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Harvesting microalgae from wastewater treatment systems with natural flocculants: Effect on biomass settling and biogas production

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ABSTRACT

Research on new sources of bioenergy is nowadays driving attention to microalgae. Cost-effective biomass harvesting and thickening pose a challenge for massive microalgae production for biofuels. In this study, coagulation–flocculation and sedimentation with natural flocculants (*Ecotan* and *Tanfloc*) was evaluated on microalgae grown in an experimental high rate algal pond treating urban wastewater. Jar tests showed how flocculant doses of 10 and 50 mg/L of *Ecotan* and *Tanfloc* enabled over 90% biomass recovery. Furthermore, settling column tests showed that both flocculants increased microalgae settling velocity, performing fast and efficient biomass recovery (>90% recovery in 10–20 min). Thus, the use of either flocculant would enhance microalgal biomass reducing the HRT and settler volume. Finally, the potential toxicity of flocculants upon biomass production was assessed in biochemical methane potential tests. Results indicated that doses of 10–50 mg/L of *Ecotan* and *Tanfloc* did not affect anaerobic digestion, leading to the same methane yield (162–166 mL CH_4/g VS) with the same methane content (70%) as the control without flocculants. This study demonstrates that *Ecotan* and *Tanfloc* flocculants would be appropriate for microalgae biomass harvesting and subsequent biogas generation.

1. Introduction

Treatment of wastewater with microalgal cultures has the major advantage of producing biomass that can be valorized to produce bioenergy or molecules of interest. In fact, energy production and resource recovery have been identified as one of the main challenges for wastewater treatment systems of the future by relevant initiatives such as the recently created European Innovation Partnership on Water. However, microalgal wastewater treatment systems such as high rate algal ponds (HRAP) have some bottlenecks like biomass separation [1,2]. Since the invention and development of HRAP in California in the 1950s, the problem of algal biomass separation has remained unsolved. The main constraint is related to the fact that wastewater is a product without market value, and therefore any added cost to the treatment system (such as the implementation of an intensive harvesting system) cannot be recovered. Nevertheless, this paradigm may change in the near future if biomass is valorized to obtain bioenergy or resources, since biomass will then have a market value.

Microalgal harvesting and thickening can be achieved by means of several techniques including coagulation–flocculation and sedimentation, flotation, centrifugation, magnetic separation and electrophoresis [3–7]. However, in the context of wastewater treatment, only low-cost techniques capable of managing large volumes of water and biomass can be applied, such as coagulation–flocculation followed by a solid/liquid separation. Indeed, coagulation–flocculation and sedimentation may lead to a solid concentration in microalgal biomass from 1 to 5% w/w [7], which is appropriate for downstream processes such as biogas production.

Coagulation consists of neutralizing negative surface charges of colloidal particles (in this case microalgae), while flocculation is the aggregation of neutralized particles followed by floc formation. Coagulants that have been traditionally used in water and wastewater treatment are salts of aluminum or iron. However, these substances have a limited application in microalgal systems because they can contaminate downstream products restricting biomass valorization [3,8]. This drawback may be overcome by using natural organic coagulants like tannin based polymers or modified starch which are being increasingly used since the 80s [9]. These types of coagulants (also referred to "flocculants", as from now in the text) are becoming very popular in the field of water treatment as substitutes for polyacrylamide based flocculants due to health concerns [2]. Previous studies on microalgae coagulation–flocculation and sedimentation with different types of organic polymers have shown promising results in terms of separation efficiency (Table 1).

In the field of wastewater treatment, biogas production is perhaps the most straightforward option for microalgal biomass valorization [16,17]. Indeed, anaerobic digestion has a long tradition in the context

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Table 1
Literature results on microalgal biomass harvesting by coagulation–flocculation and sedimentation with different types of organic polymers.

Microalgae	Flocculant	Dose	Biomass recovery	Reference
Tetraselmis suecica	Zetag 7650 + $Al_2(SO_4)_3$	5–50 mg/L (Zetag 7650) + 50 mg/L ($Al_2(SO_4)_3$)	~100%	[3]
Parachlorella	Cationic starch (Cargill C*Bond HR 35.849)	120 mg/L	>95%	[2]
Scenedesmus	Cationic starch (Greenfloc 120)	20 mg/L	>90%	[2]
Scenedesmus dimorphus	Cationic starch	10–100 mg/L	70 to 95%	[10]
Microalgal-bacteria consortia	Drewfloc 447, Flocudex CS/5000, Flocusol CM/78, Chemifloc CV/300 and Chitosan	25–50 mg/L	58 to 99%	[5]
Microcystis aeruginosa	Chitosan + Fe_3O_4	1.6 mg/L (Chitosan) + 4–6 mg/L (Fe_3O_4)	99%	[11]
Spirulina, Oscillatoria and *Chlorella*	Chitosan	15 mg/L	90%	[12]
Microalgal-bacterial consortia	Chitosan	214 mg/L	92%	[13]
Chlorella Sorokiniana	Chitosan	10 mg/L	90%	[14]
Phaeodactylum tricornutum	Chitosan	20 mg/L	80–90%	[15]

of wastewater treatment and this expertise fully justifies the use of microalgae for this purpose. Nevertheless, if microalgae are separated and thickened with coagulation–flocculation and sedimentation it is evident that flocculants should not be toxic or inhibit the anaerobic digestion process. Natural organic flocculants could meet this requirement; to our knowledge though it has yet to be confirmed.

The objective of the present study is to evaluate two tannin-based cationic flocculants for coagulation–flocculation and sedimentation of microalgae grown in experimental HRAP for wastewater treatment. In particular the study aimed at: 1) determining the optimal flocculant doses with jar tests, 2) studying the settling of formed flocs using settling column tests, and 3) assessing the effect of flocculants on biomass anaerobic digestion by means of biochemical methane potential tests. To the best of our knowledge, this is the first time that natural flocculants are evaluated not only on their efficiency, but also on their effect on downstream processing.

2. Material and methods

2.1. Microalgal biomass

Experiments were carried out at the laboratory of the GEMMA Research Group (Universitat Politècnica de Catalunya·BarcelonaTech, Barcelona, Spain). Microalgal biomass was grown in an experimental plant that had been in continuous operation for more than 1 year. Urban wastewater was pumped from a nearby municipal sewer and conveyed to a primary settler. Following that, primary treated wastewater was continuously fed (60 L/day) to an experimental HRAP; a raceway pond with a volume of 0.47 m^3 and a nominal hydraulic retention time of 8 days. Average loading rates of the HRAP were 24 g COD/m^2·day and 4 g NH_4-N/m^2·day. Microalgal biomass grown in the HRAP was separated in a clarifier connected in series with the HRAP (without coagulation–flocculation). A detailed description of the wastewater treatment system and its operation and performance may be found elsewhere [18].

In the present study, microalgal biomass term is referred to the microalgal–bacterial biomass grown in the HRAP. The biomass concentration of the HRAP mixed liquor ranged from 0.06 to 0.6 g TSS/L over the year and consisted of consortia of microalgae as well as bacteria, microalgae accounting for much of the biomass (over 90% of the biomass according to [19]). Average microalgal biomass production was 9.4 g TSS/m^2·day, However, without flocculants, harvested biomass corresponded to approximately 5 g TSS/m^2·day, since 45% of the produced biomass escaped from the settler. The biomass was characterized by an average VS/TS ratio of 60% VS/TS, being most of the organic matter in particulate form as indicated by the low VSS/VS (0.89%) and CODs/COD (0.72%) ratios. During the experimental period, microalgal population was mainly composed by green algae belonging to genus *Monoraphidium* sp., *Scenedesmus* sp. and *Stigeoclorium* sp. and the diatoms *Nitzchia* sp., *Navicula* sp. and *Amphora* sp. (Fig. 1).

Samples were collected from the HRAP on a weekly basis and analyzed in triplicate. Total solids (TS), total suspended solids (TSS), volatile solids (VS), volatile suspended solids (VSS), chemical oxygen demand (COD) and soluble chemical oxygen demand (CODs) were determined according to standard methods [20]. Moreover, microalgae images were taken with an optic microscope (Aixoplan Zeiss, Germany), equipped with a camera MRc5, using the software Axioplan LE. Microalgae genus was identified using conventional taxonomic books [21,22].

2.2. Natural polymeric flocculants

Harvesting properties of two cationic tannin-based flocculants were investigated on the samples of the HRAP mixed liquor. Ecotan AR® (Servyeco, Spain) and Tanfloc SG® (Tanac SA, Brazil) are natural cationic flocculants extracted from the bark of *Acacia mearnsii* having strong coagulating properties. None of the flocculants modifies the pH of the medium significantly and both of them are effective over a pH range of 4.5–8 (9 for *Ecotan*). *Ecotan* was provided in liquid form with a concentration of 0.3 g/L, while *Tanfloc* was supplied as a dry product that was dissolved in water until complete solution. Both flocculants are suitable for wastewater treatment applications, and were conceived to replace metal-based products with aluminum and iron chlorides.

Stock solutions of 1000 mg/L were prepared for each flocculant prior to jar tests, column settling tests and biochemical methane potential (BMP) tests.

2.3. Jar tests

Jar tests were used to determine the optimal dose of each flocculant following standard protocols employed in the water and wastewater treatment fields using common jar test equipment [23]. During one week, HRAP liquor samples were taken and two jar tests were carried out for each flocculant in order to determine the optimal concentration for coagulation–flocculation and sedimentation tests. The range of flocculant doses for jar tests was selected after previous trials in which it was observed that optimal doses ranged between 10 and 60 mg/L. Thus, flocculant concentrations tested were: 10, 20, 30, 40, 50 and 60 mg/L. Altogether, five jar test replicates were performed for each flocculant. In each experiment aliquots of 500 mL were placed in six beakers. Increasing flocculant concentrations were simultaneously added to each beaker, intensively stirred (200 rpm) for 1 min, stimulating the coagulation process. Following that, beakers were gently stirred (35 rpm) for 15 min, enhancing the flocculation process. Finally, formed flocs were allowed to settle (without stirring) for 15 min (sedimentation process). Images of the three jar test steps are shown in Fig. 2. At the end of the process, supernatant liquid samples were taken from each beaker; turbidity and pH were measured with a HI93703 Hanna Instruments Turbidimeter and a Crison 506 pH-meter, respectively. Turbidity and pH were also measured from the mixed liquor without