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Screening of commercial natural and synthetic cationic polymers for flocculation of freshwater and marine microalgae and effects of molecular weight and charge density

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ABSTRACT

Twenty-five natural and synthetic cationic polymers of different molecular weights and charge densities were evaluated for microalgae flocculation. Tanfloc is a natural low molecular weight tannin polymer whereas Zetag and Flopam are both synthetic high molecular weight polyacrylamide polymers. Five exponential concentrations (0.55, 1.66, 5, 15 and 45 mg L^{-1}) were tested for freshwater *Chlorella vulgaris* and marine *Nannochloropsis oculata*. All polymers were efficient (>90% at ≥ 1.66 mg L^{-1}) for *C. vulgaris*. However, for *N. oculata*, only Tanfloc was effective. Charge density positively influenced flocculation decreasing the required polymer dosage. Restabilization was observed only for synthetic polymers when overdosed. Natural polymers performed similarly for both species. Overall, Tanfloc SL and Flopam FO 4990 SH were the most efficient polymers for microalgae flocculation though Tanfloc is a more economical option (US$37 per ton^{-1} of biomass) and environmentally friendly than Flopam (US$171 per ton^{-1} of biomass).

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1. Introduction

Microalgae are attracting a lot of interest as a new source of biomass for production of food, feed, bulk chemicals, or biofuels [1]. Harvesting is currently one of the major bottlenecks to large-scale production of microalgae [2]. Because of their small size (3 to 30 μm) and low biomass concentration (<5 g L^{-1}), harvesting using centrifuges is too energy-intensive and costly, being justified only for high value bioproducts such as carotenoids or poly-unsaturated fatty acids [3–5]. For bulk production of biomass for commodities, a low-cost harvesting method is needed that can process large volumes of microalgae culture at a minimal cost.

Spontaneous flocculation of microalgae in suspension is prevented by electrostatic repulsion caused by the negative surface charge of the cells [6]. This negative charge is related to the presence of carboxyl, sulfate or phosphate groups on the microalgae cell surface. Hence, positively charged chemicals that interact with those negative surface charges can induce flocculation. In flocculation, small particles are combined into larger aggregates. These large aggregates can be much more easily separated from the liquid medium than the individual cells [2]. Thus, flocculation has a lot of potential to be used as a low-cost and high-throughput method for harvesting microalgae.

An important class of chemicals used in flocculation is metal salts, such as ferric chloride or aluminum sulfate [7]. When dissolved in water, these metal salts form positively charged hydroxides that cause flocculation by neutralizing the negative charge of the microalgae cells or by causing a positively charged precipitate that enmeshes the microalgae cells and removes them from suspension ('sweep flocculation'). Metal salts have been successfully applied for flocculating microalgae [8–10]. However, these elements have the disadvantage of requiring a relatively high dosage and that the biomass is contaminated with high concentrations of metals, limiting the application of the biomass due to metal toxicity [11].

Another class of chemicals that is widely used for microalgae flocculation is organic polymers. They can induce flocculation by neutralizing the negative surface charge, similar to metal salts, and by forming bridges between the microalgae cells. The effectiveness of such polymers depends on their size, secondary structure in solution as well as on their charge density [7]. Organic polymers are generally preferred over metal salts because they require a much lower dosage. The majority of organic polymers that are commercially available are synthetic based on polyacrylamide [7]. Some studies have successfully applied synthetic polyacrylamide polymers for flocculating microalgae (e.g. [12–16]). Nevertheless, these studies have made clear that there are often large disparities in the effectiveness of different polymers when applied to microalgae (e.g. [12,16]). It is not clear, however, which properties of polymers (e.g. charge density, polymer size, secondary structure) determine this variation in effectiveness.

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Although synthetic polyacrylamide polymers as such are non-toxic, they may contain acrylamide residues that are presumably carcinogenic or display a high toxicity towards aquatic organisms [17]. Therefore, it is preferable to use natural based polymers, particularly when fractions of the microalgae biomass are to be used for animal feed, which may be economically attractive in a biorefinery context [1]. A well-known natural cationic polymer is chitosan, a derivative of chitin obtained from shrimp shells. Several studies have shown that chitosan is quite effective for flocculating microalgae (e.g. [18,19]). Other naturally based polymers include derivatives of cassia gum [20] or starch [21]. Tanfloc is a relatively recently developed commercial biopolymer that is based on tannin [22]. It differs from other natural polymers in that it is not based on a polysaccharide but on a phenolic polymer. Tannins are branched polymers and thus have a different secondary structure than linear polymers such as chitosan or polyacrylamide. While Tanfloc has been used for removal of chemical contaminants [23] and turbidity in wastewater treatment [24], its potential for flocculating microalgae has not been thoroughly evaluated, although Roselet et al. [25] have recently analyzed the effect of pH, salinity, polymer dose and biomass concentration on Tanfloc efficiency in concentrating the marine microalga *N. oculata*, with good results.

A disadvantage of both synthetic and natural polymers is that they often undergo coiling when used in high ionic strength medium such as seawater (e.g. [8,26]). Coiling changes the secondary structure of the polymer and this generally results in a decrease in the flocculation efficiency [27]. Many species of microalgae, including those that have a lot of potential for biodiesel production, are marine species. Therefore, it is important to evaluate whether synthetic and natural polymers have potential for harvesting of marine microalgae species.

The main objective of this study was to evaluate the potential of 25 different commercially available cationic polymers for flocculating microalgae. These polymers included different charge density variants of a low molecular weight natural tannin polymer (Tanfloc) and two high molecular weight synthetic polyacrylamide polymers (Flopam and Zetag). To evaluate the potential of these polymers for harvesting marine as well as freshwater microalgae, screening was performed on two model species, the freshwater *Chlorella vulgaris* and the marine *Nannochloropsis oculata*. The effects of molecular weight and charge density on the microalgae flocculation were evaluated and cost analysis was conducted for all tested polymers and compared with hydrolyzing metal salts and chitosan.

2. Materials and methods

2.1. Microalgae cultivation

The two microalgae model species used in this study were freshwater *C. vulgaris* (SAG 211-11b) and marine *N. oculata* (SAG 38.85), obtained from the Culture Collection of Algae at Göttingen University (SAG, Germany). The microalgae were cultured in Wright's cryptophyte medium prepared from pure salts and deionized water. For *N. oculata*, synthetic sea salt (Homarsel, Zoutman, Belgium) was added at a final concentration of 30 g L^{-1}. Both species were cultured for 6 days in 30 liter plexiglass bubble column photobioreactors mixed by sparging with 0.2 μm filtered air (5 L min^{-1}) in a temperature-controlled room (20 °C) [9]. The pH was maintained at 8 by addition of CO_2 (2–3%) using a pH-controller system. Each photobioreactor was continuously irradiated with daylight fluorescent tubes (100 μmol photons m^{-2} s^{-1}).

Microalgae biomass concentration was monitored daily by measuring the absorbance at 750 nm. Optical density measurements were calibrated against dry weight measured gravimetrically on pre-weighed GF/F glass fiber filters ($R^2 = 0.998$). The marine microalga was washed with 0.5 M ammonium formate, prior to filtration to remove salts absorbed on the cell surface. The final biomass concentrations after 6 days were 260 mg L^{-1} and 290 mg L^{-1} for *C. vulgaris* and *N. oculata*, respectively. The final concentrations were later confirmed by dry weight measurements.

2.2. Flocculation experiments

After day 6, the microalgae cultures were collected from the photobioreactors to be used in the flocculation experiments. All 25 polymers were simultaneously screened and flocculation experiments lasted approximately 4 h. Microalgae may excrete large amounts of dissolved organic matter (DOM) into the culture medium and this may interfere with flocculation [9]. To avoid DOM interference in the flocculation experiments, the microalgae was centrifuged from the medium and resuspended in the same volume of fresh medium. This treatment reduced carbohydrate concentrations in the medium from 10 and 58 mg L^{-1} to 2 and 10 mg L^{-1} of glucose equivalent for *C. vulgaris* and *N. oculata*, respectively. Previous experiments had demonstrated that centrifugation and subsequent resuspension in fresh medium had no significant effect on flocculation [9].

Twenty-five cationic polymers were compared. Table 1 lists the properties of the polymers used. Tanfloc is a natural low molecular weight quaternary ammonium polymer based on tannins extracted from the black wattle tree (*Acacia mearnsii*) and manufactured by TANAC (Brazil). Flopam and Zetag are both synthetic copolymers of acrylamide and quaternized cationic monomer polymers manufactured by SNF Floerger (France) and BASF (Germany), respectively. For Flopam, a series of polymers with similar molecular weight (4.1–8.6 × 10^6 Da) but increasing charge densities (2.5–100 mol%) was used. For Zetag, we compared polymers with high (8125, 8160, 8180) and very high (7652, 8165, 8185) molecular weight and variable charge densities. For each polymer a 1 g L^{-1} stock solution was prepared by adding 50 mg of polymers to 50 mL of deionized water and mixed for 1 h. Zetag was initially moistened with 3% acetone as indicated by the manufacturer. For each polymer, five exponential concentrations (0.55, 1.66, 5, 15 and 45 mg L^{-1}) were selected to determine the order of magnitude of the dosage required to induce flocculation. All polymers used in this study were kindly provided by the manufacturers.

Jar test experiments were used to quantify the efficiency of *C. vulgaris* and *N. oculata* flocculation. During addition of polymers, the microalgae suspensions were intensively mixed (350 rpm) for 10 min, to allow uniform polymer dispersal, followed by gentler mixing (250 rpm) for 20 min to allow floc formation. Subsequently, the microalgae suspensions were allowed to settle for 30 min and then samples were collected in the middle of the clarified zone. Optical density at 750 nm was measured prior to polymer addition (OD_i) and after settling (OD_f) and the flocculation efficiency (η_a) was calculated as:

$$\eta_a = \frac{OD_i - OD_f}{OD_i} \times 100$$

Only flocculation efficiencies higher than 90% were considered effective.

2.3. Statistical analysis

Polymer doses and flocculation efficiencies were log transformed and a nonlinear regression analysis with least square iteration was performed to describe the polymer effectiveness. Each dose–response curve was compared by extra sum-of-squares F test ($P < 0.05$) and D'Agostino–Pearson omnibus test was performed to verify dataset normality.

2.4. Cost analysis

Analysis was conducted to quantify the cost of flocculating *C. vulgaris* and *N. oculata* using hydrolyzing metal salts ($Al_2(SO_4)_3$ and $AlCl_3$), synthetic (Flopam and Zetag) and natural (chitosan and Tanfloc) flocculants.

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