

## REMOVALS OF CHAIN-LIKE AND PIN-LIKE ALGAE BY POSITIVELY CHARGED BUBBLE FLOTATION

Thi Thuy Bui<sup>1</sup>, Viet Anh Nguyen<sup>2,\*</sup>

<sup>1</sup>*Environmental Engineering Division, Faculty of Environment, Water Resources University, 175 Tay Son, Dong Da Dist, Hanoi, Vietnam*

<sup>2</sup>*Institute of Environmental and Science Engineering, Hanoi University of Civil Engineering, 55 Giai Phong, Hanoi, Vietnam*

\*Email: [vietanhctn@gmail.com](mailto:vietanhctn@gmail.com)

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### ABSTRACT

The objective of this study was to investigate the effects of positive ferric-bubble on behaviors of chain-like and pin-like algae (i.e. *Phormidium specie (sp.)* and *Nitzschia pungens*, respectively). Two selected algae were cultured in a laboratory under the certain conditions. At stationary phase, algae were below 4  $\mu\text{m}$  in diameter and in the range of 50 ~ 100  $\mu\text{m}$  for chain-like algae, of 20 – 35  $\mu\text{m}$  for pin-like shape in length; with negatively charged at cultivated conditions (pH from 6.5 to 9). Positive ferric-bubbles were generated by adding coagulants (as  $\text{Fe}^{3+}$ ) and were injected at a pressure of 5 bars with a bubble rate of 30 % into a 10 L-acryl made reactor with algal-containing tap water. Removal efficiencies were assessed by the cells number, Chlorophyll *a* reduction and the morphological changes (i.e. cell structure). For cells number, about 90 % of both algae were removed whilst pin-like algae obtained the higher reduction of Chlorophyll *a*, showing by 92 % in comparison with about 85 % of chain-like shape. The breakup of algal morphologies occurred for chain-like cells only. The structure of filaments affects performance of positively charged bubble flotation.

*Keywords:* algal morphology; filamentous algal removal; bubble flotation; positively charged bubble.

### 1. INTRODUCTION

Algal blooms are one of the major concerns in water bodies due to their harmful effects on humans, water treatment facilities and ecosystem [1]. Filamentous algae are typically addressed as chain-like and pin-like cells (i.e. *Phormidium sp.* and *Nitzschia pungens*, respectively) [2, 3]. Algae presence is among main causes of filter clogging in water treatment plants [4 - 6]. Dissolved air flotation process is a potential treatment method since filamentous algae have gas vacuoles and low density so it is easy to make them float. The generation of positively charged bubble has been proven to be effective to maximization of charge neutralization [7 - 9]. In fact, there have been few studies on the collision mechanism of bubbles and filamentous cell

aggregates and optimal tools for removal of filamentous algae. Structure of filaments may have an impact in flotation efficiency in the view of bubble-algae collision. In this research, we aimed (1) to evaluate effectiveness of positive bubble on removals (i.e. cell number and Chlorophyll *a*) of filamentous algae; and (2) to investigate the change of algal cells' structure (i.e. the chain-like and pin-like shapes) during charged bubble flotation. This study would provide an evidence of potential application of charged bubble flotation, focusing on the effectiveness of positive bubble in the algae removal from natural waters.

## 2. MATERIALS AND METHODS

### 2.1. Algae culture and observation properties

In this study, two selected filamentous algae (i.e. *Phormidium sp.* and *Nitzschia pungens*) purchased from Korean Marine Microalgae Culture Center, Busan, South Korea were cultured in laboratory. Algae cells were grown in a 5 L-glass-beaker at 20 °C in Chloroflexus Broth media (containing 21.6 mg/L of NO<sub>3</sub><sup>-</sup>-N and 8.0 mg/L of PO<sub>4</sub><sup>3-</sup>-P) at a darkness/lightness cycle of 10 hrs/14 hrs in incubator [10]. In addition, a handshaking per day was undertaken to ensure the growth rate of algae.

Algal characteristics were addressed in terms of cell shape, charge (or zeta potential), and algae populations (i.e. cells number and Chlorophyll *a*). Algal shape and cells number were identified by using the image analysis method; including a haemocytometer cell, a microscope, and image analysis software. The charge of algae at cultured conditions (pH from 6.5 to 9) was measured via zeta-photometer II equipment (Sephy Company, France) – a system of a video microscope and an image analyzer. And finally, a spectrophotometer (Libra S60PC model, USA) was applied to analyze chlorophyll *a* pigments in algae. In this method, a 50-mL-algal sample was filtered through a membrane filter with a diameter of 47 mm and 5 μm pore size (Whatman, United Kingdom); the absorbance of extracted pigments in 10mL of 90% aqueous acetone were then measured at three wavelengths (i.e. 663 nm, 647 nm and 630 nm).

### 2.2. Bubble generation and algal removal testing

In this research, ferric-bubbles were produced in the presence from 1 to 5 mg/L of Fe<sup>3+</sup> (FeCl<sub>3</sub>.6H<sub>2</sub>O was used) in a saturator at a pressure of 5 bars. Zeta potential of the bubbles was measured with the electrophoresis cell, video camera, and video image analyzer and calculated based on Smoluchowski's equation [8, 11]. Microscopic focusing on the stationary level in the cell correctly measures the zeta potential of bubbles [8].

$$\zeta = \frac{\mu K A v}{\epsilon_r \epsilon_0 i} \quad (1)$$

where  $\mu$  is the dynamic viscosity of the electrolyte solution (Pa·s),  $\epsilon_r$  is the relative dielectric permittivity,  $\epsilon_0$  is the dielectric permittivity of vacuum,  $v$  is the horizontal velocity of bubble (m/s),  $K$  is the measured electrolyte conductivity (S/m), and  $A$  is the cross-sectional area of the electrophoretic unit (m<sup>2</sup>).

Generated bubbles were injected into a 10 L-acryl-made-reactor with algal-containing tap water at a bubble rate of 30 % for algal removal as provided in Figure 1. In the experiments, algae were separated from water within 3mins and the sampling was conducted for measurement of cell removal and Chlorophyll *a* reduction. Also, in order to evaluate positively charged bubble

flotation performance, the change of algal structure would be observed via an image analyzer system (as discussed in section 2.1).

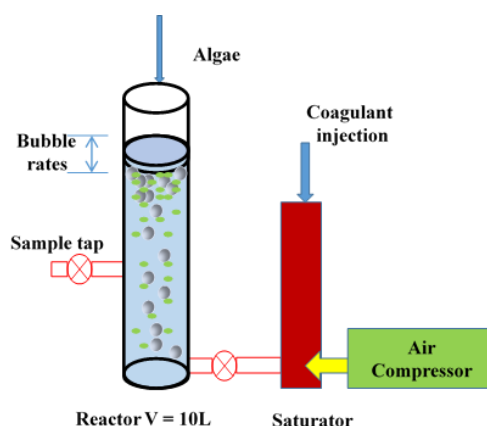




Figure 1. Schematic diagram of algal removal testing by positive bubble flotation.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Algal properties and ferric-bubble's charge

##### 3.1.1. Algal properties

Table 1. Properties of *Phormidium sp.* and *Nitzschia pungens* at stationary phase.

Algae	Shape	Characteristic	Experiment concentration	
			Cell counting (cells/mL)	Chlorophyll <i>a</i> (mg/m <sup>3</sup> )
<i>Phormidium sp.</i>		Shape: Chain-like Average diameter: 4 μm Length: 50 – 100 μm Zeta potential: -17.35 to -20.23 mV	2,000 ± 50	78.46
<i>Nitzschia pungens</i>		Shape: Pin-like Average diameter: 4 μm Length: 20 – 35 μm Zeta potential: - 19.34 to -24.13 mV	2500 ± 50	77.56

##### 3.1.2. Zeta potential of ferric-bubble

Under cultivated conditions, both *Phormidium sp.* and *Nitzschia pungens* were reached the stationary phase after 25 days. As indicated in Figure 1, *Phormidium sp.* cells were shaped in chain-like from several oval-segments with average diameter of 4 μm and length in the range of 50 – 100 μm and *Nitzschia pungens* were addressed as pin-like algae with shorter length (varying from 20 to 35 μm) and similar diameter (4 μm). Results from zeta potential measurement showing the negatively charged for both algae (i.e. minimization of -20.23 mV for *Phormidium*

*sp.* and of -24.13 for *Nitzschia pungens*) could bring a potential of high removals efficiencies by applying appropriate positive bubbles.

In the presence of  $Fe^{3+}$ , charge of generated bubble shifted from negatively (about -27 mV) to positively (above +20 mV), as illustrated in Figure 2. With an addition of 1 mg/L as  $Fe^{3+}$ , zeta potential of bubble would be neutral and seemingly unchanged at above 4 mg/L of  $Fe^{3+}$  presence. In this perspective, positive bubble would greatly attach with negative algal cells and it therefore improves removal efficiencies.

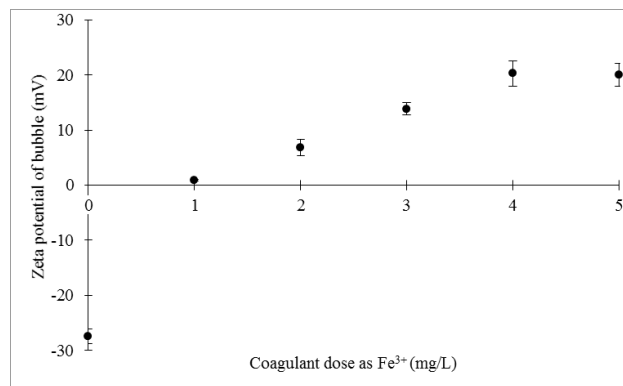


Figure 2. Zeta potential of ferric-bubble (calculated based on Smoluchowski's equation and expressed in average values and standard deviation) in various  $Fe^{3+}$  concentration.

### 3.2. Performance of flotation process

**Removal efficiencies:** Figure 3 indicates cell removal and Chlorophyll *a* reduction of chain-like and pin-like algae. In general, the greater positive bubbles were more effective than the negative and neutral ones. As seen in Figure 3-a, positive bubbles of above 4 mg/L  $Fe^{3+}$  addition obtained the greatest cells removal, showed by ~90% for both chain-like (as *Phormidium sp.*) and pin-like (as *Nitzschia pungens*) algae. In Figure 3-b, Chlorophyll *a* reduction of pin-like cell was slightly higher than it of chain-like cell (~92% comparing to ~85%, versus) at the lower  $Fe^{3+}$  concentration (3 mg/L in comparison with 4 mg/L, respectively).

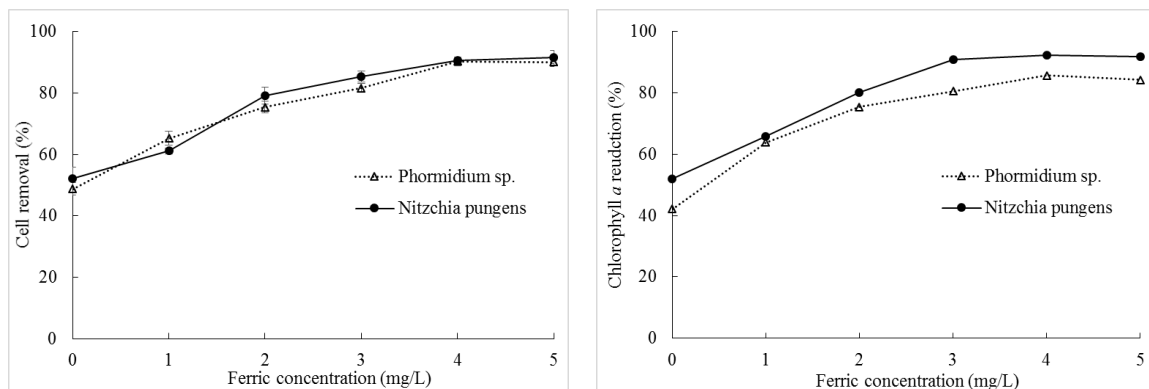


Figure 3. Filamentous algae removal efficiencies by charged bubble flotation: a) Cells removal and b) Chlorophyll *a* reduction.

The relation of the  $\text{Fe}^{3+}$  presence and shifting in zeta potential (from negatively to positively) of bubble would affect removal efficiencies. As mentioned, both filamentous algae in this research charged negatively, making them easier to be attracted and more likely removed by positive bubbles. In the range of 1 to 5 mg/L, the positivity of bubbles' charge was gradually increased upto  $\sim 20$  mV, equating to the average negativity of algae at pH from 6.5 to 9; thus enhancing removal efficiencies. At a cell number, Chlorophyll *a* pigments of pin-like algae would be less than it of chain-like form due to pin-like algae's shorter filamentous form; resulting in higher Chlorophyll *a* reduction of *Nitzchia pungens* algae in comparison with *Phormidium specie*.

**Change in cells structure:** The change of algal morphology (i.e. structure) was characterized in order to investigate the effects of filamentous types on charged bubble flotation performance. Cells shape of *Phormidium sp.* and *Nitzchia pungens* were examined in three differing cases (i.e. the negative, neutral and positive bubbles application). It is found that regardless of bubbles' charge, *Nitzchia pungens* or pin-like algae unchanged their cells structure (Figure 4 – a, b, and c); whilst *Phormidium sp.* or chain-like cells obviously divided themselves into several shorter segments in perspective of positive bubbles flotation (Figure 4 – d, e, and f).

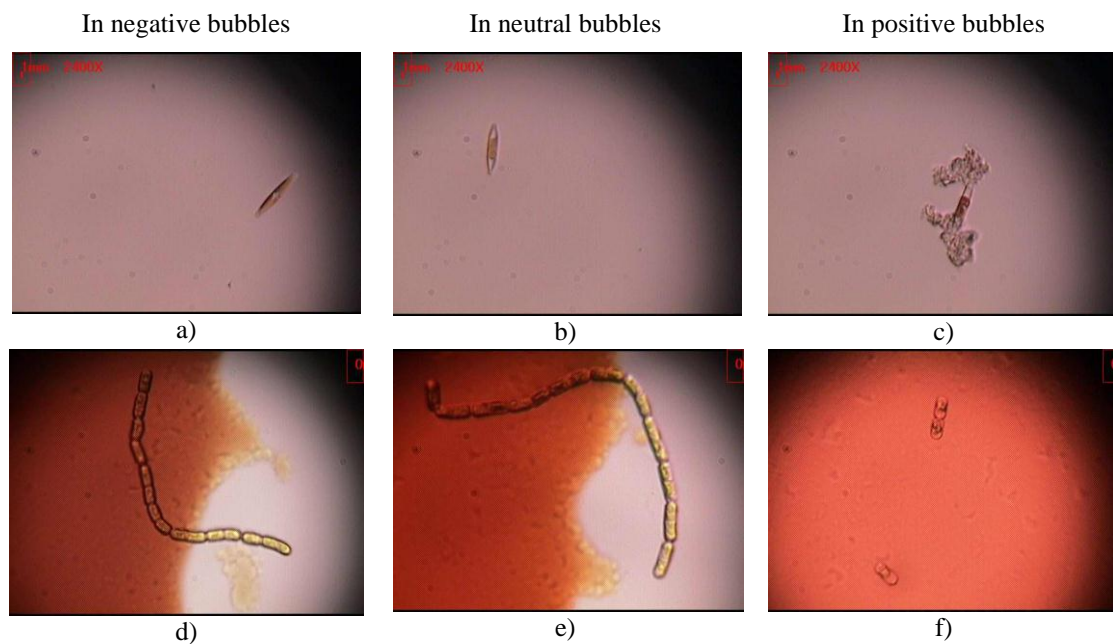


Figure 4. Cell structure in charged bubbles flotation (negatively – left; neutrally – middle, and positively – right) for pin-like algae (a, b and c) vs. chain-like algae (d, e and f).

The positivity of bubble's zeta potential and structure of filament were attributed to the breakup of *Phormidium sp.* in flotation process. Since it was formed from different oval-segments and in the cells structure, the bonding points between segments would be the weakest and easiest to be broken by appropriate positive bubbles (with high shear-force and opposite charge). Moreover, it can be discussed that an attachment of detached shorter chain-like cells and positive bubble would make the cells shorter or/and even ovally-like which were remained in the water and counted as an algal cell. This confirmed the similar cells removal of chain-like and pin-like algae while chain-like algae were easier to form cell-bubble aggregates.

#### 4. CONCLUSIONS

In this research, positive bubble has shown its effectiveness on both chain-like and pin-like algae removal. Similar number of the cells was removed for both types of filamentous algae (i.e. maximization of 90 % cells removal at 4 mg/L of ferric addition); however, due to the cell length, greater reduction of Chlorophyll *a* of pin-like algae was obtained. The breakup of chain-like cells into shorter chain-like forms at positive bubble conditions provides a conclusion of the effect of cell structure on algal removal by flotation. This research is meaningful to provide understanding of morphological effects in algae removal using dissolved air flotation. The results of the study would be practically considered for management of algal-bloom waters.

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