Algal Research 25 (2017) 1–11

Contents lists available at ScienceDirect

Algal Research

journal homepage: www.elsevier.com/locate/algal

Harvesting of microalgae *Chlorella vulgaris* using electro-coagulation-flocculation in the batch mode

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ARTICLE INFO

Article history:
Received 9 November 2016
Received in revised form 27 January 2017
Accepted 16 March 2017
Available online xxxx

Keywords:
Microalgae harvesting
Electro-coagulation-flocculation
Batch mode
Microalgal pigments
Microalgal lipids

ABSTRACT

The aim of this study was to evaluate the harvesting of microalgae *Chlorella vulgaris* by electro-coagulation-flocculation (ECF) using aluminum and iron electrodes, assess the mechanisms responsible for microalgae recovery, quantify the metal contamination in the effluent and biomass, analyze power requirements, and investigate the effect of ECF on lipid and pigment content in the biomass. The influence of six operating parameters (electrode material, sedimentation time, current density, stirring speed, initial pH (pH_i) and inter-electrode distance) on the harvesting efficiency was tested. A specific strategy involving flotation and pH-controlled ECF experiments was developed to identify the prevailing mechanism of harvesting: adhesion on flocs was shown to be negligible; flotation contributed to a maximum of 36.6% of microalgae recovery; zeta potential highlighted that the main mechanism responsible for microalgae recovery was charge neutralization at pH_i 4 and 6, and sweep flocculation at pH_i 8. The most energy saving conditions for the harvesting of *Chlorella vulgaris* involved aluminum electrodes, and 60 min electrolysis with a current density of 2.9 mA/cm^2, pH_i 4, stirring speed 250 rpm and an inter-electrode distance of 1 cm. Economic and competitive energy input (1 kWh/kg microalgae) could be achieved by adding 1.5 g/L NaCl. In addition, ECF did not affect significantly the amount of microalgal lipids and pigments.

1. Introduction

Microalgae are promising resources for bio-fuel production, as they are not exposed to many of the inconveniences of 1st and 2nd generation bio-fuels [1]. These microorganisms produce oils by photosynthesis and are approved worldwide as a source of biodiesel that can satisfy the global need for renewable and green fuels [2]. They can also play a key role in alleviating the effects of anthropic pollution. For example, they can capture CO_2 to reduce atmospheric pollution and reduce the effects of global warming and climate change. In addition to lipids as an energy source, microalgae are also able generate coproducts of great pertinence to the food, pharmaceutical, and the chemical industries, such as proteins, pigments and polysaccharides [3].

One the challenges of 3rd generation bio-fuels based on microalgal biomass is to effectively recover the tiny microalgal cells from highly dilute solutions [4]. Regarding the small size of these cells (5–30 μm), their physical separation from the culture medium using filtration techniques is difficult. Many separation processes have been proposed for recovering microalgae, such as centrifugation [5], flocculation [6,7], filtration [8], flotation [9,10], ultrasound [11], pH adjustment (at high pH about 11 [12]), and electrolysis [4]. Centrifugation is a typical method that is widely used for harvesting microalgae, but it is time consuming, complex and expensive [13]. Concentrating microalgae 30–50 times by coagulation-flocculation and gravity sedimentation before applying centrifugation, strongly lowers the energy demand for harvesting [14,15]. In filtration process, filter clogging is the most common issue in harvesting of microalgae; clogging considerably raises head loss and needs frequent maintenance [16]. Alternatively, coagulation-flocculation requires flocculating agents, but these may have associated environmental impacts, as these flocculating agents in excess may directly cause secondary pollution, or act indirectly through the formation of by-products. Another disadvantage is the possibility of changing the profile of biomass fatty acids, in this case the type of flocculating agent determines the extent of this change [3].

Some new studies have proposed economic techniques for the recovery of microalgae as substitutes to flocculation and centrifugation, which are the conventional methods of recovery, but are too energy intensive. For example, Xu et al. [17] worked on the harvesting of two microalgae species using Fe_3O_4 and found that it is possible to regenerate and use these nanoparticles. Vandamme et al. [18] also worked on a pre-concentration method, called auto-flocculation, in which increasing pH till 11 caused flocculation as a result of magnesium precipitation.

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http://dx.doi.org/10.1016/j.algal.2017.03.015
2211-9264/

Other research studies investigated the implementation of microbial flocculants as substitutes for the known conventional chemicals [19,20].

An alternative technique consisted in recovering marine microalgae using electrolysis-based coagulation and flotation methods that markedly decreased the electric energy consumption [10]. Actually, several studies investigated the use of electro-coagulation-flocculation (ECF) for the elimination of microalgae from drinking and wastewater [21–23]. In fact, the use of ECF for recovering microalgal biomass has been intensively evaluated in these papers; however, microalgal densities were much lower than those found in microalgal production systems [4]. Even though ECF has been reported to be adequate for harvesting microalgae cultivated for bio-fuel production, another key issue is that the mechanisms of microalgae harvesting by ECF are less precisely established than in centrifugation. Compared to coagulation-flocculation with Fe^{3+} or Al^{3+} salts, ECF has the advantage that no counter anions, such as chlorides and sulfates, are added to water. The drawback is that ECF requires the electrolytic dissolution of the sacrificial anode, which requires electric power. As a result, electrolytic reactions occur both at the anode and the cathode during ECF [4]. Using an aluminum anode, one gets:

$$Al \rightarrow Al^{3+} + 3e^-$$

$$xAl^{3+} + yOH^- \rightarrow Al_x(OH)_y^{z+}$$

The speciation of the aluminum hydroxides formed during ECF is extremely variable and is greatly affected by pH [4], but $Al(OH)_3$ and AlOOH precipitates dominate when pH is between 4 and 10. Using an iron anode, the same behavior can be observed, with the particularity that Fe (II) and Fe (III) species can be obtained [24]:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_{2(s)}$$

or

$$Fe \rightarrow Fe^{3+} + 3e^-$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_{3(s)}$$

The precipitation of metal hydroxide plays the same role as in conventional coagulation: first, *charge neutralization* by cations, and then *sweep coagulation* due to precipitation and floc formation (which means an enmeshment in the precipitate). But another major advantage of ECF is that water reduction at the cathode prevents pH decrease and releases H_2 in the form of tiny microbubbles, which promotes the flotation of the flocs formed by precipitated hydroxides, leading to a combined coagulation-flotation mechanism for harvesting microalgae.

Finally, the purpose of this work is to investigate the applicability and the pros and cons of the harvesting of microalgae *Chlorella vulgaris* from its culture medium using electro-coagulation-flocculation. For this purpose, the influence of the most important operating variables of the ECF process on the harvesting efficiency will be evaluated and power requirements will be estimated. The respective effects of the various mechanisms able to favor microalgae harvesting in ECF will be assessed, while the impact of ECF on microalgal lipid and pigment contents will be measured. Finally, the pollution of microalgal biomass and process water by metal cations dissolved from the sacrificial anode will also be estimated.

2. Materials and methods

2.1. Microalgal species (Chlorella vulgaris)

All the experiments were performed with the freshwater chlorophyte *Chlorella vulgaris* (Fig. 1), which is a spherical microscopic cell of 2–10 μm diameter. *C. vulgaris* is an interesting species for the production of microalgal biomass for food, pharmaceuticals, cosmetics or bio-fuel, and is presently thoroughly studied. *Chlorella vulgaris* biomass was kindly provided by *Algosource Technologies* (France). Experiments were performed using a modified Bold Basal Medium with 3-fold nitrogen and vitamins (3N-BBM + V) prepared from pure chemicals dissolved in distilled water to simulate culture conditions of *Chlorella vulgaris*. For 1 L medium, the following components were added: 0.75 g $NaNO_3$, 0.025 g $CaCl_2 \cdot 2H_2O$, 0.075 g $MgSO_4 \cdot 7H_2O$, 0.075 g $K_2HPO_4 \cdot 3H_2O$, 0.175 g KH_2PO_4, 0.025 g NaCl, 6 mL of trace elements solution, 1 mL of both vitamin B1 and vitamin B12.

The trace elements solution was prepared by adding to 1000 mL distilled water, 0.75 g Na_2EDTA and the minerals in exactly the following sequence: $FeCl_3$ $6H_2O$ (97 mg), $MnCl_2$ $4H_2O$ (41 mg), $ZnCl_2$ (5 mg), $CoCl_2$ $6H_2O$ (2 mg) and Na_2MoO_4 $2H_2O$ (4 mg). Vitamin B1 was prepared by dissolving 0.12 g thiaminhydrochloride in 100 mL distilled water and, then, filtered sterilely. Vitamin B12 was prepared by dissolving 0.1 g cyanocobalamin in 100 mL distilled water; then, 1 mL was taken from this solution and added to 99 mL distilled water and, finally, the solution was filtered sterilely.

The ECF experiments were carried out at a microalgal concentration of 0.5 g/L.

2.2. ECF experiments

All ECF experiments were carried out at room temperature in a vessel filled with 1 L microalgal broth, and agitation was carried out by a magnetic stirrer at a constant agitation speed of 250 rpm. ECF was conducted in the galvanostatic mode by the help of a 30 V-10 A generator (ELC, France), while the cell voltage (U) was recorded (it ranged from 14.0 V to 29.5 V depending on the operating conditions) in order to calculate the electric energy consumption. The experimental setup is shown in Fig. 2. Monopolar aluminum or iron rectangular electrodes of identical dimensions (8.0 cm × 6.5 cm), were used as anode and cathode material. Electrodes were rinsed with acetone and a 0.01 N HCl aqueous solution to eliminate deposits, and then weighed before and after each experimental run. pH was measured by using a pH meter (*Mettler Toledo*, Switzerland). Flotation of the flocs containing microalgae appears as the main mechanism of harvesting in Fig. 2. This originated from the release of H_2 gas at the cathode and, to a lesser extent, O_2 gas at the anode.

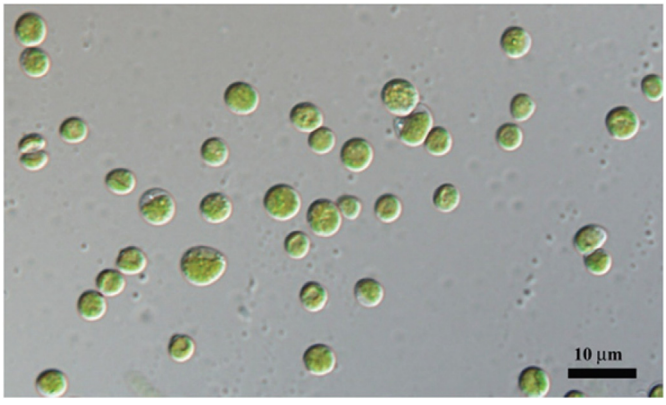

Fig. 1. Microscope image of the microalgae species, *Chlorella vulgaris* at ×100 magnification.