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Short Communication

# Effective harvesting of low surface-hydrophobicity microalgae by froth flotation

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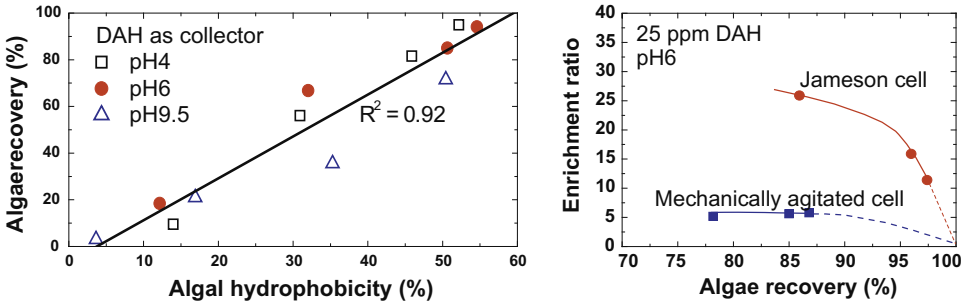
## HIGHLIGHTS

- Algal hydrophobicity and bubble size are key factors for microalgae flotation.
- Algal hydrophobicity can be improved using cationic surfactants at appropriate pHs.
- A step-wise optimization of algae flotation is demonstrated.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Microalgae harvesting by air flotation is a promising technology for large-scale production of biofuel, feed and nutraceuticals from algae. With an adherence-to-hydrocarbon method and two different types of flotation cells (mechanically agitated cell and Jameson cell), microalgal surface hydrophobicity and bubble size were identified to be critical for effective froth flotation of microalgae. Freshwater alga *Chlorella* sp. BR2 showed naturally a high hydrophobicity and an ideal response to flotation. However, many marine microalgae possess a low surface hydrophobicity and are thus difficult to harvest. This paper shows that a step-wise optimization approach can substantially improve the flotation of a low surface hydrophobicity marine microalga, *Tetraselmis* sp. M8, to near full recovery with an enrichment ratio of 11.4.



## 1. Introduction

Microalgae are considered the most efficient primary producers of biomass. They have great potential to be a future feedstock for producing biofuel and other products as their cultivation does not need to compete for arable land or biodiverse landscapes. Many marine microalgae can use brackish or seawater and are highly efficient producers of lipids. The industrial production of biofuel from microalgae can be divided into three major steps; cultivation, harvesting and processing (Ryan, 2009). Among these, one of the major impediments for commercial-scale production is the downstream processing, where algal biomass has to be concentrated and separated (dewatered) from water for further processing (Christenson and Sims, 2011; Molina Grima et al., 2003). This step can contribute to 20–30% of total biofuel production costs (Molina Grima et al., 2003). Commercial production of microalgal biodiesel requires efficient harvesting and dewatering of algal biomass (Cheng et al., 2010). Various procedures such as flocculation, sedimentation, filtration, flotation, centrifugation and membrane separation have been established for primary dewatering of microalgae from the cultivation medium (Phoochinda and White, 2003).

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However, each approach has its own limitation; typically, they are either of low efficiency or high capital cost with excessive energy consumption or cannot be applied at large scale.

Froth flotation presents a promising approach for commercial-scale harvesting of microalgae that compared to other methods, is also relatively low cost (Sharma et al., 2013). It utilizes microalgae's natural features of relatively low density and self-float (Phoochinda and White, 2003) and is considered a highly versatile method for physically separating particles with a small footprint (Chen et al., 1998; Garg et al., 2012). Microalgal cells are small particles whose size typically ranges from 1 to 20 micron. A missing link between flotation performance and algal surface hydrophobicity has recently been identified and algal hydrophobicity has now been recognized as a major factor determining microalgae flotation efficiency, irrespective of whether these are marine or freshwater microalgae (Garg et al., 2012). Addition of surfactants is commonly used to render algae surface hydrophobic, making it possible to use surfactants as carriers for flotation to separate microalgae from water (Chen et al., 1998; Garg et al., 2012; Uduman et al., 2010). Flotation efficiency can be affected by hydrodynamic and chemical factors. Variables that affect the chemical condition of froth flotation include pH, surfactant type and concentration, as these play important roles affecting the hydrophobicity and electrical charge of particle surfaces (Bulatovic, 2007). Various types of flotation devices which provide different hydrodynamic conditions may also affect flotation separation performance. For example, smaller bubbles generated by using different types of flotation machines can improve fine particle flotation (Yoon, 2000; Zhou et al., 1997). The Jameson Cell is an advanced flotation apparatus that employs a plunging jet to produce smaller air bubbles than mechanical flotation cells. The Jameson Cell technology was originally applied by Yan and Jameson to treat wastewater (Yan and Jameson, 2004), with microbial removal efficiencies over 98% (on the basis of the difference in concentration between feed and tail).

In the present work, a step-wise comparative study was carried out to understand the effects of different surfactants, pH, cell concentration, and machines on microalgae flotation efficiency with low and high hydrophobicity microalgae. Microalgal recovery for marine microalga *Tetraselmis* sp. M8 was improved from an initial 6.4% to 97.4% with a satisfactory enrichment ratio of 11.4. Microalgal surface hydrophobicity and bubble size were identified as the main underlying causes that improved froth flotation performance.

## 2. Methods

### 2.1. Algal culture and characterization

Pure cultures of the green marine microalga *Tetraselmis* sp. M8 were obtained from a coastal rock pool in Maroochydore, Queensland, Australia (26°39'39″S, 153°6'18″E; Genbank accession number JQ423158) and the green 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). Microalgae stocks are maintained in the Algae Biotechnology Laboratory at The University of Queensland, Australia (www.algaebiotech.org). Cultures were grown in silicate free f/2 medium, on an orbital shaker (100 rpm) at 26 °C ± 1 °C under 120 μmol photon $m^{-2}$ $s^{-1}$ with 12-h light/dark cycles. Using the same conditions, cultures were scaled up in two 20 L polyethylene bags with daily nutrient and continuous air supplies. When microalgal cultures reached the end of the exponential growth phase (less than 20% increase in cell numbers per day), they were nutrient-starved for 2 d for lipid induction (Hu et al., 2008). Subsequently microalgal cultures were used for flotation experiments.

### 2.2. Froth flotation

Flotation experiments were carried out using a 1.5-L bottom-driven mechanically agitated (Agitair) cell, unless otherwise stated. Microalgal cultures were stirred vigorously for 2 min, before 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 with HCl or NaOH before adding the collector, tetradecyl trimethyl ammonium bromide ($C_{14}$TAB) or dodecyl ammonium hydrochloride (DAH). First the microalgal suspension was conditioned by mixing at 800 rpm for 5 min. The agitation rate was 600 rpm or 800 rpm when $C_{14}$TAB or DAH was used for flotation tests, respectively and the air flow rate was 5 L/min. The mechanical flotation lasted for 6 min.

Once an optimal reagent scheme was determined by the above-described mechanical flotation tests, additional Jameson cell flotation tests were carried out to determine the effect of bubble size (or flotation hydrodynamics) on microalgae flotation. The diameter size of the Jameson Cell used was 150 mm and its orifice diameter was 3.83 mm. A 35-L slurry was fed into the Jameson Cell at a pressure of 150 kPa and an air flow rate of 10 L/min. The Jameson cell flotation time was around 15 min. During this procedure the tailing was continuously recycled to the feed sump and pumped back to the Jameson cell. The Jameson Cell flotation procedure has previously been well described (Bulatovic, 2007; Yan and Jameson, 2004). Microalgae cell count and dry weights were determined for concentrates collected in trays and remaining tailings left in the flotation machine. Triplicate cell counts were carried out for each sample by loading 10 μL of sample on a haemocytometer (Brightline, USA), and the averaged value was determined. Microalgae recovery ($Y$) was determined using the following equation:

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

where, $T$ is the wet mass of tailing (or sink), $F$ is the wet mass of feed, $t$ is the microalgal concentration in the tailing, and $f$ is the microalgal concentration in the feed.

The enrichment ratio ($ER$) was calculated as the ratio of the concentration of algae in the concentrate to the concentration of algae in the feed. The following formula was used:

$$ER = \frac{Y}{1 - WRR} \tag{2}$$

where $WRR$ represents the water rejection rate as equal to $T/F$.

### 2.3. Hydrophobicity test

Hydrophobicity ($H$) of microalgae was quantified by employing a modified adherence-to-hydrocarbon method (Rosenberg et al., 1980). We followed the same procedure as described by Garg et al., 2012 except that the emulsion was allowed to settle for only 20 s.

## 3. Results and Discussion

An initial comparison of the freshwater microalga *Chlorella* sp. BR2 with the marine microalga *Tetraselmis* sp. M8 showed that at pH 9.5, BR2 possessed much higher natural surface hydrophobicity than M8. The flotation recovery of *Chlorella* sp. BR2 reached more than 90% with a satisfactory enrichment ratio of 13.5, while, interestingly, only 6.4% recovery with an enrichment ratio of only 0.6 was measured for *Tetraselmis* sp. M8 under identical process conditions. Note that the enrichment ratio of M8 flotation was less than 1, which was most likely caused by the (downward) gravitational sedimentation, which counteracted the (upward) flotation of microalgae.