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Short Communication

Flotation of marine microalgae: Effect of algal hydrophobicity

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HIGHLIGHTS

- Algal hydrophobicity has a profound impact on microalgae flotation.
- The ionic strength of flotation medium has little impact on microalgae flotation.
- Algal hydrophobicity can be improved by using a cationic collector.

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ABSTRACT

This study aims to understand the underlying reasons for the poor flotation response of marine microalgae. The flotation performance and hydrophobicity of a freshwater microalga (*Chlorella* sp. BR2) were compared to those of a marine microalga (*Tetraselmis* sp. M8) at different salinities in the presence of a cationic collector, tetradecyl trimethylammonium bromide. It was found that microalgal hydrophobicity played a more important role than salinity in determining the flotation performance.

1. Introduction

Microalgae are photosynthetic organisms with great potential to harvest sunlight and convert carbon dioxide into biofuels, health food and animal feed (Chisti 2007; Walker 2005). They have a high photosynthetic efficiency, do not need to compete with edible crops and have comparatively higher oil productivity. Microalgae arguably have become the most promising candidate for the production of biodiesel and other high value products (Chisti 2007; Ota et al. 2009; Schenk et al. 2008). Biofuel production from microalgae can be divided into the following major steps: algae cultivation, biomass harvesting/dewatering, oil extraction and oil conversion to biofuel (Ryan, 2009). The operational costs for dewatering contribute from 20% to 30% to the total biofuel production costs (Brennan and Owende 2010). Dewatering is recognized as a major impediment towards the industrial-scale manufacturing of microalgae bio-products (Danquah et al. 2009; Uduman et al. 2010).

Although the selection of suitable algae harvesting techniques depends largely on the microalgae species and the desired final product, several methods have been proposed for algae harvesting, including centrifugation, filtration, membrane separation process, sedimentation with flocculation, gravity sedimentation, and froth flotation (Phoochinda and White 2003; Uduman et al. 2010). However, most of these methods are of low efficiency and have high capital costs and high energy consumption. For example, centrifugation requires high energy input, a huge cost for large-scale processing which may also damage cells due to high shear forces, resulting in a significant loss of the products of interest (Knuckey et al. 2006). Permeable membranes used for filtration and screening are also easily clogged by tiny microalgae (Uduman et al. 2010) and frequent scraping would significantly shorten the lifetime of these membranes, resulting in high operating costs (Molina Grima et al. 2003). Flocculation seems to be a promising approach for large-scale harvesting, but its application appears to be currently limited to freshwater microalgae. As the ionic strength of water increases, the efficiency of flocculating agent decreases (Uduman et al. 2010). Furthermore, depending on the flocculants, its residues in recycled water may inhibit or prevent renewed algae growth.

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Flotation is a proven technology to effectively capture small particles up to 500 μm in aqueous solution using gas bubbles (Matis et al. 1994). It is an effective method to harvest microalgae by taking advantage of their natural characteristics of relatively low density and self-float (Phoochinda and White 2003). Also with relatively rapid operation, low space requirements, high flexibility and moderate operational costs, flotation technique has the potential to overcome the bottleneck of feasible microalgal biofuel production (Liu et al. 1999). At present, there are mainly three flotation techniques reported for microalgae harvesting: dispersed air flotation (DiAF, bubble diameter 700–1500 μm), dissolved air flotation (DAF, bubble diameter 10–100 μm) and electrolytic flotation (Chisti 2007; Phoochinda et al. 2004; Uduman et al. 2010). Among these techniques, DiAF has been widely used to upgrade coal and minerals at large scale (cell volumes reaching up to 500 m^3). DiAF seems to be an economical and efficient technique for harvesting microalgae. At present, algae harvesting by flotation technique has only been developed for freshwater microalgae, such as *Chlorella vulgaris* and *Desmodesmus quadricauda* (Chen et al. 1998; Liu et al. 1999; Phoochinda and White 2003; Phoochinda et al. 2004). Although these studies inferred that the flotation efficiency could be affected by salinity (Liu et al. 1999; Phoochinda and White 2003), the flotation of marine microalgae has not been reported yet. In this study, the effectiveness of flotation on marine microalgae harvesting was investigated, through which hydrophobicity as a critical factor and a missing link between flotation performance and algal surface properties was identified.

2. Methods

2.1. Cultivation of algae

Marine microalga *Tetraselmis* sp. M8 was isolated from the Sunshine Coast, Queensland, Australia (26°39′39″S, 153°6′18″E; Genbank accession number JQ423158) and freshwater microalga *Chlorella* sp. BR2 was isolated from the Brisbane River, Tennyson, Queensland, Australia (−27°31′21.36″S, 153°0′32.87″E; Genbank accession number JQ423156; Lim et al., 2012). They were cultivated in silicate free f/2 medium, under 120 μmol photon m^{-2} s^{-1} with 12-h light/dark cycles, at 26 °C ± 1 °C on an orbital shaker (100 rpm). The cultivation was scaled up in two of 14 L cylindrical photobioreactors (one for each) with continuous supply of air and nutrients. When microalgae reached the exponential growth phase, they were nutrient-starved for two days for efficient lipid induction (Hu et al. 2008) and then collected for flotation experiments.

2.2. Dispersed air flotation test

Flotation experiments were carried out using a 1.5-L agitair flotation cell. Air was supplied to the flotation cell through its bottom, where an impeller was placed to provide the agitation necessary for breaking air into bubbles and dispersing them throughout the cell. The bubbles picked up microalgae and rose to the top, forming a microalgae-laden froth, which was subsequently removed manually. Prior to the flotation process, microalgae cultures were stirred vigorously for 2 min. Then each culture was subdivided into aliquots of 1.3 L, weighed and transferred into the flotation cell. The pH of the flotation pulp was adjusted to 9.5 by adding NaOH before adding the collector, tetradecyl trimethylammonium bromide (C_{14}TAB, molecular formula $CH_3(CH_2)_{13}N(CH_3)_3(Br)$). In the flotation cell, the microalgae suspension was first agitated by stirring at 800 rpm for 5 min. Subsequently, the stirring speed was reduced to 600 rpm and aeration was turned on at a rate of 5 L min^{-1} (superficial air velocity 0.68 cm/s). Four concentrates were sequentially collected at 1, 2, 4, and 6 min. The cell count for each sample was taken in three duplicates by loading 10 μL of sample on a haemocytometer (Brightline, USA), and the average value was reported. The microalgae recovery (Y) and water rejection rate (WRR) were determined using Eqs. (1) and (2).

$$Y = 1 - \frac{Ss}{Ff} \tag{1}$$

$$WRR = \frac{S}{F} \tag{2}$$

where S is the mass of sink (or tailing left in the flotation cell), F is the mass of feed, s is the microalgae concentration in the sink, and f is the microalgae concentration in the feed.

2.3. Hydrophobicity test

The hydrophobicity of microalgae was measured by using the modified adherence-to-hydrocarbon method (Rosenberg et al. 1980). The test assesses essentially the distribution ratio of cells between water and an organic phase. A total of 4 mL of the algae sample was placed in a test tube to which 1 mL of 98% pure n-hexane was added and shaken vigorously by hand for 1 min; the emulsion was allowed to settle for 2 min. Then, 2 mL were carefully obtained from the bottom aqueous layer of the test tube and its absorbance was read at 620 nm using a spectrophotometer (Hitachi, Model U-2800) to represent the concentration of microalgae. The extractability (H) of the hexane layer on organic substances in the algal suspension was calculated using the following expression:

$$H = \left(\frac{A_o - A_w}{A_o}\right) \times 100\% \tag{3}$$

where A_o is the initial absorbance of the microalgae suspension and A_w is the absorbance of the aqueous phase after being settled for 2 min.

3. Results and discussion

3.1. Changing collector dosage

The flotation kinetics of freshwater microalga *Chlorella* sp. (BR2) in freshwater medium and marine microalga *Tetraselmis* sp. (M8) in seawater medium in the absence of any collector were quite distinct. It was observed that within six minutes, 93% of BR2 could be recovered, whereas only 6% of M8 was recovered. It was hypothesized that M8 had a lower level of natural hydrophobicity than BR2 and that appropriate collectors were needed to render microalgae particles more hydrophobic. Most microalgae are negatively charged at natural pH values (Chen et al., 1998; Phoochinda et al., 2004). Hence, in the present work, a cationic collector, tetradecyl trimethylammonium bromide (C_{14}TAB) was used for subsequent flotation experiments.

At a given flotation time, increasing collector dosage clearly increased the flotation recovery (Fig. 1). The addition of C_{14}TAB increased BR2 recovery to almost 99%, resulting in 30–40% more algae recovery in the first two minutes of flotation (Fig. 1a). A pronounced increase in microalgae recovery was seen when the C_{14}TAB concentration was increased from 1 to 3 ppm. However, there was no further improvement in the recovery when the C_{14}TAB concentration was further increased. The experimental data of cumulative flotation recovery versus flotation time were fitted by using the first-order chemical reaction analogy:

$$Y = Y_{max}(1 - e^{-kt}) \tag{4}$$

where Y_{max} is the maximum flotation recovery when the flotation time t approaches infinity, and k is the flotation rate constant. The