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Removal of *Phormidium* sp. by positively charged bubble flotation

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ABSTRACT

The objectives of this study were to investigate the behavior of *Phormidium* sp. during flocculation and negatively or positively charged bubble flotation in order to optimize algal removal processes and identify mechanisms underlying the efficiency of flotation with positively charged bubbles. The nuisance of *Phormidium* sp. significantly decreases water quality in natural watershed and clogs filter bed in water treatment plant. Although dissolved air flotation has been recently adopted for algae removal, the best method has not been fully investigated. According to theories on dissolved air flotation, the operational conditions affect removal of the process and in this study, the optimum bubble generations was also investigated for better algal removal. Bubbles were generated at two levels of saturated pressure and measured at different bubble concentrations (10%, 20% and 30%), in the absence and presence of coagulants. Bubbles forming at 6 bars and 3 bars were observed at zeta potentials of −30 mV to + 27 mV. The chain-like algae were cultured in the laboratory for 20 days. At the stationary phase, *Phormidium* sp. sizes ranged from 2 μm to 10 μm in diameter and about 100–200 μm in length. Over a pH range of 4.0–7.0 (increments of 0.5), the negative zeta potentials were −4 mV to −12 mV. Algal removal by flocculation was determined by jar tests and by the batch dissolved air flotation (BDAF) method with bubble generation and flotation. We obtained optimal *Phormidium* sp. removal with positively charged bubble flotation at a 30% bubble rate at >16 mV and a bubble formed at 6 bars, with removal of up to 85% and 93% of cells and chlorophyll *a*, respectively. We also demonstrated the efficacy of using positively charged bubbles to remove *Phormidium* sp. cells and the importance of positively charged bubbles in the rarely reported interaction between bubbles and chain-like algae.

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1. Introduction

Filamentous algae at the base of the water column in fresh watersheds form a periphyton community under high light conditions, consisting of series of cells joined end-to-end, giving them a thread-like appearance (Bellinger and Sigee, 2010). In lakes or ponds, these normally develop into massive surface populations known as "pond moss" or "pond scum," especially in summer (Bellinger and Sigee, 2010; Canter-Lund and Lund, 1996; Sze, 1998; Paerl et al., 2001). Among the chain-like filamentous algae, *Phormidium* sp. is the one of the most common species in floating mats on the water surface (Canter-Lund and Lund, 1996; Sze, 1998). This algal nuisance reduces water quality and causes the filter bed to become clogged in conventional water treatment plants (Graham and et al., 1998; Hargenshainer and Watson, 1996; Bauer and et al., 1998). Effective removal of filamentous algae can be achieved by flocculation, negatively charged bubble flotation, and positively charged bubble flotation, of which the latter remains a challenge. Dissolved air flotation (DAF) has been widely used to remove algae due to its improved floatability and applicability in natural systems (Gao et al., 2010; Henderson et al., 2010a,b; Teixeira et al., 2010; Henderson et al., 2008; Wang et al., 2008). These studies demonstrated that bubble characteristics affect the collision mechanism of particles, and bubbles in turn affect removal efficiencies (Han et al., 2006, 2004, 2001; Han and Dockko, 1998). Bubble generation under saturated pressure with covalent metal ions can change the zeta potential from negative to positive, thus enhancing removal efficiency (Han et al., 2004). However, for spherical or spheroid algae, maintaining negative to low positive zeta potential is also key to successful algal removal (Henderson et al., 2010a, 2008; Taki and et al., 2008). Similar sized bubbles increase collisions of the bubble–particle attachment, thus improving removal efficiency (Han et al., 2001). Additionally, the similar size distribution of bubble and particle would result the better removal on flotation process; however, there have been few studies on the collision mechanism of bubbles and filamentous cell aggregates and optimal tools for removal of filamentous algae. We aimed to (1) evaluate *Phormidium* sp. removal efficiencies by flocculation and flotation (including

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negative and positive bubbles) and (2) investigate the mechanism by which chains of *Phormidium* sp. are broken by positively charged bubbles. We optimized bubble formation by determining the ideal concentration (amount of bubbles injected), zeta potential (by adding dosed coagulants), and bubble size (by changing saturating pressures) for cells removal of *Phormidium* sp. and chlorophyll *a* reduction.

2. Materials and methods

2.1. Phormidium sp. culture and observation properties

Phormidium sp., a representative chain-like algae, was purchased from Korea Marine Microalgae Culture Center (KMMCC #1218, sampled from Upo, South Korea swamp surface water) and cultured in the laboratory. Cells were grown in a 2-L de-ionized water flask at 28 °C in Jaworski's medium (JM) with a 24-h light conditions (300 lux) and 0% salinity. The culture was shaken at 150 rpm for 20 days. This culture regime was intended to mimic the optimal growth conditions of *Phormidium* sp. in nature.

We analyzed *Phormidium* sp. cell size, charge at various pH values, and populations (i.e., cell number and chlorophyll *a*). Cell size and number were determined with a hemocytometer with a cover slip, a microscope, and image analysis software. Zeta potentials at pH 4–7 were measured with a zetaphotometer (ALPHAPHOT – 2, SY2, France), and pH was adjusted with NaH_2PO_4/Na_2HPO_4 and $CH_3COOH/NaCH_3COO$. In more details, the measurement of algal charge was conducted with a system including a microscope cell, a camera and an image analyzer under experimental conditions of a temperature of 26 °C, a conductivity of 0.019 mS/cm and an electric field of 9.78 V/cm. Zeta potential of *Phormidium* sp. was then calculated from Smoluchowski's equation in an accordance with a coefficient of 12.76. To determine the concentration of chlorophyll *a*, *Phormidium* sp. cells were concentrated by filtering a volume of 50 mL of sample through a membrane filter (47 mm, 5 μm pore size); the pigments were extracted from concentrated algal sample with 10 mL of 90% aqueous acetone (90 parts acetone and 10 parts magnesium carbonate); and in order to control acetone evaporation, absorbance was immediately measured on a spectrophotometer (Libra S60PC) at three wavelengths (i.e. 664 nm, 647 nm and 630 nm) in which 90% aqueous acetone was used for calibration.

2.2. Flocculation

In the flocculation experiments, aluminum coagulant (as Al^{3+} a trivalent metal ion forming from $Al_2(SO_4)_3{\cdot}18H_2O$ – a hydrated salt with the impurity of >99.0%) at various concentrations (i.e. 0, 5, 10, 15, 20, 25 and 30 mg/L) was added to 1 L de-ionized water containing *Phormidium* sp. A standard jar test was used to assess flocculation performance with 1 min of fast mixing at 250 rpm, followed by 20 min of slow mixing with coagulant addition at 20 rpm. Samples were collected after 30-min settling to measure residual cell numbers and chlorophyll *a*.

2.3. Bubble generation and batch testing

Micro-bubbles were generated at saturated pressures in the presence of coagulants in 1 L de-ionized water (Kim et al., 2012). Zeta potential was measured with an electrophoresis cell, video camera, and video image analyzer (Han et al., 2001). This system measured electrophoretic mobility; zeta potential was calculated by using Smoluchowski's equation (Han and Dockko, 1998). An online particle counter (OPC Chemtrac System Inc., Model: PC 2400D-Laser Trac™, USA) was used to determine the size and size distribution of the generated bubbles. We compared several flotation methods of *Phormidium* sp. removal to the flocculation method, including the batch-dissolved air flotation (BDAF) method with added $Al_2(SO_4)_3{\cdot}18H_2O$ (0–30 mg/L of Al^{3+} with an increment of 5) and batch-type flotation with bubbles of varying concentration, charge, and size for better removal. Bubble concentration was controlled by changing the injection amount (10%, 20% and 30%), and size distribution was modulated by changing the pressure (3 bars and 6 bars). Zeta potential was controlled by adding various concentrations of Al^{3+} (0, 0.5, 1 and 5 mg/L) with a background solution of NaCl 0.1 M. These experiments for better removal are summarized in Table 1.

Bubbles were injected from a saturator to an acrylic cylindrical reactor containing *Phormidium* sp. in 1 L de-ionized water. After flotation, samples were collected to investigate removal efficiency (cell number and chlorophyll *a* concentration), and changes in *Phormidium* sp. morphology were observed by microscopy (Sometech, Korea) and image analysis.

3. Experimental results

3.1. Characteristics of Phormidium sp.

The morphology of *Phormidium* sp. under cultivated conditions is provided in Table 2 with an image. *Phormidium* sp. is a chain-like algae with cells formed in segments, each of which is spheroid. Most of the segments are surrounded by a continuous cuticle to form the filament. These chain-like cells range from 2 to 10 μm in diameter and about 100–200 μm in length (Table 2).

3.2. Removal efficiencies

Fig. 1 shows the separation efficiencies of the flocculation and flotation methods, with *Phormidium* sp. removal expressed in terms of cell number and chlorophyll *a*. BDAF was performed with a 30% bubble injection rate and a saturated pressure of 6 bars (Fig. 1). Overall, BDAF was more efficient than flocculation, providing greater removal at Al^{3+} concentrations less than 20 mg/L and similar results at concentrations >20 mg/L. The BDAF process was improved by adding Al^{3+} coagulant; best results were obtained at 5 mg/L Al^{3+}. The maximum separation efficiencies of DAF were 86.14% for the cells and 92.32% for chlorophyll *a*; without coagulant, we achieved separation of only ~60% of the cells and ~55% of chlorophyll *a*. BDAF was more efficient than flocculation (25–80% removal). Furthermore, the removal of *Phormidium* sp. by flotation decreased slightly regardless of increase in Al^{3+}, while in the flocculation process, it continuously increased with corresponding increases in Al^{3+} application. Thus, bubbles in the presence of 5 mg/L Al^{3+} coagulant provided better results than bubbles without coagulant or the flocculation method.

These results can be explained by the relationship between the presence of coagulant and change in zeta potential of bubbles that would have the effects on removal efficiencies. Adding Al^{3+} shifted the bubble charge from negative to positive (Han et al., 2006). The zeta potential of *Phormidium* sp. is negative, making it more likely to attach to and be removed by positively charged bubbles. Higher concentrations of Al^{3+} (10^{-5} M or 5 mg/L) slightly reduced the bubble zeta potential, thus reducing removal efficiency at

Table 1
Summary of experimental conditions for better removal.

Set 1: change of bubble rate	Set 2: change of pressure
Bubble rates: 10%, 20% and 30%	Bubble rate: 30%
Pressure: 6 bars	Pressure: 6 bars, 3 bars
Coagulant: Al^{3+}: 0, 0.5, 1 and 5 mg/L	Coagulant: Al^{3+}: 0, 0.5, 1 and 5 mg/L

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