



## Understanding the salinity effect on cationic polymers in inducing flocculation of the microalga *Neochloris oleoabundans*



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### ABSTRACT

A mechanistic study was performed to evaluate the effect of salinity on cationic polymeric flocculants, that are used for the harvesting of microalgae. The polyacrylamide Synthofloc 5080H and the polysaccharide Chitosan were employed for the flocculation of *Neochloris oleoabundans*. In seawater conditions, a maximum biomass recovery of 66% was obtained with a dosage of 90 mg/L Chitosan. This recovery was approximately 25% lower compared to Synthofloc 5080H reaching recoveries greater than 90% with dosages of 30 mg/L. Although different recoveries were obtained with both flocculants, the polymers exhibit a similar apparent polymer length, as was evaluated from viscosity measurements. While both flocculants exhibit similar polymer lengths in increasing salinity, the zeta potential differs. This indicates that polymeric charge dominates flocculation. With increased salinity, the effectivity of cationic polymeric flocculants decreases due to a reduction in cationic charge. This mechanism was confirmed through a SEM analysis and additional experiments using flocculants with various charge densities.

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### 1. Introduction

The low energy requirements for flocculation establishes it as a promising technique for concentrating microalgae (Uduman et al., 2010; Vandamme et al., 2013). Flocculation of seawater cultivated microalgae, however, is still very challenging. In sea-water, ionic hindrance occurs which inhibits the interaction of the flocculant molecules with the microalgae (Bilanovic et al., 1988; Uduman et al., 2010; Vandamme et al., 2010, 2013). Unfortunately, only a small number of techniques are reported to be successful for flocculation of marine species: i.e. pH-increase, inorganic flocculation, and polymeric flocculation (Wu et al., 2012; Chatsungnoen and Chisti, 2016; 't Lam et al., 2014). A pH-increase induces the precipitation of salts. Those precipitates will settle and, meanwhile, will sweep the biomass (Wu et al., 2012). In their study, several microalgae have been successfully flocculated by increasing the pH, resulting in a precipitation of the divalent ion magnesium. The use of inorganic flocculants in seawater salinities has also been reported (Chatsungnoen and Chisti, 2016). However, as mentioned by Uduman et al. (2010), the use of inorganic flocculants in seawater

salinities commonly requires high dosages that are about 5–10 times higher compared to polymeric flocculants. With polymeric flocculation, polymeric bridges between individual cells are formed and, subsequently, aggregates of biomass evolve (Vandamme et al., 2013; 't Lam et al., 2014).

Among polymeric flocculants, cationic polymers are regarded as successful, though not all are equally efficient in inducing flocculation of marine microalgae. Currently, only polyacrylamides are reported to be successful ('t Lam et al., 2014; König et al., 2014; Roselet et al., 2015).

Despite the success of cationic polyacrylamides in harvesting marine microalgae, 't Lam et al. (2015) reported that, when commercially available cationic polymers are applied as flocculants, the required flocculant dosage is quite high (40–100 mg<sub>flocculant</sub>/g<sub>biomass</sub>), resulting in a lower economic feasibility. Additionally, the use of polyacrylamides is forbidden for food and feed applications as several of these flocculants are reported to be toxic and non-food grade petroleum processing techniques are commonly used to manufacture them (Lee et al., 2014). To overcome these limitations, other flocculants that preferably have an equal or even better performance and that are allowed in the food and feed industry should be selected or designed. To allow the rational selection or design of novel flocculants, the mechanism that is

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responsible for successful flocculation of marine microalgae needs to be revealed.

One of the mechanisms that was proposed by Tenney et al. (1969) and by Bilanovic et al. (1988) is that adsorption is mainly due to charge attraction between flocculant and cells. These studies suggest that repulsive forces within the polymer decrease in elevated salinities due to high ionic strength, resulting in the coiling of the flocculants. Due to this coiling, flocculants lose their ability to form polymeric bridges between individual cells and this subsequently results in decreased flocculation efficiency (Tenney et al., 1969; Bilanovic et al., 1988). The lack of polymeric coiling in elevated salinities could thus be an explanation for the success of charged polymeric flocculants such as cationic polyacrylamides.

However, recent studies of Roselet et al. (2015) showed that the cationic charge of the polymeric flocculants had a positive effect on the biomass recovery where the polymer length was of minor importance and that is not in accordance with the previously specified explanation of polymeric coiling. It is, therefore, still difficult to explain why certain cationic polymers are successful in inducing flocculation in seawater salinities while others are not.

The goal of this study was to provide further information to better understand cationic polymeric flocculation in seawater salinities and possibly reveal why cationic polyacrylamides remain functional in high salinities while other cationic polymers do not. This gained insight also provided information that can be applied in optimizing the design of flocculants.

In this study, Synthofloc 5080H and Chitosan were exploited as flocculants. Synthofloc 5080H is a cationic polyacrylamide that is reported to be successful in flocculating marine microalgae ('t Lam et al., 2014). Chitosan is a natural polysaccharide which is recognized as being successful in inducing flocculation under freshwater conditions but becomes less successful in seawater salinities and in neutral pH (Bilanovic et al., 1988). The apparent polymer length and net cationic charge of both flocculants were compared with each other as a function of salinity.

The used microalga in this study was *Neochloris oleoabundans* which is able to grow in both fresh and salt water conditions. It has been reported to contain a high protein content and, under stressed conditions, a high lipid content. This makes *N. oleoabundans* an interesting species for several applications (Popovich et al., 2012; Breuer et al., 2012). In addition, *N. oleoabundans* is a spherical Chlorophyta, hence, its shape eliminates possible side-effects of the cell shape during flocculation.

## 2. Material and methods

### 2.1. Biomass cultivation

The microalgal strain *N. oleoabundans* UTEX1185 was cultivated in artificial seawater medium with various salinities: NaCl: 15 g/L (brackish), 25 g/L (seawater), 35 g/L (saline); KNO<sub>3</sub>: 1.7 g/L; Na<sub>2</sub>SO<sub>4</sub>: 0.5 g/L; 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES): 23.83 g/L; MgSO<sub>4</sub>·7H<sub>2</sub>O: 0.73 g/L; CaCl<sub>2</sub>·2H<sub>2</sub>O: 0.36 g/L; K<sub>2</sub>HPO<sub>4</sub>: 0.43 g/L; Na<sub>2</sub>EDTA·2H<sub>2</sub>O: 0.03 g/L; MnCl<sub>2</sub>·4H<sub>2</sub>O: 0.004 g/L; ZnSO<sub>4</sub>·7H<sub>2</sub>O: 0.0012 g/L; CoCl<sub>2</sub>·6H<sub>2</sub>O: 0.0003 g/L; CuSO<sub>4</sub>·5H<sub>2</sub>O: 0.0003 g/L; Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O: 0.00003 g/L; NaFeEDTA: 0.01 g/L.

Biomass was cultivated in 100 mL shake flasks in an Infors Multitron incubator (Infors AG, Bottmingen, Switzerland). The cultures were continuously illuminated at 120 μmol m<sup>-2</sup> s<sup>-1</sup> in atmospheric air enriched with 2.5% CO<sub>2</sub> at a temperature of 25° C. The flasks were orbitally shaken at 90 rpm.

Part of the cultured biomass was harvested using pipetting two days after inoculation. On the seventh day, new cultures were inoculated for further cultivation. By re-inoculating a new flask every

seven days and taking biomass after two days of cultivation, we prevented using stressed biomass in the flocculation experiments. Prior to the flocculation experiments, two cultivation cycles of nine days were performed to allow the biomass to adapt to their salinity.

### 2.2. Flocculants

1000 ppm stock solutions were prepared according to 't Lam et al. (2014) whereby the low charged flocculant 'Synthofloc 5025H', the moderately charged flocculant 'Synthofloc 5040H', and the highly charged flocculant 'Synthofloc 5080H' were dissolved in de-ionized (Milli-Q®) water. The flocculants of the 'Synthofloc'-series were generously provided by Sachtleben Wasserchemie GmbH, Germany. All flocculants are large polyacrylamides with various cationic charges and are commonly used in wastewater applications.

Chitosan (purchased from Sigma-Aldrich, product nr.: 448869-50G) was dissolved overnight in 0.1% (v/v) acetic acid after which the pH was adjusted to pH 7 ± 0.2. Flocculants were stored at 4 °C in a dark environment and were never stored longer than seven days.

### 2.3. Biomass recovery

After harvesting the biomass, the initial optical density at 750 nm was established at 0.8 ± 0.01 using culture medium (corresponds with a dry weight of 0.24 ± 0.07 g/L). After setting the OD<sub>750</sub>, 10 mL of the sample was transferred to a beaker glass and stirred at 500 rpm. From a stock solution, flocculant was added until the desired dose was achieved (ranging between 0 and 90 ppm). After five minutes of mixing at 500 rpm followed by a ten minute period of mixing at 100 rpm, samples were transferred to 4 mL polystyrene cuvettes. The mixing protocol that was used first involved a severe mixing followed by a gentle mixing time and is in accordance with protocols reported in other studies (Bilanovic et al., 1988). Using the photometric method of (Salim et al., 2012), the gradual biomass recovery was followed in a Beckman Coulter DU730 photometer. After two hours of sedimentation, the biomass recoveries were determined and calculated according to (Salim et al., 2012). All experiments were performed in duplicate:

$$\text{Recovery (\%)} = \frac{\text{OD}_{750(t_0)} - \text{OD}_{750(t_{\text{supernatant}})}}{\text{OD}_{750(t_0)}} \times 100$$

### 2.4. Viscosity

The viscosity of a polymeric solution is correlated with the apparent polymer length. To study the effect of the salinity on the apparent polymer length of the flocculants, the viscosity of the flocculant solutions in various salinities was measured. The flocculant concentrations ranged between 0 and 100 ppm. The viscosity was measured using a Physica MCR 301 Rheometer. Polymeric solutions were made with various salinities by varying the NaCl-concentration (0–10 g/L NaCl). After the addition of the flocculant solution in the rotational cylinder, the viscosity was measured at shear rates ranging from 1 to 100 s<sup>-1</sup>.

### 2.5. ζ-Potential

ζ-Potential measurements were performed to determine the effect of salinity on the net cationic charge of the flocculant. Several flocculant solutions with different NaCl concentrations were prepared. Flocculant dosages ranged between 30 and 200 ppm. The

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