Bioresource Technology 198 (2015) 789–796

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Harvesting *Chlorella vulgaris* by magnetic flocculation using Fe_3O_4 coating with polyaluminium chloride and polyacrylamide

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HIGHLIGHTS

- Polymers of PACl and PAM were combined with Fe_3O_4 to harvest *Chlorella vulgaris*.
- The optimum dosing strategy was adding the composite PACl/Fe_3O_4 first and then PAM.
- This strategy could harvest 99% of cells in less than 0.5 min.
- This strategy could avoid the influence of pH and algal organic matter.
- Charge neutralization of PACl/Fe_3O_4 and sweeping of PAM were the main mechanism.

ARTICLE INFO

Article history:
Received 12 July 2015
Received in revised form 24 September 2015
Accepted 25 September 2015

Keywords:
Microalgae harvesting
Magnetic flocculation
Polyaluminium chloride
Polyacrylamide
Composite flocculant

ABSTRACT

The harvesting of *Chlorella vulgaris* was investigated by magnetic flocculation, where the natural magnetite was used as magnetic seeds and the polyaluminium chloride (PACl) and polyacrylamide (PAM) were used as the coating polymer on the Fe_3O_4 surface. The composite modes of PACl, PAM, and Fe_3O_4 and their effects on harvesting were studied. The results showed that adding the composite PACl/Fe_3O_4 first (at (0.625 mmol Al/L)/(10 g/L)) followed by the addition PAM (at 3 mg/L) was the optimum dosing strategy. Following this strategy, 99% of cells could be harvested in less than 0.5 min, and it could overcome negative impacts from pH and algal organic matter. Compared to PACl, ζ-potentials of PACl/Fe_3O_4 were found to be increased substantially from −4.9–8.5 mV to 1.5–19.5 mV at pH range 2.1–12.3. The charge neutralization of PACl/Fe_3O_4 and sweeping of PAM play an important role in magnetic harvesting of microalgal cells.

1. Introduction

Increasing energy demands coupled with environmental concerns, regarding the generation of greenhouse gases during fossil fuel combustion, have drawn attention toward the development of renewable biofuels (Foley et al., 2011). Microalgae are considered to be one of the most promising feedstock option due to its low cost, high lipid content, and bulk biomass (Chisti, 2007). However, small size of microalgae cells and their colloidal stability in suspension result in low efficiency and expensive consumption of energy in harvesting and dewatering; this has always been a major obstacle for the algae-to-fuel approach (Slade and Bauen, 2013).

To obtain the microalgae paste for drying, a primary harvesting step is often used to concentrate the dilute microalgae suspension from 0.02% to 0.06% total suspended solids (TSS) into a slurry with 2–7% TSS, then followed by a secondary dewatering step that produces a paste of 15–25% TSS (Uduman et al., 2010). The desired microalgae concentration is important to the drying process for lipid extraction. The major methodologies currently used for harvesting and recovering microalgae include gravity sedimentation (Smith and Davis, 2013), filtration and screening (Bilad et al., 2013), flotation (Kurniawati et al., 2014), electrophoresis (Uduman et al., 2010), centrifugation (Dassey and Theegala, 2013), and flocculation (Vandamme et al., 2013). In sedimentation processes in a mass force field, the settling behavior of particles strongly depends on physico-chemical properties, concentration, and size distribution of the particles. Although it is considered to be a low-cost and simple technique, the technique is only suitable for microalgae larger than 70 μm (Gultom and Hu, 2013). For

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http://dx.doi.org/10.1016/j.biortech.2015.09.087
0960-8524/

smaller microalgae (5–20 μm), flocculants must be used to achieve higher settling velocities (Smith and Davis, 2013). Flotation is a physico-chemical type of gravity separation process, where air or gas bubbles attach to algae cells and help in carrying them to surrounding liquid's surface (Chen et al., 2011). It is suitable for harvesting small and unicellular algae and is reportedly more effective and beneficial than sedimentation (Chen et al., 2011), although is often limited by the energy requirements of bubble production. As for electrophoresis techniques, the microalgae can be separated from water-based solutions through movement using an electric field, including electrolytic coagulation, electrolytic flotation, and electrolytic flocculation (Uduman et al., 2010). In filtration process, algal culture runs through filters that allow water and small molecules to pass, while inhibiting passage of larger microalgae cells. Such filtration methods can achieve an almost complete retention of biomass, however, consumes considerable amount of energy due to the application of high pressure and liquid velocity (Bilad et al., 2013). Centrifugation is the predominant method for harvesting microalgae as it does not require addition of chemicals. It can often be used in the secondary dewatering process. However, algal broth often requires preconcentration to reduce energy demands for centrifugation and the associated costs.

Due to relatively low cost and energy consumption, flocculation receives greater attention for primary harvesting than the other aforementioned techniques. During flocculation, single cells can be concentrated from microalgae suspensions to form large aggregates that can be easily separated from medium by simple gravity sedimentation (Vandamme et al., 2013). This can be achieved using several approaches including traditional chemical flocculation methods widely used in water treatment to novel ideas based on the biology of microalgae such as bioflocculation (González-Fernández and Ballesteros, 2012).

Magnetic flocculation is a newly emerging technology, which applies modified magnetic particles that attach directly to microalgal cells and later separate them from medium using an external magnetic field (Wang et al., 2014). In the modified technique, magnetite acts as the core coated with a protective organic layer carrying specific functional groups ensuring selective separations and/or targeting, resulting in the formation of composite magnetic beads (Prochazkova et al., 2013). The coating organics can bind magnetic core with microalgae cells and make the cells to aggregate together. The binding organics in microalgae harvesting include poly(diallyldimethylammonium chloride) (Lim et al., 2012; Toh et al., 2012), chitosan (Lee et al., 2013; Toh et al., 2014), diethylaminoethyl (Prochazkova et al., 2013), polyethylenimine (Ge et al., 2015; Prochazkova et al., 2013), and cationic polyacrylamide (Wang et al., 2014). Such magnetic separation technique can achieve more than 90% of cell recovery in less than 5 min during the harvesting processes of microalgae. The magnetic harvesting combines flocculation and magnetic separation in a single process, offering quick, simple, energy-efficient, and cost effective advantages. In addition, external magnetic field enables to concentrate magnetically modified cells into compact slurry and remove large amounts of bulk liquid in a short time.

In the magnetic flocculation technique, organic polymer used for coating and the dosage of magnetic composite are the main factors influencing the harvesting efficiency (Prochazkova et al., 2013). The magnetic particles, pH value, reaction time, and stirring speed can also affect cell recovery (Wang et al., 2014; Xu et al., 2011). Due to negative surface charges on most microalgae, cationic polymers are often used as coating chemicals. In previous studies, only one cationic polymer has been tested to make composite with Fe_3O_4. Using two organic polymers for dosing is an approach that not only improves separation effects, but also shortens settling time in the conventional flocculation (Ahmad et al., 2008). However, less reports are available till date regarding two polymers dosing strategy to make composite with magnetite in harvesting microalgae. Polyaluminium chloride (PACl) is often applied coupled with polyacrylamide (PAM), and the combination has already exhibited better efficiency in removing algae and pollutant during water treatment (Ahmad et al., 2008; Lou et al., 2013). Hence, PACl and PAM were selected as the two polymers to combine with natural magnetite in this study.

The present study examines the composite modes of PACl, PAM, and Fe_3O_4 and their effects on harvesting of oleaginous microalgae *Chlorella vulgaris* (*C. vulgaris*) from freshwater. Natural magnetite was selected as the magnetic material and characterized its surface properties using field emission scanning electron microscopy (FE-SEM), energy-dispersive spectroscopy (EDS), and X-ray diffraction (XRD) patterns. The harvesting efficiency of different dosages, dosing strategy of composite flocculants and the ratio of polymer to Fe_3O_4 were also investigated. Moreover, the ζ-potentials of the composite flocculants and the supernatant after flocculation were measured. The influence of pH of microalgal broth, settling time, and algal organic matter (AOM) on cell harvesting were also evaluated.

2. Methods

2.1. Algae culture

C. vulgaris (FACHB-31) was obtained from the Institute of Hydrobiology, Chinese Academy of Sciences. It was cultured in a 10 L round bottom flask containing 7 L sterilized BG-11 media. Algae culture was incubated at room temperature (22–25 °C) under a fluorescent lamp with an illumination of 34 $\mu mol/m^2/s$ (light:night = 20:4) with constant air feeding at 6.5×10^{-2} m^3/h. After 24 days, algae broth was used directly without any pretreatment. The pH of the final broth was 8.4.

2.2. Preparation of composite flocculants

Magnetite powder was purchased from the Baotou Bally Ken Industrial Technology Co., Ltd., China. PACl was obtained from Adamas Reagent Co., Ltd., China, while PAM (molecular weight ⩾ 3,000,000) was purchased from Sinopharm Chemical Reagent Co., Ltd., China.

Before preparing composite flocculants, magnetite powder was washed three times using distilled water and then dried at room temperature. Stock solutions of concentrations 125 mmol Al/L and 1.00 g/L were prepared for PACl and PAM, respectively. The composite flocculants of PACl/Fe_3O_4 and PAM/Fe_3O_4 were synthesized by mixing magnetite powder with PACl or PAM stock solution at a given ratio with continuous shaking for 5 min in a shaking incubator. To obtain the composite PAM/PACl/Fe_3O_4 and PACl/PAM/Fe_3O_4, PAM and PACl stock solutions were added to the PACl/Fe_3O_4 and PAM/Fe_3O_4 composite solution, respectively and mixed thoroughly. The dosages of composite flocculants are described using ratio *x*/*y* or *x*/*y*/*z* for expressing the doses of PACl, PAM or Fe_3O_4; the concentration units used for calculations are mmol Al/L, mg/L and g/L, respectively.

2.3. Magnetic flocculation

The experiments were carried out in a jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co., Ltd., China). The flocculant was first added to 400 mL algae suspension ($2–3 \times 10^{10}$ cells/L), freshly taken from broth. After stirring for 1 min at 500 rpm, the beaker was placed inside a magnetic field created by a cubic NdFeB permanent magnet