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Electro-flotation of *Chlorella* sp. assisted with flocculation by chitosan

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ABSTRACT

Harvest of algal biomass from dilute culture medium at low cost remains a major hurdle to industrial scale processing. Conventional harvesting methods are not only costly, but also affect any later downstream processes partly because of the metal ions contamination by flocculants. This work constructed an electro-flotation technique including two steps of flocculation by chitosan first and then sequential bubbling flotation by non-sacrificial graphite electrodes. Laboratory work has been carried out to investigate the influences of chitosan dosage, pH value, cell density of algal culture, stirring rate and mixing time on flocculation efficiency, and the voltage and current intensity imposed on electrodes and the space between electrodes on flotation efficiency. Moreover, a 1000 L pilot bench of electro-flotator constructed to harvest *Chlorella* sp. was tested. Around 90% of total recovery efficiency and 50 times concentration rate have been reached, and only 23.7 g chitosan and 0.43 kWh of electricity are required to harvest 1 kg biomass. Above results proved electro-flotation by graphite electrodes assisted with chitosan is a safe and cost effective approach for microalgae harvesting.

1. Introduction

Microalgae have been widely used as fish baits, healthcare products and food additives due to their richness of nutrients including lipids, proteins and variety of functional components [1–2]. Moreover, recently, the potential and prospect of microalgae for sustainable energy production have been extensively reviewed. In fact, microalgae biofuels have been placed globally as one of the leading research fields which could bring enormous benefits to human beings and environment [3–5]. However, the production of either bio-products or biofuels using algal biomass in commercial purpose has been handicapped by certain problems, one of them is the high cost of algal biomass harvesting from dilute culture [6]. In fact, the algal biomass density of most conventional cultivation systems including open ponds and variety of photobioreactors is less than 5 g L^{-1}, which means large volumes of water is processed during biomass harvesting [7–8]. If centrifugation was directly used for such solid dilute suspension, harvesting has been estimated to contribute more than 30% of the total cost of algal biomass production [9]. Therefore, concentrating the culture to small volume as dense algal slurry and then deeply dewatering of the slurry by centrifugation to obtain algal pastes is a reasonable strategy in order to cut the harvesting cost. Of all the concentrating methods, flotation has been proved to be efficient and operated continuously at large scales.

Flotation is by the aid of the attachment of micro-bubbles on floc to form bubble-floc aggregates and then the bubble-floc aggregates rise to the surface of water-gas interface due to the density difference between aggregates and water. It has been found that bubble characteristics affect the collision mechanism of particles, and in turn affects removal efficiencies [10–13]. Thus, before flotation, the algal cells should form well sized bubble-floc aggregates [14]. Generally, microalgae cells are surface electronegative, while bubbles generated by pressure release or dissolved air pump are neutral or slight electronegative [13,15–17], flocculants addition can induce the formation of bubble-floc aggregates. Although aluminum and ferrous salts are usually used as the common electropositive flocculants nowadays, residual metal ions of Al^{3+} or Fe^{3+} in the harvested algal biomass and effluent water may bring negative effects towards the final product quality and contaminate the culture medium. Fortunately, chitosan, a linear polysaccharide composed of randomly distributed β-(1–4)- linked D-glucosamine (deacetylated unit) and *N*-acetyl-D-glucosamine (acetylated unit) is electropositive. It is made from shrimp and other crustacean shells and has well been proved biodegradable and safe. Sirin et al. [18] used chitosan as flocculent for *Phaeodactylum tricornutum* harvesting and found that the chitosan concentration of 20 mg L^{-1} in medium has the same flocculation efficiency as aluminum polychloride or aluminum sulphate. In addition, the flocculation efficiency of chitosan was influenced by both pH value and the density of algal culture [19]. Ahmad et al. [20] optimized the conditions of flocculation for *Chlorella* sp. with chitosan addition and obtained 99% recovery rate.

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Another factor to influence the flotation of microalgae is the size of bubbles. Small sized and well distributed bubbles have more probability of collisions for bubble–particle attachment and improve removal efficiency [11,14]. For conventional flotation, the bubbles produced by pressure release or dissolved air pump are usually too big and distributed unevenly [21–25]. Currently, electro-flotation has attracted many attention, because this technique could produce dense micro-bubbles by water electrolysis [26–27]. Vandamme et al. [28] used this method successfully to harvest fresh *Chlorella vulgaris* and marine *Phaeodactylum tricornutum* under optimized conditions. The efficiency of electrolysis is dependent on the voltage, current intensity of imposed electricity and the electric conductivity of water. Algal medium has good electric conductivity because it contains rich metal ions, so it has higher recovery efficiency of flotation compared with pure water. Generally in electro-flotation system, the electrodes could be sacrificial or non-sacrificial materials, but sacrificial anode like aluminum is preferable because the dissolved aluminum ions could improve the electric conductivity of water and enhance the flocculation of particles to reduce the usage of flocculants. But, if electro-flotation is used for harvesting microalgae for food additives production, such sacrificial anode is unacceptable due to the dramatically accumulation of metal ions from dissolved sacrificial anode. Vandamme et al. [28] have assessed aluminum ions content in harvested microalgae and residual medium by electro-flotation with aluminum anode and found it reached 3% of dry weight and 2 mg L^{-1} respectively. Misra et al. [29] adopted graphite electrodes instead of metal electrode to harvest *Scenedesmus obliquus* cells, but the recovery efficiency reduced to 80% and the power consumption increased to 3.84 kWh per kg biomass. In spite of this, electro-flotation by graphite electrode is a safer harvesting option especially for the production of microalgae as food additives.

Chlorella sp. is popularly used as healthcare products, however, because of the small size (2–5 μm) of cells, traditional methods including sedimentation, filtration and centrifugation are ineffective to harvest this algae. In this work, electro-flotation process of non-sacrificial graphite electrodes assisted with food safe chitosan as flocculants was constructed for *Chlorella* sp. harvesting. The influences of chitosan dosage, pH value, algal density and stirring rate on flocculation of *Chlorella*, and the effects of voltage of electricity and the distance between graphite electrodes on the flotation recovery efficiency were systematically investigated in laboratory. Finally its harvesting practice in pilot scale which was constructed by modifying a traditional air dissolving pump driven flotator was also performed. Results showed electro-flotation with non-sacrificial graphite electrodes assisted with chitosan is a promising way for economical and safe harvesting of small size microalgae.

2. Materials and methods

2.1. Microalgae strain and cultivation methods

The freshwater microalgae species *Chlorella* sp. 0217 was locally screened in Qingdao, China, and maintained in BG11 medium in Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences. Laboratory cultivation was carried out in bubbling glass column with a diameter of 50 mm, containing 800 mL medium, in which, CO_2 enriched gas (1.5%, v/v) was continuously aerated at 0.1 vvm and the light intensity and temperature were maintained at 100 μmol photons m^{-2} s^{-1} by fluorescent lamps and 20 °y respectively.

2.2. Flocculation conditions of Chlorella sp.

Chitosan was purchased from Aladdin Industrial Corporation, and 1 g L^{-1} of chitosan solution was prepared with 1% acetate acid solution and stored in refrigerator at 4 °o for later use. The flocculation of *Chlorella* sp. was carried out in a 500 mL beaker containing 200 mL microalgae suspension. Different dosages of chitosan solution were added into the beaker to make the chitosan concentration of 0–32 mg L^{-1}. Mechanic stirring (by JJ-1DS, Hongye, China) was used to mix the solution for a certain time and then the solution was settled down for 20 min. 5 mL supernatant was taken for measuring optical density (OD) at 680 nm. Single factor experiments were arranged in order to investigate the effects of pH (5.0, 5.5, 6.0, 6.5, 7.0, 8.5), microalgae biomass density (0.17, 0.32, 0.47, 0.63, 0.94, 1.25 g L^{-1}), stirring rate (30, 60, 90, 120, 150, 180, 210 rpm) and stirring time (0–180 s) on flocculation efficiency. The pH was adjusted with 1.0 mol L^{-1} sulfuric acid or sodium hydroxide solution.

The flocculation efficiency (FE) was calculated according to Eq. (1).

$$FE = (1 - OD_t/OD_0) \times 100\% \quad (1)$$

where, OD_0 is the initial optical density of microalgae suspension and OD_t is the optical density of the supernatant after flocculation. The relationship between OD at 680 nm and the concentration of microalgae in dry weight (DW) was calibrated as shown in Eq. (2).

$$DW = 0.1567 \times OD_{680} \left(g\ L^{-1}\right), R^2 = 0.992. \quad (2)$$

2.3. Electro-flotation of Chlorella sp.

The electro-flotation was carried out in a plexiglas column with the diameter of 50 mm and the height of 600 mm. The micro-bubble generator, a couple of graphite electrode plates connected with a current DC power (KXN-305D, Zhaoxin, China), was fixed at the bottom of the column. Of which, both the plates have the diameter of 44 mm and thickness of 5 mm. As most of the micro-bubbles were produced in the space between two electrode plates by electrolysis, the upper anode plate was designed as pectinate plate which was concatenated by 14 pieces of graphite slice (1 mm in thickness) with space of 2.0 mm between the adjacent slices (Fig. 1A) in order to avoid the micro-bubbles coalescence and lead a well distribution. A 1000 mL flocculated solution of *Chlorella* sp. at an optimal condition which was determined in Section 2.2 was gently poured into the flotation column, and then switched on the flotation at different voltage according to the experimental arrangements. Samples at the half-depth of suspension were taken to measure OD value for calculating the recovery efficiency (RE). The influences of the space between anode and cathode plates (1, 2, 5, 10 mm) and the imposed voltage (3, 3.5, 4, 5, 6 V) on recovery efficiency of electro-flotation were investigated. The recovery efficiency of flocculation-electro-flotation at optimized conditions was compared with two controls of only flocculation by chitosan or only electro-flotation.

The recovery efficiency (RE) of electro-flotation was calculated by Eq. (3).

$$RE = (1 - OD_t/OD_0) \times 100\% \quad (3)$$

where OD_0 is the initial optical density of microalgae solution, and OD_t is the optical density of the residual solution after electro-flotation.

The power consumption (PC) was calculated according the following Eq. (4) by Vandamme et al. [28].

$$PC = (P \times t)/(1000 \times V \times C_0 \times RE_t) \quad (4)$$

where, P (W) is output power of DC power, t (h) is the minimum time when the recovery efficiency of Electro-flotation reached 90% above, RE_t is the very recovery efficiency at time t, C_0 (g L^{-1}) and V (L) is the initial concentration and volume of microalgae solution.

2.4. Pilot practice of harvesting of Chlorella sp. by Electro-flotation

The pilot electro-flotator is modified from a conventional air dissolved flotator which originally used air dissolving pump as bubble