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Evaluation of electro-coagulation-flocculation for harvesting marine and freshwater microalgae

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Running Title

Evaluation of ECF for harvesting microalgae

Abstract

Although microalgae are considered as a promising feedstock for biofuels, the energy efficiency of the production process needs to be significantly improved. Due to their small size and low concentration in the culture medium, cost efficient harvesting of microalgae is a major challenge. In this study, the use of electro-coagulation-flocculation (ECF) as a method for harvesting a freshwater (*Chlorella vulgaris*) and a marine (*Phaeodactylum tricornutum*) microalgal species is evaluated. ECF was shown to be more efficient using an aluminum anode than using an iron anode. Furthermore it could be concluded that the efficiency of the ECF process can be substantially improved by reducing the initial pH and by increasing the turbulence in the microalgal suspension. Although higher current densities resulted in a more rapid flocculation of the microalgal suspension, power consumption, expressed per kg of microalgae harvested, and release of aluminum were lower when a lower current density was used. The aluminum content of the harvested microalgal biomass was less than 1 % while the aluminum concentration in the process water was below 2 mg l⁻¹. Under optimal conditions, power consumption of the ECF process was around 2 kWh kg⁻¹ of microalgal biomass harvested for *Chlorella vulgaris* and ca. 0.3 kWh kg⁻¹ for *Phaeodactylum tricornutum*. Compared to centrifugation, ECF is thus more energy efficient. Because of the lower power consumption of ECF in seawater, ECF is a particularly attractive method for harvesting marine microalgae.

Introduction

Due to the combination of a high areal productivity, a high lipid content and limited competition with food crops for arable land, microalgal biomass is an attractive feedstock for the production of biofuels. At present, however, microalgae are only produced on a limited scale for high-value products such as food supplements, natural pigments and polyunsaturated fatty acids (Cardozo et al., 2007; Raja et al., 2008; Spolaore et al., 2006). Energy inputs during the production of microalgal biomass are very high and often exceed the energy content of the microalgal biomass (Pienkos and Darzins, 2009; Wijffels and Barbosa, 2010). To use microalgal biomass as a feedstock for biofuels, the cost and energy efficiency of the process needs to be improved dramatically (Greenwell et al., 2010; Tredici, 2010).

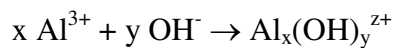
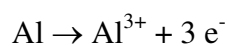
Because of their small size (typically a few micrometer) and low concentration in the culture medium (0.5 – 2 g/l), harvesting microalgal biomass is a major challenge. Most existing microalgal production systems use energy intensive centrifuges to harvest microalgae (Heasman et al., 2000). Consequently, harvesting represents a major fraction of the total energy demand of the production process (Grima et al., 2003; Uduman et al., 2010). If the microalgae could be preconcentrated 30-50 times by coagulation-flocculation and gravity sedimentation prior to centrifugation, the energy demand for harvesting could be strongly reduced (Harun et al., 2010; Tredici, 2010; Uduman et al., 2010).

Microalgae can easily be flocculated using metal coagulants such as Fe^{3+} or Al^{3+} salts (Ahmad et al., 2006; Bernhardt and Clasen, 1991; Papazi et al., 2009). In wastewater treatment, electro-coagulation-flocculation (ECF) has been proposed as an alternative for chemical coagulants (Mollah et al., 2001; Mollah et al., 2004). In ECF, iron or aluminum ions are

released from a sacrificial anode through electrolytic oxidation. Compared to coagulation-flocculation with Fe^{3+} or Al^{3+} salts, ECF has the advantage that no anions such as chlorine and sulphate are introduced in the process water. The electrolytic oxidation of the sacrificial anode, however, requires electricity.

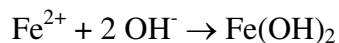
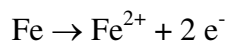
During ECF, the following reactions occur at the anode:

Using an aluminum anode :

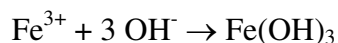
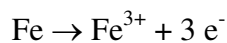


The speciation of the aluminum hydroxides formed during ECF is highly variable and is strongly influenced by pH (Mouedhen et al., 2008).

Using an iron anode :

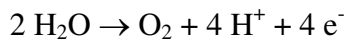


or

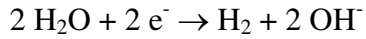


It is not clear whether ferrous or ferric ions are formed during ECF (Sasson et al., 2009). Moreover, Fe^{2+} can be rapidly oxidized in solution to Fe^{3+} in the presence of oxygen. Release of Fe^{2+} during ECF leads to green hydroxide precipitates, while Fe^{3+} ions results in yellow hydroxide precipitates.

At both the Al and Fe anodes, water is oxidized as a side reaction and oxygen is produced:



The main reaction at the cathode is the reduction of water and the formation of hydrogen gas:



So far, the use of ECF for harvesting microalgal biomass has not been thoroughly evaluated. Some studies have investigated the use of ECF for removal of microalgae from drinking or wastewater (Alfafara et al., 2002; Azarian et al., 2007; Gao et al., 2010a; Gao et al., 2010b; Poelman et al., 1997; Sridhar et al., 1988). In these studies, however, microalgal densities were much lower than those typically occurring in microalgal production systems. Moreover, these studies all focused on freshwater and not on marine microalgae. The chemical composition and conductivity of fresh water and seawater differ strongly and this may have a strong effect on the efficiency of the ECF process. It is relevant to evaluate the use of ECF as a harvesting method for marine microalgae because marine microalgae are attractive as a source of biofuels due to their limited dependence on freshwater resources.

The general aim of this study was to demonstrate the proof of principle for harvesting of microalgae using electro-coagulation flocculation (ECF) in both a freshwater and marine environment. Specific goals were (1) to study the influence of several important variables on the efficiency of the ECF process, (2) to evaluate contamination of the microalgal biomass and process water with metals released from the sacrificial anode and (3) to estimate the electricity demand of the ECF process.

Materials & Methods

Cultivation of microalgae

Because we expected large differences in the efficiency of ECF for harvesting microalgae from marine and freshwater medium, all experiments were carried out with the freshwater chlorophyte *Chlorella vulgaris* (SAG, Germany, 211-11B) and the marine diatom *Phaeodactylum tricornutum* (UGent, Belgium, Pt 86). Both *Chlorella* and *Phaeodactylum* are promising species for the production of microalgal biomass for food, feed or fuel, and are currently intensively studied. *Chlorella vulgaris* was cultured in Wright's cryptophytes (WC) medium prepared from pure chemicals dissolved in disinfected tap water (Guillard and Lorenzen, 1972). *Phaeodactylum tricornutum* was cultured in WC medium prepared in deionised water to which 30 g L⁻¹ synthetic sea salt (Homarsel, Zoutman, Belgium) was added. Table I illustrates the differences in chemical composition and conductivity between both media. Both species were grown in 30 L plexiglas bubble column photobioreactors (diameter 20 cm). Degassing was carried out with humidified and filtered air at a rate of 5 L min⁻¹. The pH was controlled at 8.5 by addition of CO₂ (2-3%) using a pH-stat system. The ECF experiments were carried out at the beginning of the stationary phase, corresponding to a microalgal density of 0.3-0.6 g dry weight L⁻¹.

ECF experiments

All the ECF experiments were carried out at room temperature in a PVC batch reactor of 20 cm (length) × 5 cm (width) × 15 cm (height) filled with 1L of microalgal broth. The electrodes consisted of two parallel flat metal plates with a surface area of 200 cm², placed 4.4 cm apart

near the walls of the reactor. Aluminum or iron plates were compared as anodes while an inert net of IrO₂/TiO₂ was used as the cathode. The anode and cathode were connected to the positive and negative outlets of a DC power supply (EHQ Power PS3010), respectively. The current density was controlled by changing the current of the DC power supply, which was operated in the constant current mode. The microalgal broth in the vessel was stirred using an overhead stirrer (IKA Labortechnik Eurostar digital Model RW-16).

To determine the microalgal recovery efficiency η_a of microalgal biomass, samples were collected at different time points (t) during the ECF process. 10 mL samples were collected at 5 cm below the water surface in the ECF reactor. In the samples, flocs of microalgae either settled to the bottom or floated to the surface of the sample tube. Flotation of the flocs was caused by the formation of H₂ at the cathode and O₂ at the anode. The microalgal recovery efficiency η_a was determined based upon the decrease in optical density of the microalgal suspension (measured at 550 nm with a UV-VIS spectrometer Thermo Scientific Nicolet Evolution 100). The recovery efficiency was subsequently calculated as:

$$\text{Microalgal recovery efficiency } \eta_a = \frac{OD_i - OD_f}{OD_i} \text{ (Eq. 1)}$$

where OD_i is the optical density of the suspension prior to the start of the ECF process, and OD_f is the optical density of the suspension at time t.

Influence of variables on the ECF process

The influence of several important variables on the ECF process was studied using a one-variable-at-the-time-approach. Consecutively, the influence of the anode material (Fe or Al), the sedimentation time after finishing the ECF-treatment, the current density, the (initial) pH,

and the stirring speed were investigated. The influence of a specific variable was studied using the best values found for the variables that were already investigated.

Calculation of the power consumption

The power consumption E (in kWh kg⁻¹ of recovered microalgae) was calculated as:

$$E = \frac{UIt}{1000V\eta_a c_i} \quad E = \frac{U \times I \times t}{1000 \times V \times \eta_a \times c_i} \quad (\text{Eq. 2})$$

Where U is the voltage (V), I the current (A), t the time of the ECF treatment (h), V the volume of the microalgal solution treated (m³), η_a the microalgae recovery efficiency and c_i the initial microalgae biomass concentration (kg m⁻³).

Al, Ca and Mg analyses in the harvested algal biomass and the process water

To determine the degree of contamination of the microalgal biomass and the process water, the Al, Ca and Mg content of the microalgal biomass recovered during the ECF process as well as of the supernatant remaining after the ECF treatment was determined. Al, Ca and Mg in solution were determined by atomic absorption spectroscopy (AAS, Solaar UNICAM 989). For measurements on the microalgal biomass, it was first calcinated in a furnace at 550 °C during 4 hours and then the ashes were dissolved in 37% fuming hydrochloric acid. The total amount of metals released during ECF was estimated by assuming that the electrical efficiency for the release of metal was 100 %. This is in reality an overestimation, as the formation of O₂ competes with Al³⁺ formation at the anode.

Results & Discussion

Influence of variables

In all ECF experiments, η_a increased with time following a sigmoid pattern. This observation is in accordance with a model in which metal ions such as Al^{3+} or $\text{Fe}^{2+}/\text{Fe}^{3+}$ are continuously released from the anode during the ECF treatment. These aluminum and iron ions react with water to form metal hydroxides (Duan and Gregory, 1996). Positively charged soluble metal hydroxides bind to the negative surface of the microalgal cells and destabilize the microalgal suspension by charge neutralization. Insoluble metal hydroxides can destabilize the microalgal suspension through a mechanism known as sweeping flocculation, resulting in enmeshment of microalgae and insoluble precipitates (Duan and Gregory, 2003). For both mechanisms, the inflection point of the sigmoidal curve corresponds to the time required to produce a sufficient amount of aluminum or iron hydroxides to destabilize the microalgal dispersion (Mollah et al., 2001; Mollah et al., 2004).

Visual observation of the solution during the ECF process revealed the formation of insoluble metal hydroxides, either as brown-green precipitates when using an iron anode, or as a milky precipitate when using an aluminum anode. The brown-green color of the precipitates formed when an iron anode was used, suggests that Fe^{2+} rather than Fe^{3+} was released from the anode during ECF. The metal hydroxide precipitates interfered to some extent with the spectrophotometric quantification of microalgal biomass. On the one hand, they may have caused a residual turbidity in the solution after η_a reached a plateau and therefore may have caused a slight underestimation of the maximum η_a . These insoluble metal hydroxides also explain why in some cases negative recovery efficiencies were measured prior to the destabilization of the microalgal suspension.

In Fig. 1, the performance of aluminum and iron electrodes is compared. For both *Chlorella vulgaris* and *Phaeodactylum tricornutum*, dispersion destabilization of the microalgal suspension occurred much faster with aluminum electrodes than with iron electrodes. The lower efficiency of the iron electrodes is probably due to the lower current efficiency generated by iron electrodes when compared to aluminum electrodes (Cañizares et al., 2006; Zongo et al., 2009). Also, iron hydroxides are relatively inefficient coagulants compared to aluminum hydroxides (Emamjomeh and Sivakumar, 2009). In a study on the use of ECF for removal of microalgae from eutrophic surface waters, Gao et al. (2010b) also noted a higher efficiency of aluminum compared to iron electrodes. Because of this higher efficiency, aluminum electrodes were selected as the anode material in further experiments.

When samples were taken from the ECF reactor, destabilization of the microalgal suspension continued after sampling. This is illustrated for *Chlorella vulgaris* and *Phaeodactylum tricornutum* in Table II and III respectively. Particularly for samples collected at time points close to the inflection point of the sigmoidal curve, this continued coagulation-flocculation-sedimentation of microalgae after sampling resulted in a substantial increase of η_a , up to 25% over a period of 30 minutes. This can be ascribed to continued reaction between dissolved metal hydroxides and microalgal cells and to the fact that some time is needed for sedimentation of the flocs. Because of this continued coagulation-flocculation-sedimentation after sampling, η_a was determined in further experiments 30 min after sampling.

As electricity is the driving force for the reactions occurring at the anode, current density is an important variable in the ECF process (Fig. 2). For *Chlorella vulgaris*, current densities between 1.5-12 mA cm⁻² were evaluated. It was not possible to maintain a lower current density in a stable way in the freshwater medium. For *Phaeodactylum tricornutum*, current densities between 0.6-3 mA cm⁻² were used. The use of higher current densities in the salt water medium resulted in the electrolytic formation of NaClO or bleach, which visually led to

the disappearance of microalgae flocs. This bleach formation was also reported by Gao et al. (2010a) and should be avoided. For both *Chlorella vulgaris* and *Phaeodactylum tricornutum*, the time required to destabilize the microalgal suspension decreased with increasing current density. To reach an η_a of 95% for *Chlorella vulgaris*, 50 min ECF was required using 1.5 mA cm⁻², while only 10 min ECF was required using 12 mA cm⁻². For *Phaeodactylum tricornutum*, an η_a of 80% was reached after 30 min using a current density of 0.5 mA cm⁻², while only 10 min was required using 3 mA cm⁻².

In Fig. 3, the influence of the initial pH on the ECF process is shown. For both *Chlorella vulgaris* and *Phaeodactylum tricornutum*, the efficiency of the process decreased with increasing pH. This influence of pH was more pronounced for *Phaeodactylum tricornutum* than for *Chlorella vulgaris*. It is well known that pH is an important variable in ECF (Mouedhen et al., 2008), as it determines speciation of aluminum hydroxides in the solution (Duan and Gregory, 2003; Gregory, 2006). Under acidic conditions, the formation of positively charged monomeric aluminum hydroxides such as Al(OH)²⁺, or polymeric aluminum hydroxide cations such as Al₆(OH)₁₅³⁺, Al₇(OH)₁₇⁴⁺, Al₈(OH)₂₀⁴⁺, Al₁₃O₄(OH)₃₄⁷⁺ and Al₁₃(OH)₃₄⁵⁺ is promoted (Cañizares et al., 2006; Mollah et al., 2001). These react with the negatively charged surface of the microalgal cells and are able to destabilize the microalgal suspension by charge neutralization. At more alkaline pH levels, the formation of the negatively charged aluminum hydroxide Al(OH)₄⁻ is promoted, which will not react with the negatively charged microalgal cells. Under these conditions, coagulation-flocculation of microalgal cells is probably mostly due to sweeping coagulation-flocculation by insoluble aluminum hydroxide Al(OH)₃. In their study on the use of ECF for removal of microalgae from eutrophic surface waters, Goa et al. (2010a) also noted that a low pH had a positive effect on the recovery efficiency of microalgae during ECF. Because of this positive effect of a low initial pH, an initial pH value of 4 was used in all subsequent experiments.

Fig. 4 illustrates the influence of stirring during the ECF process on η_a . 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 two. At the maximum stirring speed of 200 rpm, however, the time required to achieve destabilization increased again. Previous studies on ECF for other applications have also demonstrated that stirring can improve the coagulation-flocculation efficiency (Cañizares et al., 2006). Stirring improves the recovery efficiency by enhancing contact rates between the coagulants and the microalgal cells (Mollah et al., 2004). The highest stirring rate, however, probably caused break-up of microalgal flocs due to the high shear forces applied, resulting in a longer time needed to achieve a similar recovery efficiency. Because the time needed to achieve a maximal η_a was shortest for a stirring speed of 150 rpm, this stirring speed was used in subsequent experiments.

The reproducibility of the ECF process was evaluated in a new set of experiments in triplet, working under the following (optimal) experimental conditions: aluminum anode, pH 4, sedimentation time of 30 minutes and stirring speed of 150 rpm. For both types of microalgae, the two lowest current densities from the range tested above were used (1.5 and 3 mA/cm² for *Chlorella vulgaris* and 0.6 and 1.5 mA/cm² for *Phaeodactylum tricornutum*). Fig. 5 illustrates that, for both species, the time required to initiate flocculation as well as the final recovery efficiencies are reproducible.

Accumulation of aluminum during ECF

During the above-mentioned experiment, we also investigated the accumulation of aluminum in both the recovered microalgal biomass and in the liquid phase during the course of the ECF process (Fig. 5). As predicted by Faraday's law, the concentration of aluminum in both the biomass and the liquid phase increased with time and with current density. Aluminum content in the recovered microalgal biomass was about twice as high at the higher current density than

at the lower current density. For both species, the aluminum content in the microalgal biomass continued to increase after the maximal η_a was reached, which can be ascribed to continued precipitation of aluminum hydroxides. In the experiment with *Chlorella vulgaris*, aluminum concentration in the liquid phase was relatively high and continued to increase after the maximal η_a was reached. In *Phaeodactylum tricornutum*, on the contrary, the Al concentration in the liquid phase was much lower and appeared to stabilize when the maximal η_a was reached.

The difference in aluminum concentration in the water between the marine and freshwater species are most likely due to differences in the chemical composition of the freshwater and the seawater medium. The seawater medium contains high concentrations of sulphate anions. These sulphate anions are known to facilitate precipitation of aluminum hydroxides (Duan and Gregory, 2003; Gregory and Duan, 2001). This probably explains the low residual aluminum concentrations in the process water in the experiments with *Phaeodactylum tricornutum*. The seawater medium also contains high concentrations of magnesium and calcium cations (Table I). Electrolytic release of hydroxyl anions at the cathode may lead to high pH levels near the cathode. This is known to cause precipitation of carbonates and hydroxides of calcium and magnesium (Mameri et al., 1998; Wijesekara et al., 2005). We monitored calcium and magnesium concentrations in the experiments with *Phaeodactylum tricornutum* at a current density of 1.5 mA cm^{-2} . Calcium concentrations did not decrease appreciably in the medium during the course of the experiment but magnesium concentrations decreased by about 15%, suggesting that precipitation of magnesium carbonates or hydroxides did indeed occur. Magnesium concentrations in the biomass did not increase during the experiment, most likely because magnesium was precipitated on the cathode. In long term operation, this may lead to an increased current consumption during the ECF process.

Both in the marine and the freshwater medium, it is clear that the aluminum content in both the water and the microalgal biomass can be minimized by using a lower current density. To avoid accumulation of excess aluminum in either the liquid phase, the biomass or both, ECF should not be continued beyond the point where η_a reaches the saturation phase. Taking this into account, the aluminum content in the microalgal biomass could be kept below 1% in the harvested biomass. In the process water it could be kept below 2 mg l⁻¹ for *Chlorella vulgaris* or 0.5 mg l⁻¹ for *Phaeodactylum tricornutum* in the process water.

In the experiments described in this research, microalgae were coagulated-flocculated by aluminum hydroxides. This mechanism of coagulation-flocculation is comparable to coagulation-flocculation of microalgae using aluminum salts like alum. According to the literature (Shelef et al., 1984), 80 to 250 mg alum l⁻¹ corresponding to 7.2 to 23 mg Al l⁻¹ is needed to coagulate/flocculate a microalgal suspension. For harvesting *Chlorella minutissima*, Papazi et al. (2009) used 750 mg l⁻¹ alum, which corresponds to 120 mg l⁻¹ of aluminum. If we assume that only aluminum oxidation occurred at the anode, we estimated that in the experiments in which the lowest current density was used, only 3.5 mg Al l⁻¹ was released in the experiment with *Chlorella vulgaris* and 1.7 mg Al l⁻¹ in the experiment with *Phaeodactylum tricornutum*. This suggests that ECF is more efficient in terms of aluminum consumption than coagulation-flocculation using alum. These findings coincide with the results of Cañizares et al. (2009) on the use of ECF for treatment of textile waters.

Power consumption

The experimental results indicated that similar microalgal recovery efficiencies could be obtained by applying a high current density during a short time as by applying a low current density during a longer time. From an energy consumption point of view, it is unclear which strategy is best. Therefore, for the data presented in Fig. 2, the global power consumption,

expressed as kWh kg⁻¹ dry weight microalgal biomass recovered during the ECF process was calculated using Equation (2) for each sampling time (Tables IV and V). For each ECF run, a point in time could be identified at which the power consumption per unit of microalgal biomass recovered was minimal. This point in time generally corresponded to the time at which η_a reached the saturation phase. For *Chlorella vulgaris*, for instance, this corresponded to an ECF time of 40 min at a current density of 1.5 mA cm⁻² and 20 min at 6 mA cm⁻². For *Phaeodactylum tricornutum*, this point in time was situated at 20 min at a current density of 0.6 mA cm⁻² and 3 to 5 min at 3 mA cm⁻².

These analyses clearly indicated that the minimal power consumption per unit of microalgal biomass recovered is much lower if lower current densities are used than when higher current densities are used. For *Chlorella vulgaris*, 1.3 kWh kg⁻¹ recovered microalgae was consumed at a current density of 1.5 mA cm⁻² while 9.5 kWh kg⁻¹ recovered microalgae was consumed at 6 mA cm⁻². For *Phaeodactylum tricornutum*, the difference was smaller, with 0.2 kWh kg⁻¹ recovered microalgae consumed at 0.6 mA cm⁻², and 0.4 kWh kg⁻¹ recovered microalgae was consumed at 3 mA cm⁻². Previous studies, in which ECF was used to remove microalgae from surface waters, have also indicated that the energy consumption to achieve coagulation-flocculation is lower when a lower current density is used (Gao et al., 2010b). Although a higher current density thus leads to a more rapid coagulation-flocculation of the microalgae, the use of a low current density is more efficient, from an energy consumption point of view,. It should be noted, however, that the use of a low current density requires relatively long retention times of the water in the reactor. It is not unusual, however, to use retention times in other applications of ECF (e.g. Deng & Huang 2006, Zodi et al. 2011). Nevertheless, the retention time should be taken into account when the process is applied at an industrial scale.

A long retention time will require a larger reactor to process the same volume of water. A long retention time may also influence the quality of the algal biomass that is harvested.

For the experiments depicted in Fig. 5, the minimum value of the power consumption was 2.1 kWh kg⁻¹ of biomass harvested for *Chlorella vulgaris* and 0.2 kWh kg⁻¹ of biomass harvested for *Phaeodactylum tricornutum*, at a current density of 1.5 and 0.6 mA cm⁻² respectively. These data confirm the low power requirements of ECF, especially for the marine species. The lower power consumption needed for the marine species is mainly due to the higher conductivity of the marine medium when compared to the freshwater medium, which results in a higher efficiency of the electrolytic release of aluminum from the anode (Kim et al., 2002), but other phenomena could also play a role here. Mouedhen et al. (2008) reported that chloride ions present in seawater attack the aluminum oxide layer formed on the surface of the anode, thereby enhancing the release of aluminum from the anode.

In existing microalgal production systems for high value applications, centrifugation is currently the most commonly used technology for harvesting microalgae. For low value applications, however, the use of conventional centrifuges is not economically feasible (Grima et al., 2003). Power consumption of conventional centrifugation has been estimated at 8 kWh m⁻³ of microalgal suspension (Danquah et al., 2009). Assuming a microalgal biomass concentration of 0.5 kg m⁻³, which is typical for microalgal production systems and comparable to the microalgal biomass concentration used in our experiments, this would correspond to a power consumption of 16 kWh kg⁻¹ microalgal biomass recovered. The experiments in this study indicate that, for the freshwater microalgae *Chlorella vulgaris*, power consumption of ECF is an order of magnitude lower than for centrifugation. For *Phaeodactylum tricornutum*, the difference is nearly two orders of magnitude. Because ECF

is a complex process involving electrolysis, coagulation-flocculation and sedimentation/flotation, there is no straightforward approach for estimating the challenges and costs associated with scaling-up of the technology (Holt et al. 2005). Pilot-scale tests are therefore required to confirm whether rates of power consumption can be extrapolated to industrial scale ECF reactors, and to estimate additional costs of a full-scale setup. An important parameter that will influence power consumption in large-scale systems which was not investigated in this study is the distance between the electrodes, which has an important influence on power consumption (Holt et al., 2005; Kim et al., 2002). Nevertheless, our results indicate that ECF may be a promising technology for harvesting microalgae, in particular for species cultivated in seawater.

Conclusions

Although both aluminum and iron anodes achieved destabilization of the microalgal suspensions, aluminum anodes proved to be more efficient. During ECF, Al^{3+} and Fe^{2+} are released from the sacrificial anode and form metal hydroxides in the solution. Destabilization of the microalgal suspension was probably achieved through a combination of charge neutralization by positively charged metal hydroxides and sweeping coagulation-flocculation by insoluble metal hydroxides. The efficiency of the ECF process using aluminum as an anode could be significantly improved by reducing the initial pH and by increasing the turbulence. It is also recommended to include a sedimentation period between ECF and the removal of the microalgal flocs as destabilization of the microalgal suspension continues after removal of the microalgal suspension from the ECF reactor. Although higher current densities resulted in a more rapid destabilization of the microalgal suspension, this also resulted in a higher power consumption and release of aluminum from the sacrificial anode. Release of aluminum in the process water is lower, probably due to enhanced precipitation of aluminum hydroxides related to the presence of sulphates in seawater. When ECF is compared to chemical coagulation-flocculation using alum, consumption of aluminum appears to be lower when ECF is used. Power consumption of ECF was an order of magnitude lower than centrifugation when applied to the freshwater microalgae *Chlorella vulgaris* and nearly two orders of magnitude lower when applied to the marine microalgae *Phaeodactylum tricorutum*. ECF is therefore an attractive technology for harvesting microalgae, particularly for harvesting marine microalgae.

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Figure captions

Figure 1: Microalgae recovery efficiency η_a as function of ECF time using different electrodes.

Conditions: (A) *Chlorella vulgaris*, (B) *Phaeodactylum tricornutum*, 3 mA cm⁻², pH = 8, no stirring and no sedimentation time.

Figure 2: Microalgae recovery efficiency η_a as function of ECF time using different current intensities.

Conditions: (A) *Chlorella vulgaris*, (B) *Phaeodactylum tricornutum*, pH = 8, no stirring, sedimentation time = 30 min.

Figure 3: Microalgae recovery efficiency η_a as function of ECF time using different pH levels.

Conditions: (A) *Chlorella vulgaris*, (B) *Phaeodactylum tricornutum*, 3 mA cm⁻², no stirring, sedimentation time = 30 min.

Figure 4: Microalgae recovery efficiency η_a as function of ECF time at different stirring speeds.

Conditions: (A) *Chlorella vulgaris*, (B) *Phaeodactylum tricornutum*, 3 mA cm⁻², pH = 4, sedimentation time = 30 min.

Figure 5: (A & B) Microalgae recovery efficiency η_a , Al in (C & D) liquid phase and (E & F) in residual biomass measured using two different current densities.

Conditions: (A, C, E) *Chlorella vulgaris*, (B, D, F) *Phaeodactylum tricornerutum*, pH = 4,
stirring speed = 150 rpm, sedimentation time = 30 min (n=3).

Table headings

Table I: Main differences in chemical composition of freshwater and marine cultivation medium.

Table II: Microalgae recovery efficiency η_a (%) as function of additional sedimentation time for different ECF times. Conditions: *Chlorella vulgaris*, 3 mA cm⁻², pH = 8, no stirring.

Table III: Microalgae recovery efficiency η_a (%) as function of additional sedimentation time for different ECF times. Conditions: *Phaeodactylum tricornutum*, 3 mA cm⁻², pH = 8, no stirring.

Table IV: Power consumption (kWh kg⁻¹ dry weight recovered microalgae) using different current densities for *Chorella vulgaris* based on previous experiment (Fig. 2).

Table V: Power consumption (kWh kg⁻¹ dry weight recovered microalgae) using different current densities for *Phaeodactylum tricornutum* based on previous experiment (Fig. 2).

Table I

	Freshwater (mM)	Marine water (mM)
Cl	1.7	442.1
Na	1.9	338.6
Mg	1.0	80.5
Ca	2.7	9.1
K	0.3	6.4
SO ₄	1.3	40.2
Conductivity (mS cm ⁻¹)	0.8	43.0

Table II

ECF (min)	Sedimentation time (min)			
	0	10	20	30
10	16	19	19	32
20	87	88	91	91
30	88	89	92	91

Table III

ECF (min)	Sedimentation time (min)			
	0	10	20	30
10	58	56	58	60
20	53	72	78	77
30	54	76	72	78

Table IV

CD* (mA cm ⁻²)	ECF time (min)							
	10	20	30	40	50	60	70	80
1.5	5.3	8.4	2.3	1.3	1.5	1.9	2.1	2.4
3	11.3	3.6	4.1	5.7	7.0	8.3	-	-
6	13.4	9.5	14.1	-	-	-	-	-
12	25.4	34.3	-	-	-	-	-	-

* CD = current density

* - = no data available: ECF process completed

Table V

CD* (mA cm ⁻²)	ECF time (min)					
	3	5	8	10	20	30
0.6	-	-	-	0.4	0.2	0.3
1.5	-	-	1.1	0.4	0.5	0.8
3	0.4	0.4	0.5	0.5	0.8	1.7

* CD = current density

* - = no sufficient microalgae recovery achieved to calculate realistic values

Figure 1

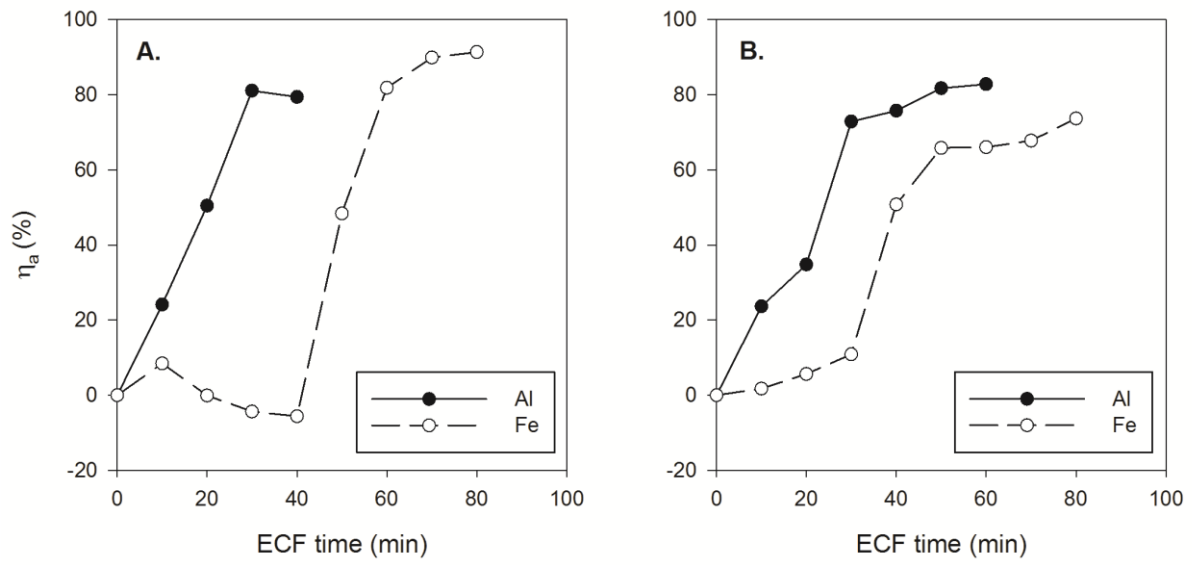


Figure 2

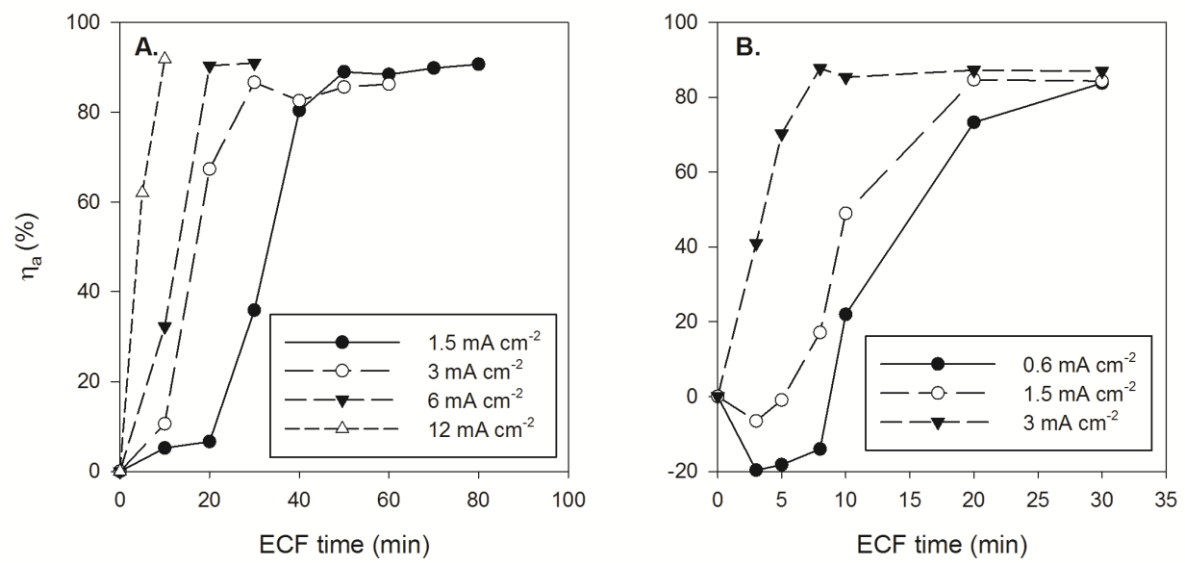


Figure 3

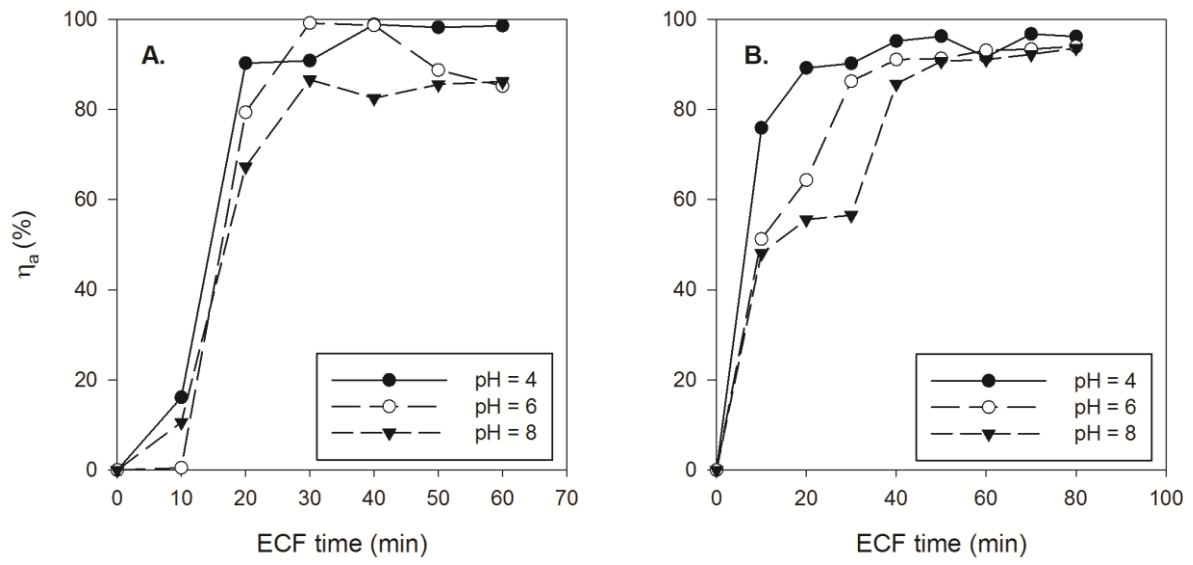


Figure 4

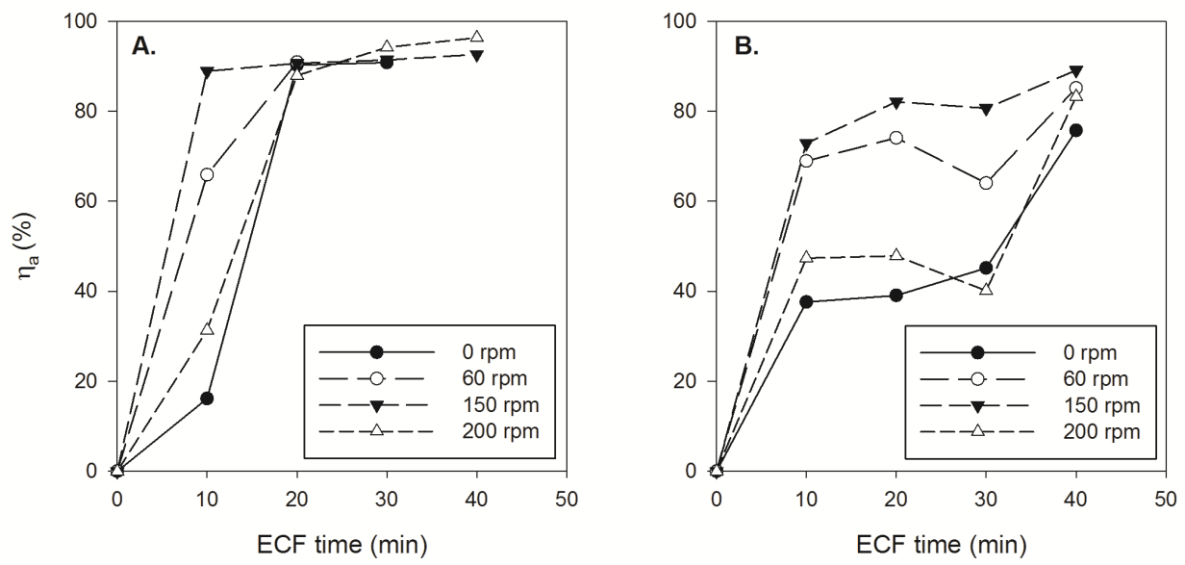


Figure 5

