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A novel low cost microalgal harvesting technique with coagulant recovery and recycling

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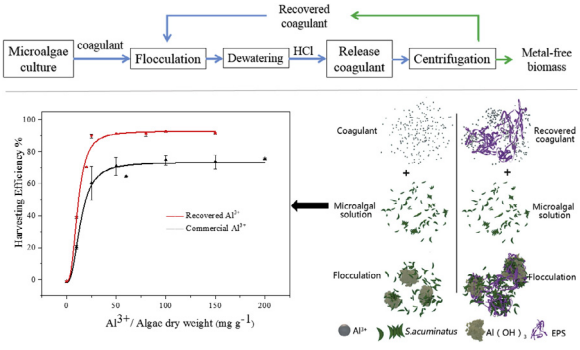
GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a novel low cost and sustainable microalgal harvesting technique was developed using the concept of coagulant recovery concentration and recycling. Al^{3+} can be recovered from harvested *Scenedesmus acuminatus* biomass with 0.1 M HCl, at an acid solution-biomass ratio of 250 ml g^{-1}. The residual Al^{3+} content in the purified biomass was reduced to 0.11 ± 0.0006 mg g^{-1}, while a higher content of 59.74 ± 3.11 mg g^{-1} was found in the coagulation harvested biomass. The recovered Al^{3+} solution was concentrated 25 times and then reused for the harvesting of *S. acuminatus*. The Al^{3+} recovery and reuse were repeated 5 times, and the harvesting efficiencies were found higher than the fresh Al^{3+} as a result of the presence of extracellular polymeric substances in the recovered coagulant solution which aided the coagulation process. According to the technical-economic analysis, the cost of chemicals decreased 50% after 5 times recycling.

1. Introduction

Nowadays, the application of microalgae has attracted great attention for producing biofuels and environmental remediation (Shi et al., 2017). As the third generation biofuel feedstock, microalgae presented numerous economic and ecological advantages, such as high productivity, less land occupation, and more environmentally sustainable (Barros et al., 2015; Pragya et al., 2013). However, the low biomass

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concentration of microalgal culture suspension which is typically less than 1 g L^{-1} in large scale (Das et al., 2016; Wan et al., 2015) and the small size of microalgal cells (2–30 μm) remain the huge challenges in microalgal harvesting (Wan et al., 2015).

So far, a lot of separation techniques have been used to harvest microalgae: filtration including microfiltration/ultrafiltration/forward osmosis (Ye et al., 2018), centrifugation (The microalgal suspension was centrifuged directly without any sedimentation or filtration) (Molina Grimaa et al., 2003), coagulation-sedimentation/flotation (Abomohra et al., 2018), as well as the combination of these techniques (Barros et al., 2015). In most commercial production, microalgae are harvested by centrifugation, which is energy-intensive and not suitable for production of low-value products such as biofuel (Abdul Hamid et al., 2014; Granados et al., 2012). Microalgal harvesting using membrane filtration is also reported, but the membrane fouling is still a challenge which limits its large scale application (Gerardo et al., 2015; Rawat et al., 2011).

Due to high loading rate and low energy consumption, coagulation-flocculation-sedimentation/flotation appears to be the least expensive solution for large scale microalgal harvesting (Granados et al., 2012). However, biomass contamination is another barrier for the coagulation based harvesting, as metal ions can interfere with the subsequent lipid extraction and conversion process. Although chitosan and charge-tunable polymers induced coagulation has been introduced, they are either too expensive, or have the problems of eco toxicity (Milledge and Heaven, 2012; Morrissey et al., 2015; Vandamme et al., 2013).

If biomass contamination and high cost of coagulant-the two main barriers impeding the large scale application of coagulation based harvesting-can be solved, the current cost of biofuel would be greatly reduced, and the application of the biomass or lipid extracted biomass could be extended greatly. In previous studies, aluminum and ferric ions were recovered from activated sludge by acid solution combined with stirring and ultrasonic, and reused in water treatment (Ishikawa et al., 2007; Xu et al., 2009a; Xu et al., 2009b). Ferric ion recovery and reuse by acid solution were also investigated in microalgal harvesting (Das et al., 2016; Kim et al., 2017), however, the factors influencing the recovery efficiency, as well as the concentration of the recovered coagulant have not been investigated comprehensively. Moreover, it is very important to explore the reusability of the recovered coagulant, as its composition may differ from the fresh one.

In this study, a novel coagulant recover, concentration and recycling technique was developed, using *Scenedesmus acuminatus* and Al^{3+} as model microalgal strain and coagulant. The objectives of this study are, 1) developing an appropriate technique to recover and concentrate Al^{3+} from harvested *S. acuminatus* biomass effectively, and to purify the biomass 2) exploring the effect of multiple times of coagulant recycling on the harvesting efficiencies, and 3) analyzing the savings on the chemical consumption using coagulant recover and recycling technique.

2. Materials and methods

2.1. Microalgal cultivation

The freshwater microalgae *Scenedesmus acuminatus* (GT-2, SDIC Microalgae Biotechnology Center, China) was cultured in 15 L acrylic panel photobioreactors in batch mode. Culture temperature was controlled at 25 °C and mixing the culture was performed by continuously bubbling air with 3% CO_2 at a rate of 6 L min^{-1}. The initial NO_3^- - N concentration of the modified BG-11 was reduced to 32 mg L^{-1} to increase lipid production in the environment of the nitrogen starvation (Liu et al., 2016; Zhang et al., 2012). Fluorescent lighting was provided at an intensity of 180 μmol m^{-2} s^{-1}, 24 h of photoperiod per day, and the pH of the cultures ranged from 6.5 to 7.0. The dry weight reached 1 g L^{-1} before harvesting.

For the experiment of 5 times coagulant recovery and recycling, 1.5 g L^{-1} *S. acuminatus* biomass was used, which was obtained from an indoor 200 L tubular photobioreactor with light intensity of 130 μmol m^{-2} s^{-1}. Tap water was used to prepare the modified BG11 culture media for this cultivation.

2.2. Coagulation-flocculation-sedimentation harvesting of S. acuminatus

The microalgal harvesting experiment was performed using jar test with 500 ml beakers (Phipps Bird, Richmond, VA 23230, USA). Aluminum sulfate ($Al_2(SO_4)_3{\cdot}18H_2O$) was used as coagulant for *S. acuminatus* harvesting. Aluminum was quickly added into the beaker with rapid mixing (200 rpm, for 2 min). Meanwhile the pH was adjusted to 6.2 ± 0.2 by adding 1 M NaOH, followed by slow stirring (30 rpm, for 10 min). Then the suspension was settled for 15 min. 10 ml supernatant (in the middle of the surface and flocculation layer) was collected and the dry weight was measured. Harvesting efficiency was calculated by the following formula.

$$Harvesting\ efficiency = \frac{DW_i - DW_f}{DW_i} \times 100\% \quad (1)$$

where DW_i is initial cell dry weight of the culture, and DW_f is cell dry weight of supernatant after the settlement.

2.3. Al^{3+} recovery

Biomass containing Al^{3+} was collected after jar testing. The biomass was transferred into 50 ml tubes, and centrifuged at 3000*g* for 5 min (Beckman Coulter, Allegra X-15R) to collect the microalgal pellet. The pellet was then washed with hydrochloric acid for Al^{3+} recovery and biomass purification. After complete mixing, all the tubes were fixed on the rotary agitator rotated at 50 rpm for 15 min, and then the suspension was centrifuged at 3000*g* for 5 min to collect the Al^{3+} containing supernatant. The Al^{3+} concentrations were analyzed using ICP-OES (OPTIMA 8000DV, PekinElmer, USA), and the Al^{3+} recovery efficiency was calculated using the following equation:

$$Recovery\ efficiency = \frac{C_r \times V_r}{C_i \times V_i} \times 100\% \quad (2)$$

where $C_r$is Al^{3+} concentration in the recovered solution; V_r is volume of recovered solution; C_i is initial Al^{3+} concentration, and V_i is volume of Al^{3+} used in the coagulation process.

The influence of acid concentration, initial dosage of aluminum, ratio of acid solution-biomass (called liquid-solid ratio below, ml g^{-1}), and washing times on Al^{3+} recovery efficiencies were studied. To explore the effect of acid concentration, *S. acuminatus* pellet was collected with an initial Al^{3+} dosage of 100 mg g^{-1}, and different concentrations of acid solution, namely 0.01 M, 0.1 M, 0.5 M, and 1.0 M were added into the pellet at liquid-solid ratio of 250 ml g^{-1}. For the study of the effect of liquid-solid ratio, different liquid-solid ratios of 17, 85, 256, 854 ml g^{-1} were tested, and the initial dosage of Al^{3+} and acid concentration was kept 100 mg g^{-1} and 0.1 M, respectively. For the study of the effect of initial aluminum dosage, different dosages of 5, 30, 100, 200 mg g^{-1} were investigated with the acid concentration of 0.1 M, and the liquid-solid ratio of 250 ml g^{-1}.

To obtain sufficient amount of recovered Al^{3+} for five times sequential coagulation recovery and recycling experiment, 18 L 1.5 g L^{-1} *S. acuminatus* was harvested with 100 mg Al^{3+} g^{-1} initially, and then the subsequent acid washing was conducted in several 500 ml beakers with the acid concentration of 0.1 M, and liquid-solid ratio of 250 ml g^{-1}.

2.4. Residual Al^{3+} in the Al^{3+} recovered (purified) biomass

After Al^{3+} recovery, certain amount of purified biomass was collected and freeze dried using freeze dryer (FreeZone-12L, Labconco, USA). The dried biomass was fixed on the conductive adhesive tape and