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Harvesting green algae from eutrophic reservoir by electroflocculation and post-use for biodiesel production

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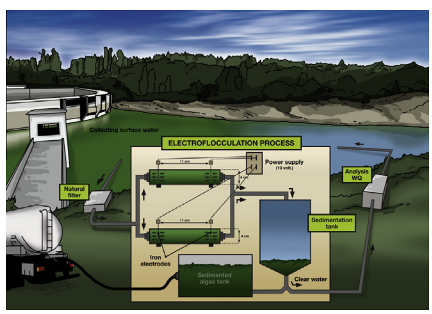
HIGHLIGHTS

- Harvesting by electroflocculation is effective with green algae mixture in freshwater.
- Cyanobacterial blooms can be solvent without fluvial ecosystem damage.
- A real pilot plant can be design from these results.

GRAPHICAL ABSTRACT



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ABSTRACT

Each year there are more frequent blooms of green algae and cyanobacteria, representing a serious environmental problem of eutrophication. Electroflocculation (EF) was studied to harvest the algae which are present in reservoirs, as well as different factors which may influence on the effectiveness of the process: the voltage applied to the culture medium, run times, electrodes separation and natural sedimentation. Finally, the viability of its use to obtain biodiesel was studied by direct transesterification. The EF process carried out at 10 V for 1 min, with an electrode separation of 5.5 cm and a height of 4 cm in culture vessel, obtained a recovery efficiency greater than 95%, and octadecenoic and palmitic acids were obtained as the fatty acid methyl esters (FAMEs). EF is an effective method to harvest green algae during the blooms, obtaining the greatest amount of biomass for subsequent use as a source of biodiesel.

1. Introduction

The eutrophication process is a specific consequence of water pollution caused by the increase of nutrients, particularly phosphorus and nitrogen (Paerl et al., 2011; Khan et al., 2014). The increase of these nutrients allows the algae population to improve their growth and development, especially when weather conditions are favorable such as temperature (Xue et al., 2005) and solar radiation (Liu et al., 2011). All this leads to algal blooms, affecting the coloration of the water, especially when green algae are present, and implying a negative impact on the ecosystem of rivers, lakes, reservoirs, etc. (Smith, 2003), as well as some alterations in the physical–chemical conditions (Alvarez Cobelas and Arauzo, 1994; Lee et al., 2012).

Nowadays, eutrophication is one of the effects triggered by the population growth and economic development (Khan et al., 2014) affecting 53% of lakes and reservoirs in Europe (ILEC, 1994). For this

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reason and the implications that it involve, water managers and the proper authorities on issues of nature conservation are concerned about how to solve this phenomenon, specifically if we take into account that in many algal blooms and eutrophication processes there are toxic cyanobacteria, whose environmental effects are worse, even to human health (Kim et al., 2010; Xuguang et al., 2011), as is the case of *Microcystis* sp., which has not solution when bloom occurs.

One possible solution is to harvest algae from the medium (lakes, reservoir, estuaries, coasts, etc.). There are several methods of harvesting algae such as sedimentation, this method of particle separation is popular in wastewater treatment, and is relatively inexpensive to install and operate and it does not require specialized operations (Timmons et al., 2002). According to Pienkos and Darzins (2009) centrifugation is very expensive in an integrated system producing lower-value products, such as algal oils for biofuel production. There are several recent studies in others techniques such as the coagulation, flocculation, electrocoagulation and electroflocculation process, such as the research of Matos et al. (2013), who studied Electrocoagulation as a process to harvest the marine *Nannochloropsis* sp. microalga; Wang et al. (2012) investigated the combination of algaecide and flocculants to control cyanobacterial blooms. Some researchers have separated microalgae by electroflocculation, such as Xu et al. (2010) who developed an electroflocculation technology for harvesting microalgae (*Botryococcus braunii*). Lee et al. (2013) concluded in their study that electroflocculation is potentially a low cost *Tetraselmis* sp. microalgal harvesting technique; and Alfafara et al. (2002) who combined the electroflocculation with electrocoagulation. Highlight the researched carried out by Liang et al. (2008) who tried to eliminated the microcystin-LR during the cyanobacterial inactivation by electooxidation, obtaining more than 98% removal for total.

On the other hand, the microalgae are been recognized as a source for obtaining biodiesel (Phukan et al., 2011) and the transesterification represents a key process for biodiesel production (Griffiths et al., 2010). Particularly, vegetable oils, after transesterification with methanol produce fatty acid methyl ester (FAME) as the precursor to biodiesel and glycerol as a by-product (Demirbas and Demirbas, 2010).

Recent studies carried out by the Regional Government of Galicia concluded that there are eutrophication and algae blooms in A Baxe reservoir (Augas de Galicia, 2011). The aim of this research is to harvest the green algae without damage to the ecosystem. This means that chemical flocculants, which remain in the aquatic ecosystem affecting the organisms that inhabit, cannot be used. The electroflocculation technique (EF) was selected to apply it separately and without affect natural water composition. Therefore, in this investigation the microalgae present in water samples from "A Baxe" reservoir (with no isolated strains) have been cultivated.

Different factors which may influence the effectiveness of the process were evaluated, specifically, the voltage applied, runs, distance between electrodes and the height of the culture column, as well as EF/gravity sedimentation effectiveness at different temperatures. Finally, the algae harvested in this process have been used as a direct source for the biodiesel production, for alae valorisation.

2. Methods

2.1. Microalgae

Water samples collected in March of 2014 from the "A Baxe" reservoir (Umia River, Northwest of Spain) were used in the study. The microalgae were grown in a medium with two different solutions: one of macronutrients ($NaNO_3$, KH_2PO_4, $MgSO_4 \cdot 7H_2O$ and Na_2CO_3) and the second solution was micronutrients ($MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$, H_3BO_3, $MnCl_2 \cdot 4H_2O$, $ZnCl_2$, $FeCl_3 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, $Na_2MoO_4 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$ and $Na_2EDTA \cdot 2H_2O$) provided by the ECIMAT (Estación de Ciencias Mariñas de Toralla, University of Vigo, Spain). The experimental work was carried out in six 250 ml Erlenmeyer flasks. The microalgae from the reservoir were grown for 20 days at 28 °C, with constant stirring (Magnetic Mini-Stirrer 220/230 V) and a light cycle of 24:0 Light/Dark. There were three different algae growing together: *Scenedesmus* spp. (24%), *Kirchneriella* sp (1%). and *Microcystis* sp. (75%). Cultures raised to a density of 10^6 cell ml^{-1}.

2.2. Harvesting by electroflocculation

The EF experiments were performed with a power source (DC Power Supply, FREAK EP-603) in three different vessels (1000; 250 and 150 ml) with a wall thickness of 2 mm. Different factors that could influence the process of collecting the algae by EF were evaluated: (1) separation of iron electrodes (Lee et al., 2013). The distance between the two electrodes was varied in order to evaluate which is the most effective for harvesting green algae. To this purpose, the height of the culture column was kept constant (4 cm). (2) The column height of culture (h), (3) natural sedimentation, (4) application of different current applied (Ilhan et al., 2008; Vandamme et al., 2011), and (5) run times of the electric current (Matos et al., 2013).

Measurement runs have been made three times each. For specific details of each process see Figs. 1–3. As was carried out each EF processes, the decisions were made based on the best results obtained in the previous process. The most efficient separation between electrodes (Test No. 1) was chosen and fixed for the next tests where the effect of the height of the culture column were evaluated (Test No. 2). For this reason, subsequent experiments were carried out with the best results obtained in previous test.

The iron electrode plate had an area of 2×9 cm and a thickness of 2 mm. Two iron electrode plates were placed along two opposite walls in the vessels and were submerged 7 cm. When these kinds of electrodes are used, the following reactions occur (Ilhan et al., 2008):

At the cathode

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

and at the anode

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

The distance between cathode and anode was studied during the process of EF number 1 (Fig. 1) and it varied depending on the vessels used. In the second test, different water column heights were evaluated through the variation of culture volumes according to Fig. 2. The influence of different electric current intensities, as well as the natural sedimentation of algae without electricity were evaluated at 8 and 22 °C. On the other hand, different run times of this electric current were assessed in the third test (Fig. 3).

2.3. Microalgae biomass characterisation

Cell growth was measured by means of absorbance of the suspension at 690 nm in accordance to Becker (1994) with a digital spectrophotometer Spectro 22 (Labomed, USA). Correlations between absorbance and cell concentration were previously established by a polynomial equation as:

$$y = 0.0011x^2 + 0.0113x - 0.012 \, (R^2 = 0.9991, P < 0.05)$$