

MICROALGAE BIOMASS HARVESTING BY ELECTRO-COAGULATION

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Abstract *The use microalgae biomass for the production of biofuels has received great attention in the last decades. Microalgae biofuels could be important alternative to conventional biofuels since microalgae could be produced at high rates without the need of neither arable land, potable water or competition with food. However, the high energy intensive harvesting processes are limiting the commercial production of microalgae biofuels. In this study, Electro-Coagulation (EC) was used for harvesting the freshwater microalga Chlorella vulgaris and the marine microalga Nannochloropsis sp. The results show that EC could be an alternative to the conventional harvesting processes since it is efficient and produces good quality biomass with low energy requirements.*

1. INTRODUCTION

Microalgae biomass composition allows the production of different added value compounds with applications in pharmaceutical/medical, food, cosmetic and energy industries [1].

Microalgae are able to grow without the need of arable land and potable water and therefore, could be an important alternative to conventional biofuels production, which require arable land and directly compete with food production. Additionally, microalgae cultivation allows for the fixation of green house gases.

After cultivation, the microalgae biomass has to be harvested. However, due to microalgae poor volumetric concentration, the energy requirements for the harvesting process are very high and often exceed the energy content of the microalgae biomass [2,3].

Electro-Coagulation (EC) has been proposed for wastewater treatment and showed to be an efficient technology with low energy requirements and in opposition to conventional flocculation it prevents the need of adding flocculants. Therefore, EC could be an interesting technology for microalgae harvesting.

During EC occurs the coagulation/flocculation of the microalgae followed by sedimentation or flotation, which allows for the separation. In EC an electrical current is applied through two reactive electrodes (e.g. aluminium electrodes) submerged in the microalgae suspension. The anode electrode suffers an electrolytic oxidation realising metal ions that will serve as coagulant agents for the formation of microalgae flocs. Additionally, oxygen and hydrogen microbubbles are generated due to the water oxidation and reduction [4].

In this studied EC was used for the recovery of *Nannochloropsis sp.* (a marine microalga) and *Chlorella vulgaris* (freshwater microalga) biomass. Both this microalgae have important applications for biofuel and pigment production, *Nannochloropsis sp.* can accumulate up to 53% w/w of its content in lipids (that can be used for biodiesel production) with a lipid productivity of 37.6–90.0 mg.L⁻¹.day⁻¹ [5]. The microalgae recovery efficiency of EC was evaluated under different EC operation conditions, such as: EC operation time and current density applied, for both microalgae. The performance of EC in the recovery of the marine *Nannochloropsis sp.* was compared with the recovery achieved for the freshwater *Chlorella vulgaris* and the energy required for both separations, was analysed.

2. MATERIALS AND METHODS

2.1. Microalgae cultivation

The Electro-Coagulation (EC) recovery studies were performed using the marine microalga *Nannochloropsis sp.* (NANNO-2 from SERI algotec) and the freshwater *Chlorella vulgaris* (INETI/58).

Nannochloropsis sp. was grown in modified GPM medium with the following composition per litre: 0.200 g KNO₃, 0.038 g K₂HPO₄, 0.034 g H₃BO₃, 0.030 g Na₂EDTA, 4.30 mg MnCl₂.4H₂O, 1.45 mg FeCl₃.6H₂O, 0.30 mg ZnCl₂, 0.13 mg CoCl₂.6H₂O in 75% of filtered seawater (GF/C filter Ø 1.2 lm pore) and 25% of de-ionised water.

Chlorella vulgaris Beijerinck (INETI 58) was grown in a medium adapted from Gouveia et al. (1996) [6] in a 50 mM PBS solution.

The microalgae was grown firstly in 1 L glass bubble column photobioreactors (PBRs) and then transferred to 10 L plastic bubble column PBRs.

The growth conditions included bubbling filtered air at 1 vvm ($\text{mL L}^{-1} \text{min}^{-1}$) at a constant temperature of $25 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$ and under $25.7 \text{ } \mu\text{E} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ light intensity by fluorescence lamps (Philips TL-D 36 W/54-765). The lights were positioned behind the PBR's at a distance of 20 cm, and the light intensity was measured at the surface of the vessels.

2.2. Electro-Coagulation experiments

All EC tests were performed with 500 mL of microalgae samples collected from the 10 L PBRs and the average microalgal biomass concentration was around 2.5 g dry weight.

The EC system consisted of two reactive aluminium electrodes connected to an external DC power source. All the EC tests were performed under batch conditions at room temperature in a glass flask of 600 mL filled with 500 mL of microalgae culture. The electrodes were coupled at the distance of 1 cm to each other and consisted of two parallel flat metal plates of aluminium of $2 \times 7.5 \text{ cm}^2$. The anode and cathode were connected to a DC power supply (model HY3005D, MASTECH) to control the current density applied (current densities from 3.3 to $33.3 \text{ mA} \cdot \text{cm}^{-2}$ were applied) during the EC operation period (from 5 to 50 min). Throughout EC operation the microalgae suspension was stirred using a magnetic stirrer at 150 rpm (model HEIDOLFH). This agitation was stopped immediately after EC current ceased to allow microalgae sedimentation/flotation.

To determine the recovery efficiency of the microalgae biomass, samples of 1 mL were collected at 30 min and 24 h after stopping the EC process. The samples were collected very carefully without disturbing the suspension; the tested variation was below 0.3% of EC efficiency. The optical density of the samples was measured and compared with the optical density of the culture before being subjected to EC (both measured at 540 nm in a UV-VIS spectrometer Hitachi-2000).

The recovery efficiency was calculated as following:

$$\text{Microalgae recovery efficiency} = (\text{OD}_0 - \text{OD}_{\text{st}}) / \text{OD}_0$$

where: OD_0 is the optical density of the suspension before the EC treatment and OD_{st} is the optical density at the chosen sedimentation time (st) after EC treatment.

3. RESULTS AND DISCUSSION

Electro-Coagulation EC operation depends on several parameters such as: the electrodes (material, design, separation distance), the current density applied, operation time, temperature, pH and conductivity of the microalgae suspension. In this study all the EC tests were performed at constant temperature of $25 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$ and two microalgae were tested under

different operation conditions. The *Nannochloropsis sp.* growth medium had a conductivity of 40-45 ms while the *Chlorella vulgaris* medium had a conductivity of 6.8 ms.

Table 1 depicts the results achieved for the recovery of *Nannochloropsis sp.* after 30 min of sedimentation following the EC operation. The maximum recovery efficiency was obtained using 16.67 mA.cm⁻² of applied current and 10 min of operation time (after 30 min of sedimentation). However, the results showed that an increase from 8.33 to 16.67 mA.cm⁻² resulted only in an increase of 1.4% of the recovery efficiency, which may not justify the increment in the energy required. Ten minutes of an applied current of 8.33 mA.cm⁻² were sufficient to achieve a recovery efficiency of 96.1%, which is higher than results reported in the literature [4].

		<i>Nannochloropsis sp.</i>	
Current density (mA.cm ⁻²)	Time (min)	Recovery Efficiency after 30 min of sedimentation (%)	Recovery Efficiency after 24 hours of sedimentation (%)
0	0	0.0	45.8
3.33	10	70.9	98.4
8.33	5	77.4	96.7
	10	96.1	99.7
	15	97.2	99.9
16.67	10	97.5	99.2

Table 1. Recovery efficiencies of *Nannochloropsis sp.* using different EC operation conditions

Table 2 depicts the results achieved for the recovery of *Chlorella vulgaris* after 30 min of sedimentation. For this microalga it was not possible to achieve removal efficiencies higher than 88.7%, even with current densities as high as 33.33 mA.cm⁻² and operation times higher than 30 min. Higher removal efficiencies could be achieved with higher sedimentation times.

		<i>Chlorella vulgaris</i>	
Current density (mA.cm ⁻²)	Time (min)	Recovery Efficiency after 30 min of sedimentation (%)	Recovery Efficiency after 24 hours of sedimentation (%)
0	0	29.9	81.6
8.33	15	52.8	87.6
	20	65.2	85.6
	30	78.1	90.9
	50	81.5	91.8
	30	87.3	94.7
16.67	30	87.3	94.7
33.33	30	88.7	94.9

Table 2. Recovery efficiencies of *Chlorella vulgaris* using different EC operation conditions

Comparing the results achieved for both microalgae is possible to conclude that to achieve recovery efficiencies of *Chlorella vulgaris* similar to the ones attained for the *Nannochloropsis sp.* more energy is required. Figure 1 show the energy used to achieve each

EC microalgae recovery. It is possible to conclude that to obtain a recovery efficiency of 80% the energy required for *Nannochloropsis sp.* is two folds lower (around 0.03 kWh.m⁻³ of microalga suspension) than for *Chlorella vulgaris* (around 1 kWh.m⁻³ of microalga suspension). This result can be explained due to the high difference between the microalgae suspensions conductivity, which is more than six times lower for *Chlorella vulgaris* (a freshwater microalga) comparing with the marine microalga *Nannochloropsis sp.* Therefore, the *Chlorella vulgaris* suspension imposes higher resistance to the electron conduction during EC, increasing the energy required for higher recovery efficiencies. This can be improved by adding salt to the suspension before EC treatment, increasing conductivity.

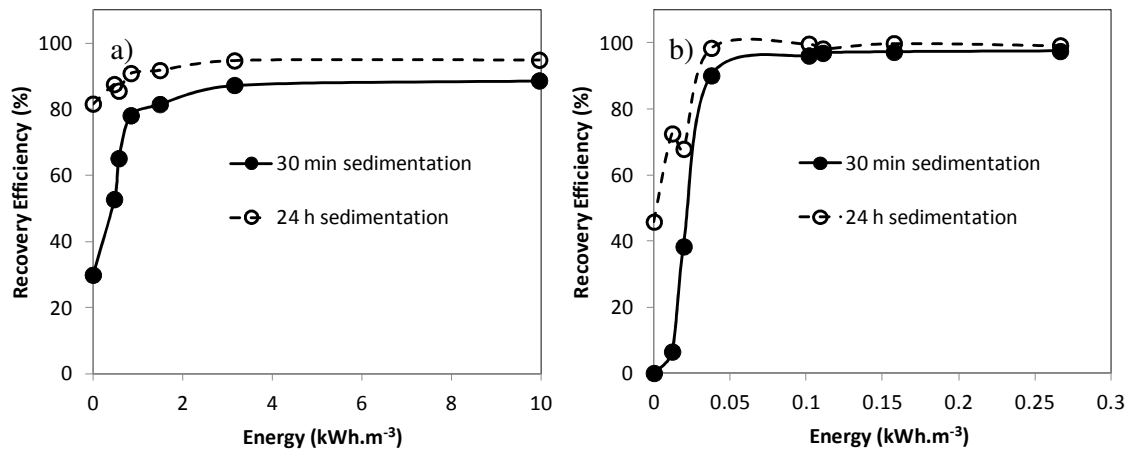


Figure 1. EC microalgae biomass recovery efficiency vs energy demand for each EC trial (after 30 min and 24 h of sedimentation time) (a) for *Chlorella vulgaris* (b) for *Nannochloropsis sp.*

Microalgae harvesting is conventionally performed by centrifugation, which can consume up to 8 kWh.m⁻³. Therefore, the combination of EC with conventional centrifugation will decrease significantly the energy demand of the *Nannochloropsis sp.* harvesting process [7]. Lower energy efficiencies will be achieved for *Chlorella vulgaris*, however with an increase in the salt content it will be possible to increase EC performance.

For the *Nannochloropsis sp.* the authors had previously demonstrated the capacity of this microalga to accumulate 45% w/w of its content in oils and the fatty acid oil composition of the oil extracted after EC treatments maintained an adequate profile for biodiesel production [7,8].

4. CONCLUSIONS

Electro-Coagulation could be an alternative to the conventional harvesting of microalgae biomass since it is efficient, with low energy requirements and prevents the need of adding flocculants that may compromise the biomass quality. The EC allowed to recover more

than 97% of the marine *Nannochloropsis sp.* and more than 80% of the freshwater *Chlorella vulgaris*, spending less than 0.06 and 1 kWh.m⁻³, respectively.

REFERENCES

- [1] L. Gouveia, *Microalgae as a Feedstock for Biofuels*, Springer Briefs in Microbiology, Springer, Heidelberg, Germany, (2011).
- [2] P.T. Pienkos and A. Darzins, *The promise and challenges of microalgal derived biofuels*, *Biofuels, Bioproducts and Biorefining*, 3 (2009), pp. 431–440.
- [3] R.H. Wijffels and M.J. Barbosa, *An outlook on microalgal biofuels*, *Science*, 329 (2010), pp. 796–799.
- [4] D. Vandamme, S.C.V. Pontes, K. Goiris, I. Foubert, L.J.J. Pinoy and K. Muylaert, *Evaluation of electro-coagulation–flocculation for harvesting marine and freshwater microalgae*. *Biotechnology and Bioengineering*, 108 (2011), pp. 2320–2329.
- [5] T.M. Mata, A.A. Martins and N. Caetano, *Microalgae for biodiesel production and other applications: a review*, *Renewable and Sustainable Energy Reviews*, 14 (2010), pp. 217–232.
- [6] L. Gouveia, V. Veloso, A. Reis, H. Fernandes, J. Novais and J. Empis, *Evolution of pigment composition in Chlorella vulgaris*, *Bioresource Technology*, 57 (1996), pp. 157–159.
- [7] C.T. Matos, M. Santos, B.P. Nobre and L. Gouveia, *Nannochloropsis sp. biomass recovery by Electro-Coagulation for biodiesel and pigment production*, *Bioresource Technology*, 134 (2013), pp. 219–226.
- [8] B.P. Nobre, F.V. Castillejos, B.E. Barragán, A.C. Oliveira, A.P. Batista, P.A.S.S. Marques, R.L. Mendes, H. Sovová, A.F. Palavra and L. Gouveia, *Biorefinery from Nannochloropsis sp. microalga – extraction of microalgal oils and pigments and biohydrogen production from biomass leftover*, *Bioresource Technology*, 135 (2013), pp. 128 – 136.

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