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Short Communication

Ferrofluid-assisted rapid and directional harvesting of marine microalgal *Chlorella* sp. used for biodiesel production

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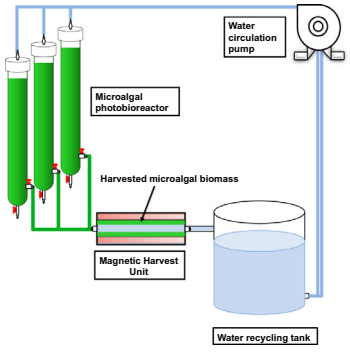
HIGHLIGHTS

- High harvesting efficiency of 95–100% was achieved within 1 min with a ferrofluid dosage of 25 mg L^{-1}.
- A simple and effective strategy for microalgal harvesting by ferrofluid was demonstrated.
- The harvesting efficiency reached over 80% after five recycles by the ferrofluid-harvesting system.
- The growth reached 80% after three recycles by the ferrofluid-harvesting system.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a novel harvesting strategy using ferrofluids coupled with flocculation as a magnetic directional harvesting system was developed, providing a fast and easy way to effectively collect microalgae with no further modifications made to the ferrofluids. With a ferrofluid dosage of 25 mg L^{-1}, a high harvesting efficiency of 95–100% was achieved within 1 min. In addition, we successfully performed a wastewater recycling strategy coupled with a microalgal ferrofluid-harvesting dynamic flow-through system to harvest biomass of *Chlorella* sp. MTF-7 which could achieve over 80% of the maximum level after three repeated recycling cultivations. This work demonstrated the use of an integrated microalgal ferrofluid-harvesting dynamic flow-through system to develop a simple and effective strategy to enhance microalgal harvesting efficiency, along with wastewater recycling, in a marine microalgal *Chlorella* sp. MTF-7.

1. Introduction

The dilute nature of mass microalgal cultivation, with concentrations of approximately 1 – 2 g L^{-1}, causes many difficulties during the harvesting process due to the low density, motility and its

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morphological characteristics (Seo et al., 2015;Wyatt et al., 2012). To date a number of microalgal harvesting techniques have been proposed, including centrifugation, flocculation, flotation, filtration, sedimentation and electro-coagulation (Barros et al., 2015). However, most of these techniques have disadvantages, not only because of the relatively high operating cost but the frequently low separation efficiencies (Wan et al., 2015).

Several recent studies have shown that flocculation coupled with filtration or centrifugation is a more promising and cost-effective method (Schenk et al., 2003). However, centrifugation is also one of the most expensive methods due to its high-energy consumption, and thus is only suitable for the separation of high-value products (Barros et al., 2015). Nowadays, magnetic separation is noticed as a promising technology for use in water treatment. In addition, the use of magnetic methods for the separation of microalgal biomass from culture broth has also been explored (Hu et al., 2014; Xu et al., 2011). However, little is known about the feasibility of this approach with regard to practical downstream applications, such as the effect of lipid extraction efficiency after magnetic harvesting, the reusability of magnetic materials, and the possibility of the recycling of used media.

Thus, the aim of this work was to develop a novel process of magnetic ferrofluid separation coupled with flocculation (MFS-F) for efficient microalgal harvesting. The effects of different dosages of ferrofluids on microalgal harvesting and the sustainability of the ferrofluids, as well as the growth potential of *Chlorella*sp. MTF-7 by the recycled broth. The knowledge obtained from this study could be useful in assessing the applicability of the MFS-Fprocess for enhancing the efficiency of microalgal harvesting with lower energy consumption.

2. Materials and methods

2.1. Microalgal cultures, medium and chemicals

The microalga *Chlorella* sp. MTF-7 was originally obtained from the collection of the Taiwan Fisheries Research Institute (Tung-Kang, Ping-Tung, Taiwan) and isolated by chemical mutagenesis. The *Chlorella* sp. MTF-7 cells were grown in modified f/2 medium in artificial sea water prepared as previous study (Chiu et al., 2011).

2.2. Determination of microalgal biomass and growth rate

The biomass concentration (dry weight of gram per liter) of cultures was measured according to previous method (Chiu et al., 2011). Regression equations of the relationship between optical density and cell dry weight were established as follows:

$$\text{Biomass conc.}(g \cdot L^{-1}) = 0.2631A_{682} - 0.0142 \quad R^2 = 0.9896$$

2.3. Preparation of aqueous ferrofluids

In order to produce particles with a specific size distribution, it is important to perform the reaction in an aqueous ammonia solution with a molar ratio (Fe(II)/Fe(III)) of 0.5 and a pH of 11–12, shown as follows:

$$2FeCl_3 + FeCl_2 + 8NH_3 + 4H_2O \rightarrow Fe_3O_4 + 8NH_4Cl$$

2.4. Experimental system of an indoor photobioreactor

The microalgal cells were cultured in photobioreactors with a working volume of 800 mL incubated at 25 ± 1 °C with a surface light intensity of approximately 300 μmol m^{-2} s^{-1}. The 2% CO_2 was supplied from the bottom of the photobioreactor with a flow rate of 0.1 vvm (Chiu et al., 2011).

2.5. Determination of microalgal harvesting efficiency by ferrofluids

The algal culture suspension (50 mL) was placed in a 100 mL beaker. The test beaker was stirred for 1 min at room temperature and left for 10 min to settle. The magnetic material was then separated from the solution by a magnetic process using a neodymium magnet and the residual concentrations of algae were analyzed. Microalgal harvesting efficiency was calculated by the following equation:

Microalgal harvesting efficiency (%) = weight of sample/weight of reference

2.6. Harvest capacity of ferrofluids

The harvest capacity of the ferrofluids for microalgal cells (R_c, g-dry cell weight/g- ferrofluids) was calculated according to the following equation (Hu et al., 2014):

$$R_c = (C_t - C_o)V/m$$

where C_0 is the initial cell concentration in the culture medium (g L^{-1}), C_t is the cell concentration after harvesting (g L^{-1}) in 1 min, V is the volume of microalgal cultures used for harvesting (L), and m is the amount of ferrofluids used for harvesting (g).

2.7. Experimental system of microalgal harvesting dynamic flow-through system

The initial biomass concentration was approximately 0.2 g L^{-1}. First, the culture was grown for four days, and the microalgal cells were partially flocculated and harvested by the magnetic harvesting unit. The culture broth without microalgal cells, as harvested by ferrofluids, was transported into the following photobioreactors. The remaining microalgal cultures were fed with 225 mg L^{-1} nitrate and the system was operated for three repeats. The microalgal cells were sampled every 24 h for growth measurement.

2.8. Microalgal lipid extraction, transesterification and fatty acid analysis

Microalgal lipid extraction was carried out according to the modified method reported in a previous work (Chiu et al., 2011). The dried biomass (200 mg) was used for lipid extraction and transesterification. Finally, the organic (lower) phase containing fatty acid methyl esters (FAMEs) was collected. The fatty acid composition was determined using a FOCUS Gas Chromatograph (GC) (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a flame ionization detector (FID). The operation procedures are followed previous work (Chiu et al., 2011).

3. Results and discussion

3.1. Behaviors of microalgal flocs treated with ferrofluids

Early studies on microalgal flocculation have shown that microalgal cells could be flocculated by inorganic flocculants that neutralize their surface charge (Seo et al., 2015; Wyatt et al., 2012). For solid-liquid separation, $FeCl_3$ was used as the inorganic flocculant in this study. The magnetic ferrofluid was then added as the magnetic absorbent for microalgal magnetic harvesting. The particle sizes of ferrofluids were controlled at approximately 20–30 μm. The suspended microalgal cells without flocculant and the microalgal flocs flocculated by $FeCl_3$ showed no magnetic