph on conventional and cutting-edge harvesting and extraction technologies, *Algal Res.* 6 (2014) 250–270, <https://doi.org/10.1016/j.algal.2014.08.005>.
- [14] A. Alam, D. Vandamme, W. Chun, X. Zhao, I. Foubert, Z. Wang, K. Muylaert, Z. Yuan, Bioflocculation as an innovative harvesting strategy for microalgae, *Rev. Environ. Sci. Biotechnol.* 15 (2016) 573–583, <https://doi.org/10.1007/s11157-016-9408-8>.
- [15] N. Deconinck, K. Muylaert, W. Ivens, D. Vandamme, Innovative harvesting processes for microalgae biomass production: A perspective from patent literature, *Algal Res.* 31 (2018) 469–477, <https://doi.org/10.1016/j.algal.2018.01.016>.
- [16] I.A. Matter, V.K. Hoang Bui, M. Jung, J.Y. Seo, Y.E. Kim, Y.C. Lee, Y.K. Oh, Flocculation harvesting techniques for microalgae: A review, *Appl. Sci.* 9 (2019), <https://doi.org/10.3390/app9153069>.
- [17] G. Singh, S.K. Patidar, Microalgae harvesting techniques: A review, *J. Environ. Manage.* 217 (2018) 499–508, <https://doi.org/10.1016/j.jenvman.2018.04.010>.
- [18] D. Ghernaout, Electrocoagulation Process for Microalgal Biotechnology-A Review, *Appl. Eng.* 3 (2019) 85–94, <https://doi.org/10.11648/j.ae.20190302.12>.
- [19] N. Uduman, V. Bourniquel, M.K. Danquah, A.F.A. Hoadley, A parametric study of electrocoagulation as a recovery process of marine microalgae for biodiesel production, *Chem. Eng. J.* 174 (2011) 249–257, <https://doi.org/10.1016/j.cej.2011.09.012>.
- [20] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC)-Science and applications, *J. Hazard. Mater.* 84 (2001) 29–41, [https://doi.org/10.1016/S0304-3894\(01\)00176-5](https://doi.org/10.1016/S0304-3894(01)00176-5).
- [21] M.Y.A. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals, present and future perspectives of electrocoagulation, *J. Hazard. Mater.* 114 (2004) 199–210, <https://doi.org/10.1016/j.jhazmat.2004.08.009>.
- [22] G. Chen, Electrochemical technologies in wastewater treatment, *Sep. Purif. Technol.* 38 (2004) 11–41, <https://doi.org/10.1016/j.seppur.2003.10.006>.
- [23] D.T. Moussa, M.H. El-Naas, M. Nasser, M.J. Al-Marri, A comprehensive review of electrocoagulation for water treatment: Potentials and challenges, *J. Environ. Manage.* 186 (2017) 24–41, <https://doi.org/10.1016/j.jenvman.2016.10.032>.
- [24] E. Molina Grima, E.H. Belarbi, F.G. Acien Fernández, A. Robles Medina, Y. Chisti, Recovery of microalgal biomass and metabolites: Process options and economics, *Biotechnol. Adv.* 20 (2003) 491–515, [https://doi.org/10.1016/S0734-9750\(02\)00050-2](https://doi.org/10.1016/S0734-9750(02)00050-2).
- [25] G. Shelief, A. Sukenik, M. Green, *Microalgae Harvesting and Processing: A Literature Review*, Springfield, VA, 1984. doi:http://dx.doi.org/10.2172/6204677.
- [26] C.M. Monteiro, P.M.L. Castro, F.X. Malcata, Metal uptake by microalgae: Underlying mechanisms and practical applications, *Biotechnol. Prog.* 28 (2012) 299–311, <https://doi.org/10.1002/btpr.1504>.
- [27] J. Sun, J. Cheng, Z. Yang, K. Li, J. Zhou, K. Cen, Microstructures and functional groups of Nannochloropsis sp. cells with arsenic adsorption and lipid accumulation, *Bioresour. Technol.* 194 (2015) 305–311. doi:10.1016/j.biortech.2015.07.041.
- [28] A. Ozkan, H. Berberoglu, Physico-chemical surface properties of microalgae, *Colloids Surfaces B Biointerfaces.* 112 (2013) 287–293, <https://doi.org/10.1016/j.colsurfb.2013.08.001>.
- [29] B.V. Derjaguin, L.D. Landau, Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes, *Acta Physicochim. URSS.* 14 (1941) 733–762.
- [30] E.J.W. Verwey, J.T.G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier Inc., Amsterdam, 1948.
- [31] C. Wan, M.A. Alam, X.Q. Zhao, X.Y. Zhang, S.L. Guo, S.H. Ho, J.S. Chang, F. W. Bai, Current progress and future prospect of microalgal biomass harvest using various flocculation technologies, *Bioresour. Technol.* 184 (2015) 251–257, <https://doi.org/10.1016/j.biortech.2014.11.081>.
- [32] P.K. Holt, G.W. Barton, M. Wark, C.A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, *Colloids Surfaces A Physicochem. Eng. Asp.* 211 (2002) 233–248, [https://doi.org/10.1016/S0927-7757\(02\)00285-6](https://doi.org/10.1016/S0927-7757(02)00285-6).
- [33] D. Vandamme, S.C.V. Pontes, K. Goiris, I. Foubert, L.J.J. Pinoy, K. Muylaert, Evaluation of electro-coagulation-flocculation for harvesting marine and freshwater microalgae, *Biotechnol. Bioeng.* 108 (2011) 2320–2329, <https://doi.org/10.1002/bit.23199>.
- [34] A. Golzary, S. Imanian, M.A. Abdoli, A. Khodadadi, A. Karbassi, A cost-effective strategy for marine microalgae separation by electro-coagulation-flotation process aimed at bio-crude oil production: Optimization and evaluation study, *Sep. Purif. Technol.* 147 (2015) 156–165. doi:10.1016/j.seppur.2015.04.011.
- [35] J.C. Crittenden, R.R. Trussell, D.W. Hand, K.J. Howe, G. Tchobanoglous, *MWH's Water Treatment: Principles and Design*, Third edit, John Wiley & Sons Inc, Hoboken, New Jersey, 2012.
- [36] J. Kim, B.G. Ryu, K. Kim, B.K. Kim, J.I. Han, J.W. Yang, Continuous microalgae recovery using electrolysis: Effect of different electrode pairs and timing of polarity exchange, *Bioresour. Technol.* 123 (2012) 164–170, <https://doi.org/10.1016/j.biortech.2012.08.010>.
- [37] V. Kuokkanen, T. Kuokkanen, J. Rämö, U. Lassi, Recent Applications of Electrocoagulation in Treatment of Water and Wastewater—A Review, *Green Sustain. Chem.* 03 (2013) 89–121, <https://doi.org/10.4236/gsc.2013.32013>.
- [38] I. Kabdaşlı, I. Arslan-Alaton, T. Ölmez-Hancı, O. Tünay, Electrocoagulation applications for industrial wastewaters: a critical review, *Environ. Technol. Rev.* 1 (2012) 2–45, <https://doi.org/10.1080/21622515.2012.715390>.
- [39] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, 2nd Ed., National Association of Corrosion Engineers, Houston, Texas (USA), 1974.
- [40] L.L. Pesterfield, J.B. Maddox, M.S. Crocker, G.K. Schweitzer, Pourbaix (E–pH–M) Diagrams in Three Dimensions, *J. Chem. Educ.* 89 (2012) 891–899, <https://doi.org/10.1021/ed200423n>.
- [41] H. Elnakar, I. Buchanan, Soluble chemical oxygen demand removal from bypass wastewater using iron electrocoagulation, *Sci. Total Environ.* 706 (2020), 136076, <https://doi.org/10.1016/j.scitotenv.2019.136076>.
- [42] A.J. Dassej, C.S. Theegala, Reducing electrocoagulation harvesting costs for practical microalgal biodiesel production, *Environ. Technol. (United Kingdom)* 35 (2014) 691–697, <https://doi.org/10.1080/09593330.2013.842602>.
- [43] P. Cañizares, C. Jiménez, F. Martínez, C. Sáez, M.A. Rodrigo, Study of the electrocoagulation process using aluminum and iron electrodes, *Ind. Eng. Chem. Res.* 46 (2007) 6189–6195, <https://doi.org/10.1021/ie070059f>.
- [44] P. Cañizares, M. Carmona, J. Lobato, F. Martínez, M.A. Rodrigo, Electrodissolution of aluminum electrodes in electrocoagulation processes, *Ind. Eng. Chem. Res.* 44 (2005) 4178–4185, <https://doi.org/10.1021/ie048858a>.
- [45] G. Chen, X. Chen, P.L. Yue, Electrocoagulation and electroflotation of restaurant wastewater, *J. Environ. Eng.* 126 (2000) 858–863.
- [46] D. Ghosh, C.R. Medhi, M.K. Purkait, Treatment of fluoride containing drinking water by electrocoagulation using monopolar and bipolar electrode connections, *Chemosphere.* 73 (2008) 1393–1400, <https://doi.org/10.1016/j.chemosphere.2008.08.041>.
- [47] S. Tchamango, C.P. Nansu-Njiki, E. Ngameni, D. Hadjiev, A. Darchen, Treatment of dairy effluents by electrocoagulation using aluminium electrodes, *Sci. Total Environ.* 408 (2010) 947–952, <https://doi.org/10.1016/j.scitotenv.2009.10.026>.
- [48] E. Gençec, M. Kobya, E. Demirbas, A. Akyol, K. Oktor, Optimization of baker's yeast wastewater using response surface methodology by electrocoagulation, *Desalination.* 286 (2012) 200–209, <https://doi.org/10.1016/j.desal.2011.11.023>.
- [49] J.T. Overbeek, Recent developments in the understanding of colloid stability, *J. Colloid Interface Sci.* 58 (1977) 408–422, [https://doi.org/10.1016/0021-9797\(77\)90151-5](https://doi.org/10.1016/0021-9797(77)90151-5).
- [50] N. Fayad, T. Yehya, F. Audonnet, C. Vial, Harvesting of microalgae *Chlorella vulgaris* using electro-coagulation-flocculation in the batch mode, *Algal Res.* 25 (2017) 1–11, <https://doi.org/10.1016/j.algal.2017.03.015>.
- [51] R. Misra, A. Gulde, P. Singh, I. Rawat, F. Bux, Electrochemical harvesting process for microalgae by using nonsacrificial carbon electrode: A sustainable approach for biodiesel production, *Chem. Eng. J.* 255 (2014) 327–333, <https://doi.org/10.1016/j.cej.2014.06.010>.
- [52] A. Gulde, R. Misra, P. Singh, I. Rawat, F. Bux, An innovative electrochemical process to alleviate the challenges for harvesting of small size microalgae by using

- non-sacrificial carbon electrodes, *Algal Res.* 19 (2016) 292–298, <https://doi.org/10.1016/j.algal.2015.08.014>.
- [53] A.I. Barros, A.L. Gonçalves, M. Simões, J.C.M. Pires, Harvesting techniques applied to microalgae: A review, *Renew. Sustain. Energy Rev.* 41 (2015) 1489–1500, <https://doi.org/10.1016/j.rser.2014.09.037>.
- [54] R. Misra, A. Guldhe, P. Singh, I. Rawat, T.A. Stenström, F. Bux, Evaluation of operating conditions for sustainable harvesting of microalgal biomass applying electrochemical method using non sacrificial electrodes, *Bioresour. Technol.* 176 (2015) 1–7, <https://doi.org/10.1016/j.biortech.2014.11.014>.
- [55] W. Zhou, L. Gao, W. Cheng, L. Chen, J. Wang, H. Wang, W. Zhang, T. Liu, Electroflotation of *Chlorella* sp. assisted with flocculation by chitosan, *Algal Res.* 18 (2016) 7–14, <https://doi.org/10.1016/j.algal.2016.05.029>.
- [56] A.K. Lee, D.M. Lewis, P.J. Ashman, Harvesting of marine microalgae by electroflocculation: The energetics, plant design, and economics, *Appl. Energy.* 108 (2013) 45–53, <https://doi.org/10.1016/j.apenergy.2013.03.003>.
- [57] L. Xu, F. Wang, H.Z. Li, Z.M. Hu, C. Guo, C.Z. Liu, Development of an efficient electroflocculation technology integrated with dispersed-air flotation for harvesting microalgae, *J. Chem. Technol. Biotechnol.* 85 (2010) 1504–1507, <https://doi.org/10.1002/jctb.2457>.
- [58] C. Cominellis, G. Chen, eds., *Electrochemistry for the Environment*, Springer New York, New York, NY, 2010. doi:10.1007/978-0-387-68318-8.
- [59] S. Luo, R. Griffith, W. Li, P. Peng, Y. Cheng, P. Chen, M.M. Addy, Y. Liu, R. Ruan, A continuous flocculants-free electrolytic flotation system for microalgae harvesting, *Bioresour. Technol.* 238 (2017) 439–449, <https://doi.org/10.1016/j.biortech.2017.04.061>.
- [60] S. Gao, J. Yang, J. Tian, F. Ma, G. Tu, M. Du, Electro-coagulation-flotation process for algae removal, *J. Hazard. Mater.* 177 (2010) 336–343, <https://doi.org/10.1016/j.jhazmat.2009.12.037>.
- [61] N.S. Abuzaid, A.A. Bukhari, Z.M. Al-Hamouz, Ground water coagulation using soluble stainless steel electrodes, *Adv. Environ. Res.* 6 (2002) 325–333, [https://doi.org/10.1016/S1093-0191\(01\)00065-X](https://doi.org/10.1016/S1093-0191(01)00065-X).
- [62] T.R. Shuman, G. Mason, D. Reeve, A. Schacht, A. Goodrich, K. Napan, J. Quinn, Low-energy input continuous flow rapid pre-concentration of microalgae through electro-coagulation-flocculation, *Chem. Eng. J.* 297 (2016) 97–105, <https://doi.org/10.1016/j.cej.2016.03.128>.
- [63] A. Rahmani, D. Zerrouki, L. Djafer, A. Ayral, Hydrogen recovery from the photovoltaic electroflocculation-flotation process for harvesting *Chlorella pyrenoidosa* microalgae, *Int. J. Hydrogen Energy.* 42 (2017) 19591–19596, <https://doi.org/10.1016/j.ijhydene.2017.06.123>.
- [64] E. Poelman, N. De Pauw, B. Jeurissen, Potential of electrolytic flocculation for recovery of micro-algae, *Resour. Conserv. Recycl.* 19 (1997) 1–10, [https://doi.org/10.1016/S0921-3449\(96\)01156-1](https://doi.org/10.1016/S0921-3449(96)01156-1).
- [65] E. Valero, X. Álvarez, Á. Cancela, A. Sánchez, Harvesting green algae from eutrophic reservoir by electroflocculation and post-use for biodiesel production, *Bioresour. Technol.* 187 (2015) 255–262, <https://doi.org/10.1016/j.biortech.2015.03.138>.
- [66] Y.K. Wong, Y.H. Ho, H.M. Leung, K.C. Ho, Y.H. Yau, K.K.L. Yung, Enhancement of *Chlorella vulgaris* harvesting via the electro-coagulation-flotation (ECF) method, *Environ. Sci. Pollut. Res. Int.* 24 (2017) 9102–9110, <https://doi.org/10.1007/s11356-016-7856-x>.
- [67] F. Baierle, D.K. John, M.P. Souza, T.R. Bjerck, M.S.A. Moraes, M. Hoeltz, A.L. B. Rohlfes, M.E. Camargo, V.A. Corbellini, R.C.S. Schneider, Biomass from microalgae separation by electroflotation with iron and aluminum spiral electrodes, *Chem. Eng. J.* 267 (2015) 274–281, <https://doi.org/10.1016/j.cej.2015.01.031>.
- [68] R.V. Pearsall, R.L. Connelly, M.E. Fountain, C.S. Hearn, M.D. Werst, R.E. Hebner, E.F. Kelley, Electrically dewatering microalgae, *IEEE Trans. Dielectr. Electr. Insul.* 18 (2011) 1578–1583, <https://doi.org/10.1109/TDEI.2011.6032827>.
- [69] H.M. Maleki, M. Almassi, M. Amin, S. Minaei, Harvesting of microalgae by electro-coagulation-flocculation for biodiesel production: an investigation of the effect of operational parameters and forecast model using response surface methodology, *Int. J. Biosci.* 6655 (2014) 258–269, <https://doi.org/10.12692/ijb/4.7.258-269>.
- [70] N. Fayad, The application of electrocoagulation process for wastewater treatment and for the separation and purification of biological media, Université Clermont Auvergne, 2017. <https://tel.archives-ouvertes.fr/tel-01719756>.
- [71] D. Parmentier, D. Manhaeghe, L. Baccini, R. Van Meirhaeghe, D.P.L. Rousseau, S. Van Hulle, A new reactor design for harvesting algae through electrocoagulation-flotation in a continuous mode, *Algal Res.* 47 (2020), 101828, <https://doi.org/10.1016/j.algal.2020.101828>.
- [72] A. Pugazhendhi, S. Shobana, P. Bakonyi, N. Nemesóthy, A. Xia, R. Banu J, G. Kumar, A review on chemical mechanism of microalgae flocculation via polymers, *Biotechnol. Reports.* 21 (2019) e00302. doi:10.1016/j.btre.2018.e00302.
- [73] R. Henderson, S.A. Parsons, B. Jefferson, The impact of algal properties and pre-oxidation on solid-liquid separation of algae, *Water Res.* 42 (2008) 1827–1845, <https://doi.org/10.1016/j.watres.2007.11.039>.
- [74] I. Branyikova, G. Prochazkova, T. Potocar, Z. Jezkova, T. Branyik, Harvesting of Microalgae by Flocculation, *Fermentation.* 4 (2018) 93, <https://doi.org/10.3390/fermentation4040093>.
- [75] K.K. Sharma, S. Garg, Y. Li, A. Malekizadeh, P.M. Schenk, Critical analysis of current microalgae dewatering techniques, *Biofuels.* 4 (2013) 397–407, <https://doi.org/10.4155/bfs.13.25>.
- [76] A.L. Gonçalves, C. Ferreira, J.A. Loureiro, J.C.M. Pires, M. Simões, Surface physicochemical properties of selected single and mixed cultures of microalgae and cyanobacteria and their relationship with sedimentation kinetics, *Bioresour. Bioprocess.* 2 (2015), <https://doi.org/10.1186/s40643-015-0051-y>.
- [77] S. Garg, Y. Li, L. Wang, P.M. Schenk, Flotation of marine microalgae: Effect of algal hydrophobicity, *Bioresour. Technol.* 121 (2012) 471–474, <https://doi.org/10.1016/j.biortech.2012.06.111>.
- [78] C. José de Andrade, L. Maria de Andrade, An overview on the application of genus *Chlorella* in biotechnological processes, *J. Adv. Res. Biotechnol.* 2 (2017) 1–9, <https://doi.org/10.15226/2475-4714/2/1/00117>.
- [79] W. Zhou, Q. Lu, P. Han, J. Li, Microalgae Cultivation and Photobioreactor Design, in: *Microalgae Cultiv. Biofuels Prod.*, Elsevier, 2020. pp. 31–50. doi:10.1016/B978-0-12-817536-1.00003-5.
- [80] J. Liu, F. Chen, Biology and Industrial Applications of *Chlorella*: Advances and Prospects, *Adv. Biochem. Eng. / Biotechnol.* 153 (2014) 1–35, [https://doi.org/10.1007/10\\_2014\\_286](https://doi.org/10.1007/10_2014_286).
- [81] Sarawak Biodiversity Centre, The official website of Sarawak biodiversity centre, (n.d.). <https://www.sbc.org.my/programmes/bioinformatics/187-english-categories/programmes/r-d-laboratories/algae-research/featured-algae>.
- [82] A. Pudney, C. Gandini, C.K. Economou, R. Smith, P. Goddard, J.A. Napier, A. Spicer, O. Sayanova, Multifunctionalizing the marine diatom *Phaeodactylum tricornutum* for sustainable co-production of omega-3 long chain polyunsaturated fatty acids and recombinant phytase, *Sci. Rep.* 9 (2019) 11444, <https://doi.org/10.1038/s41598-019-47875-1>.
- [83] X.-N. Ma, T.-P. Chen, B. Yang, J. Liu, F. Chen, Lipid Production from *Nannochloropsis*, *Mar. Drugs.* 14 (2016) 61, <https://doi.org/10.3390/md14040061>.
- [84] M.A. Borowitzka, *The mass culture of Dunaliella salina*, *Food Agric. Organ, United Nations*, 1990 <https://agris.fao.org/agris-search/search.do?recordID=XF9107059>.
- [85] S. Gao, M. Du, J. Tian, J. Yang, J. Yang, F. Ma, J. Nan, Effects of chloride ions on electro-coagulation-flotation process with aluminum electrodes for algae removal, *J. Hazard. Mater.* 182 (2010) 827–834, <https://doi.org/10.1016/j.jhazmat.2010.06.114>.
- [86] P.E. Wiley, J.D. Trent, Clarification of algae-laden water using electrochemical processes, *Water Supply.* 16 (2016) 314–323, <https://doi.org/10.2166/ws.2015.140>.
- [87] D. Gheraout, M.W. Naceur, A. Aouabed, On the dependence of chlorine by-products generated species formation of the electrode material and applied charge during electrochemical water treatment, *Desalination.* 270 (2011) 9–22, <https://doi.org/10.1016/j.desal.2011.01.010>.
- [88] T. Ball, J. Bridges, B. De Angelis, D. Han, D. Hoskins, J. Jones, D. Walker, CURE Electrocoagulation Technology - Innovative Technology Evaluation Report, Cincinnati, Ohio, USA, 1998. papers2://publication/uuid/0F25391B-9A90-4453-B601-AD7B4EA0FBED.
- [89] C.T. Matos, M. Santos, B.P. Nobre, L. Gouveia, Microalgae biomass harvesting by electro-coagulation, in: *Energy Sustain.* 2013, Coimbra, 2013. pp. 1–6.
- [90] D.W. Sparling, T.P. Lowe, Environmental hazards of aluminum to plants, invertebrates, fish, and wildlife, *Rev. Environ. Contam. Toxicol.* 145 (1996) 1–127, [https://doi.org/10.1007/978-1-4612-2354-2\\_1](https://doi.org/10.1007/978-1-4612-2354-2_1).
- [91] J. Zhou, Z. Ai, H. Wang, G. Niu, J. Yuan, Phosphorus alleviates aluminum toxicity in *Camellia oleifera* seedlings, *Int. J. Agric. Biol.* 21 (2019) 237–243, <https://doi.org/10.17957/IJAB/15.0886>.
- [92] J. dos Santos Neto, J. Delfini, T. Willian Silva, A. Akihido Hirose, J. Marcos Novais, L. Simões Azeredo Gonçalves, V. Moda-Cirino, Response of Common Bean Cultivars and Lines to Aluminum Toxicity, *Agronomy.* 10 (2020) 296. doi:10.3390/agronomy10020296.
- [93] REGULATION (EU) 2019/1009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 5 June, Laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003, *Off. J. Eur. Union.* (n.d.).
- [94] *FAO Regional Office for the Near East, Users Manual for Irrigation with Treated Wastewater*, Egypt, Cairo, 2003.
- [95] T.M. Chiroma, R.O. Ebeuele, *Comparative Assessment Of Heavy Metal Levels In Soil, Vegetables And Urban Grey Waste Water Used For Irrigation In Yola And Kano*, *Int. Ref. J. Eng. Sci.* ISSN. 3 (2014) 2319–3183.
- [96] J. Lindemann, E. Holtkamp, R. Herrmann, The impact of aluminium on green algae isolated from two hydrochemically different headwater streams, Bavaria, Germany, *Environ. Pollut.* 67 (1990) 61–77, [https://doi.org/10.1016/0269-7491\(90\)90172-9](https://doi.org/10.1016/0269-7491(90)90172-9).
- [97] EPA, Final 2018 Aquatic Life Ambient Water Quality Criteria for Aluminum in Freshwaters, 2018.
- [98] *FAO/WHO Food Standards Programme Codex Committee on Contaminants in Foods*, Working Document for Information and Use in Discussions Related to Contaminants and Toxins in GSCTF, Utrecht, The Netherlands, 2018.
- [99] L.K. Wang, N.K. Shammam, B.C. Wu, *Electroflotation, in: Flotat. Technol., Humana Press, Totowa, NJ, 2010. pp. 165–197. doi:10.1007/978-1-60327-133-2\_5.*
- [100] Eurostat, Statistiche sul prezzo dell'energia elettrica, *Stat. Explain.* (2019). [https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Electricity\\_price\\_statistics/#Prezzi\\_dell\\_27energia\\_elettrica\\_per\\_i\\_consumatori\\_non\\_domestici](https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Electricity_price_statistics/#Prezzi_dell_27energia_elettrica_per_i_consumatori_non_domestici) (accessed May 22, 2020).
- [101] Meps, The Latest Global Steel Prices, Indices & Forecasts, (2020). <https://www.meps.co.uk/gb/en/pages/the-latest-global-steel-prices-indices-forecasts>.
- [102] Trefis Team, Great Speculations, Year Price Analysis And Production-Demand-GDP Dynamics, *Forbes.* (2019). <https://www.forbes.com/sites/>

- greatspeculations/2019/11/05/aluminum-prices-15-year-price-analysis-and-production-demand-gdp-dynamics/#7fab64a1dadab%0D.
- [103] J. Ge, J. Qu, P. Lei, H. Liu, New bipolar electrocoagulation–electroflotation process for the treatment of laundry wastewater, *Sep. Purif. Technol.* 36 (2004) 33–39, [https://doi.org/10.1016/S1383-5866\(03\)00150-3](https://doi.org/10.1016/S1383-5866(03)00150-3).
- [104] A.B. Aragón, R.B. Padilla, J.A.F. Ros de Ursinos, Experimental study of the recovery of algae cultured in effluents from the anaerobic biological treatment of urban wastewaters, *Resour. Conserv. Recycl.* 6 (1992) 293–302, [https://doi.org/10.1016/0921-3449\(92\)90053-5](https://doi.org/10.1016/0921-3449(92)90053-5).
- [105] A. Papazi, P. Makridis, P. Divanach, Harvesting *Chlorella minutissima* using cell coagulants, *J. Appl. Phycol.* 22 (2010) 349–355, <https://doi.org/10.1007/s10811-009-9465-2>.
- [106] R.R. Soomro, T. Ndikubwimana, X. Zeng, Y. Lu, L. Lin, M.K. Danquah, Development of a two-stage microalgae dewatering process – A life cycle assessment approach, *Front. Plant Sci.* 7 (2016) 1–12, <https://doi.org/10.3389/fpls.2016.00113>.
- [107] W.A. Barton, S.A. Miller, C.J. Veal, The Electrodewatering of Sewage Sludges, *Dry. Technol.* 17 (1999) 498–522, <https://doi.org/10.1080/07373939908917548>.
- [108] A. Mahmoud, J. Olivier, J. Vaxelaire, A.F.A. Hoadley, Electrical field: A historical review of its application and contributions in wastewater sludge dewatering, *Water Res.* 44 (2010) 2381–2407, <https://doi.org/10.1016/j.watres.2010.01.033>.
- [109] M.H.M. Raats, A.J.G. Van Diemen, J. Lavèn, H.N. Stein, Full scale electrokinetic dewatering of waste sludge, *Colloids Surfaces A Physicochem. Eng. Asp.* 210 (2002) 231–241, [https://doi.org/10.1016/S0927-7757\(02\)00380-1](https://doi.org/10.1016/S0927-7757(02)00380-1).
- [110] H. Saveyn, P. Van der Meer, G. Pauwels, R. Timmerman, Bench- and pilot-scale sludge electrodewatering in a diaphragm filter press, *Water Sci. Technol.* 54 (2006) 53–60, <https://doi.org/10.2166/wst.2006.725>.
- [111] Y. Zhang, M. Cao, H. Lv, J. Wei, Y. Gu, D. Liu, W. Zhang, M.P. Ryan, X. Wu, Electrodeposited nanometer-size IrO<sub>2</sub>/Ti electrodes with 0.3 mg IrO<sub>2</sub>cm<sup>-2</sup> for sludge dewatering electrolyzers, *Electrochim. Acta.* 265 (2018) 507–513. doi: 10.1016/j.electacta.2018.01.190.
- [112] M. Citeau, J. Olivier, A. Mahmoud, J. Vaxelaire, O. Larue, E. Vorobiev, Pressurised electro-osmotic dewatering of activated and anaerobically digested sludges: Electrical variables analysis, *Water Res.* 46 (2012) 4405–4416, <https://doi.org/10.1016/j.watres.2012.05.053>.
- [113] S. Visigalli, A. Turolla, P. Gronchi, R. Canziani, Performance of electro-osmotic dewatering on different types of sewage sludge, *Environ. Res.* 157 (2017) 30–36, <https://doi.org/10.1016/j.envres.2017.05.015>.
- [114] H. Saveyn, G. Pauwels, R. Timmerman, P. Van Der Meer, Effect of polyelectrolyte conditioning on the enhanced dewatering of activated sludge by application of an electric field during the expression phase, *Water Res.* 39 (2005) 3012–3020, <https://doi.org/10.1016/j.watres.2005.05.002>.
- [115] J. Feng, Y.L. Wang, X.Y. Ji, Dynamic changes in the characteristics and components of activated sludge and filtrate during the pressurized electro-osmotic dewatering process, *Sep. Purif. Technol.* 134 (2014) 1–11, <https://doi.org/10.1016/j.seppur.2014.07.019>.
- [116] Z. Xue, X. Tang, Q. Yang, Influence of voltage and temperature on electro-osmosis experiments applied on marine clay, *Appl. Clay Sci.* 141 (2017) 13–22, <https://doi.org/10.1016/j.clay.2017.01.033>.
- [117] A.T. Lima, P.J. Kleingeld, K. Heister, J.P.G. Loch, Removal of PAHs from contaminated clayey soil by means of electro-osmosis, *Sep. Purif. Technol.* 79 (2011) 221–229, <https://doi.org/10.1016/j.seppur.2011.02.021>.
- [118] J. Ling, B. Han, Y. Xie, Q. Dong, Y. Sun, B. Huang, Laboratory and Field Study of Electroosmosis Dewatering for Pavement Subgrade Soil, *J. Cold Reg. Eng.* 31 (2017) 1–16, [https://doi.org/10.1061/\(ASCE\)CR.1943-5495.0000136](https://doi.org/10.1061/(ASCE)CR.1943-5495.0000136).
- [119] A. Mahmoud, J. Olivier, J. Vaxelaire, A.F.A. Hoadley, Electro-dewatering of wastewater sludge: Influence of the operating conditions and their interactions effects, *Water Res.* 45 (2011) 2795–2810, <https://doi.org/10.1016/j.watres.2011.02.029>.
- [120] B. Cao, Y. Zhang, Y. Shi, R. Ren, H. Wu, W. Zhang, D. Wang, T. Zhang, J. Xiong, Extracellular organic matter (EOM) distribution characteristic in algae electro-dewatering process, *J. Environ. Manage.* 265 (2020), 110541, <https://doi.org/10.1016/j.jenvman.2020.110541>.