Bioresource Technology 204 (2016) 152–156

Contents lists available at ScienceDirect

Bioresource Technology

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

Pellets valorization of waste biomass harvested by coagulation of freshwater algae

Ángeles Cancela [a], Ángel Sánchez [a], Xana Álvarez [b,*], Alejandro Jiménez [c], Luis Ortiz [b], Enrique Valero [b], Paloma Varela [c]

[a] Chemical Engineering Department, Industrial Engineering College, University of Vigo, Campus Lagoas-Marcosende s/n, 36310 Vigo-Pontevedra, Spain
[b] Department of Natural Resources and Environment Engineering, E E. Forestal, University of Vigo, Campus A Xunqueira s/n., 36005 Pontevedra, Spain
[c] E E. Forestal, University of Vigo, Campus A Xunqueira s/n., 36005 Pontevedra, Spain

HIGHLIGHTS

- The blooms of green algae can be reduced by using tannins from forest waste.
- Tannins of *Eucalyptus globulus* bark were a suitable coagulants of freshwater algae.
- Waste biomass from freshwater algae can be used as fuel by their pelletization.

ARTICLE INFO

Article history:
Received 29 October 2015
Received in revised form 30 December 2015
Accepted 4 January 2016
Available online 7 January 2016

Keywords:
Renewable energy
Pellet
Tannins
Eucalyptus globulus
Freshwater algae

ABSTRACT

There is a comparison of different coagulants: calcium chloride (20, 60, 120 and 180 mg/L); sodium alginate (10 and 20 mg/L) and tannins of *Eucalyptus globulus* bark (10 and 20 mg/L) in order to make the most of each method. The results show that 20 mg/L of tannin achieved a recovery efficiency of 95.35 ± 1.16, sodium alginate 90.49 ± 0.53 and 84.04 ± 2.29 for calcium chloride. Taking into account the economic side of the coagulants, obtaining tannins is a profitable process. Bark is waste biomass obtained in the forestry process; therefore it does not involve extra costs. Finally, the feasibility of making pellets from harvested algae was studied, and the results suggest that waste biomass pellets may be used as fuel in boilers in a mixture <54% with other waste sources as *Eucalyptus* g. branches.

1. Introduction

Unfortunately, freshwater algae have more influence on the environment than ecological benefit for the biodiversity of fluvial ecosystems. The eutrophication of rivers, reservoirs, lakes etc., is one of the main effects of high algae concentration, and affects different aspects of their physical, chemical, biological and ecological characteristics (Zamparas and Zacharias, 2014). A special case are cyanobacteria, due to their effect on quality of drinking water, as Augas de Galicia (2011) identified in the study area of this research (Galicia, Spain).

There are comprehensive research works on freshwater microalgae. They analyze different aspects about energy applications such as cultivation conditions and growth (Ashokkumar et al., 2014; Yang et al., 2012), harvesting methods (Xu et al., 2007; Lin et al., 2015), raw material of biodiesel (Abou-Shanab et al., 2011), biogas (Mussgnug et al., 2010), bioethanol synthesis (John et al., 2011) and biohydrogen (Dasgupta et al., 2015).

However, these studies have been based on species with a high energetic potential in order to obtain profitable processes. On the other hand, some researchers have obtained isolated strains of microalgae from specialized laboratories (Zeng et al., 2012), while other studies were collected from water samples from eutrophic environments and, subsequently isolated as single species (Ashokkumar et al., 2014) for further analysis. But none of them has focused on the set of blue-green algae growth in river ecosystems just as microalgae are in their natural habitat.

In the process of harvesting algae, many studies have been carried out about flocculation, coagulation and electroflocculation. The last method was analysed by the authors in a previous research, as well as the feasibility of green algae as feedstock to produce biodiesel. Now, in order to advance on understanding

* Corresponding author. Tel.: +34 986 801959.
E-mail address: giaf4_5@uvigo.es (X. Álvarez).

http://dx.doi.org/10.1016/j.biortech.2016.01.002
0960-8524/

the problems increasingly affecting river ecosystems, other alternatives were studied.

We have specifically studied the coagulation of algae from a reservoir using tannins of bark from *Eucalyptus globulus*. This species is one of the main forest species in Galicia, representing 27% of total wood volume (Vázquez et al., 2008), and its bark is separated as a waste product and used as fuel. In order to compare the coagulant potential of Eucalyptus bark, sodium alginate and calcium chloride as coagulants were used, too. Tannins are complex polymers, which can be classified in condensed tannins (found in the wood of woody species) and hydrolysable tannins. They present a slight characteristic smell, a bitter and astringent taste, and a color from yellow to dark brown. Tannins have been used for tanning animal skins, but many of them have been used as flocculants, especially in water treatment with the advantage that it is not necessary coagulants or flocculants (Wilderer, 2004). The use of tannins as a coagulant, was tested for surfactants elimination in municipal wastewater, obtaining very good results (Sánchez-Martín et al., 2010). They were used for microalgae harvesting from wastewater treatment too (Gutiérrez et al., 2015). But most of these studies investigated its use with a chemical modification, as Wang et al. (2013) who used a modified larch tannin to flocculate *Microcystis aeruginosa*.

Finally, as a form of energy recovery, the possibility of obtaining pellets from the harvested algae biomass was analysed in this article. For this purpose, the products from the combustion of these pellets, resulting from the mixture of freshwater algae, were analyzed.

2. Methods

2.1. Microalgae

Scenedesmus sp., *Kirchneriella* sp., and *M. aeruginosa* algae were collected by sampling from a reservoir of Northwest Spain. This sample was taken in March of 2015. After that, this sample with algae was cultivated in a polyethylene 50 L bag photobioreactor. The culture medium used was a mixture of two 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 culture went on for twenty days, with 14:10 light/dark cycles and 23 ± 3 °C of temperature. Cell growth was measured by means of the algal suspension absorbance at 690 nm. The absorbance values were measured every day at the same time slots with SPECTRO 22 Digital Spectrophotometer. Microalgae were identified microscopically and the cell count was obtained in a Neubauer chamber using an optical microscope (BX 51, Olympus, Japan) with each specie in order to associate absorbance value with the proportion of the different microalgae present in the culture. The concentration of algae (*Scenedesmus* sp., *Kirchneriella* sp., and *M. aeruginosa*) at the end of the culture process was 2.76×10^7 cells/mL. The pH was 7.7. All experiments in this research were carried out from one single harvest.

2.2. Separation method

Coagulation may be induced by adding chemical species to the culture, both inorganic and organic compounds. This process shows a lower energy requirement than other separation techniques and it increases biomass concentration. Coagulation experiments were made in 0.5 L glass vessels. Considering all inorganic and organic coagulants, and taking into account that $AlCl_3$, $FeCl_3$, cationic starch and chitosan have been well studied, in this experiment the coagulants used were calcium chloride, sodium alginate, as well as a tannin, which was obtained of eucalyptus bark.

After the coagulant addition, mixtures were stirred in two steps. In the first, rapid mix at 200 rpm for 1 min, in order to distribute the coagulant through the water. In the second step, coagulation occurred, so a low speed mixture at 50 rpm for 3 min was necessary. The concentrations of inorganic coagulant, calcium chloride, were 20, 60, 120, 180 mg/L. Concentrations of sodium alginate, the organic coagulant, were 10 and 20 mg/L, as well as of tannins. Absorbance values were measured at 550 nm from a digital spectrophotometer Spectro 22 (Labomed, USA), at time intervals of 5 min for a one-hour period. Then, the time distribution of measures was changed to 120, 180 and 1440 elapsed minutes. All experiments were performed in triplicate, for each time environment, at pH 7.7. Finally, environmental conditions were analysed with natural sedimentations at 22 ± 0.5 °C, in order to compare these results with the coagulants used.

To compare coagulants, the recovery efficiency of microalgae for different samples, at different times, was a determining factor. The efficiency (biomass recovery percentage) was calculated from the absorbance data. Absorbance samples were taken from the superior part of the vessel.

Microalgae recovery efficiency (RE) was determined, as:

$$\text{Recovery efficiency} = \frac{Ab_i - Ab_f}{Ab_i}$$

where Ab_i is the initial absorbance to the start and Ab_f is absorbance at time t.

2.3. Harvesting by tannin

Tannins that have been used as coagulants in this paper were obtained in the laboratory from *E. globulus* bark. Two different extraction methods were used, Soxhlet extraction and stirring and heating. The solvent extractor was pure water (Varela et al., 2015).

2.4. Biomass methods

Biomass produced during the growth period was harvested by coagulation, using both inorganic and organic compounds and tannins as coagulants. From this dry biomass, the feasibility of its use for pellet manufacturing was studied. A manual pellet press was used to obtain 12 mm diameter and 15 mm length pellets. Pellet characterization was based on moisture content [UNE 14774-3: ES (2010a)], heating power, volatile matter (UNE 15148: ES (2009)), ash content [UNE 141775: ES (2010b)], and fixed carbon (calculated by difference). The heating power was obtained (Parr 1261 calorimetric bomb) according to UNE 14918 (ES, 2011).

2.5. Statistical analysis

Harvesting was carried out at room temperature, 22 ± 3 °C. All experiments were conducted in triplicate sampling and testing. The results are given as mean values ± standard deviation of three independent experiments. Differences about the harvesting method and coagulant concentrations were tested for significance using one-way analysis of variance at a significant level of 0.001 at 60 min, for every experiment. One-way ANOVA was used to compare harvesting efficiency in experimental treatments with the control treatment (environment conditions). Statistical analysis was run using the software program IBM SPSS Statistics 23.0.