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Flotation separation of marine microalgae from aqueous medium

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ABSTRACT

Harvesting of oleaginous marine microalgae by dewatering is an important step for cost-effective algal biomass feedstock production. This paper reports separation of marine microalgae (*Tetraselmis* sp. M8) from aqueous medium by froth flotation using various collectors (surfactants) with equal carbon chain length, such as dodecyl pyridinium chloride (DPC), N-dodecylpropane-1,3-diamine hydrochloride (DN2), dodecyl amine hydrochloride (DAH), and sodium dodecyl sulphate (SDS), at different pHs. Algal hydrophobicity, froth stability, and surfactant precipitation were characterised. The laboratory-scale mechanical flotation tests showed that at natural pH 9.5 and a lower pH, DPC outperformed DAH, DN2 and SDS in separating *Tetraselmis* sp. M8 from seawater. DPC was capable of rendering the microalgae hydrophobic, producing metastable froth, and dissolving readily in water, which are all desirable features of a collector for flotation separation of microalgae from water. Use of DPC at 15 ppm in pilot-scale Jameson cell flotation tests for M8 after outdoor cultivation led to a 23-fold increase in algal concentration with over 99% algal recovery.

1. Introduction

Substituting the use of fossil fuel with biofuel that is more sustainably sourced can minimise the carbon foot print [4]. Microalgae are highly productive photosynthetic microorganisms that can provide biofuel independent of using fresh water or arable land [9,10,33,35]. The overall production of biofuel from microalgae can be divided into three major steps; algae cultivation, harvesting and processing [32]. Among these steps, the major bottleneck for commercial-scale production of biofuels is algae harvesting [10,28]. The algae harvesting step can consume 20–30% of total biofuel production costs [28,30]. Mass production of microalgal biodiesel requires efficient harvesting of the biomass from cultivation media [8].

Froth flotation is one of the most promising methods for commercial-scale harvesting of microalgae and concentrating the algal biomass from approx. 0.05–0.1% to 1–3% by weight [19]. Flotation is a highly versatile method for physically separating the suspended particles in liquid [7,18]. It consists of three phases: water, solid particles and air bubbles. During the initial stages of collision due to the deformation of bubbles, a thin liquid film referred to as wetting film is formed between the bubble and the particle [29]. Destabilisation of this film results in adhesion of hydrophobic particle to the air bubble, which is the basis for froth flotation [37,24]. An important factor affecting microalgae flotation is the hydrophobicity of microalgal cells [19]. The surfaces of microalgae vary from being naturally hydrophilic to slightly hydrophobic. Addition of surfactants can effectively render microalgal surfaces more hydrophobic, making it easier to separate algae from water [7,18,27,38]. A surfactant molecule consists of a charged hydrophilic head and a hydrophobic carbon tail, and its adsorption onto microalgae helps these microorganisms to adhere to air bubbles after which they are transported to the froth zone [5,15]. Surfactant adsorption can be affected by multiple factors such as concentration and pH. With operating costs taken into consideration, low surfactant dosage and natural pH should be employed wherever possible.

pH plays a very important role in affecting collector adsorption onto particles and thus flotation performance. At alkaline pHs, microalgae are often negatively charged; reducing pH could make the microalgal surface charge neutral or even positively charged. For a cationic surfactant or anionic surfactant, there should be an optimum pH range at which one can take advantage of the strong electrostatic interaction between microalgae and surfactant to hydrophobize the surface of microalgae [7,27]. Various studies demonstrate that cationic collectors tend to have better flotation performance in slightly alkaline pH whereas anionic collectors work better when the pH of suspensions becomes acidic

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[7,27,30]. pH modification can lead to various changes, including changes in interfacial chemistry (including surface charges), solubility of particles such as collectors, and changes in water chemistry [17].

Air bubbles generated in flotation not only provide a platform for hydrophobic microalgae to attach but also enhance particle recovery by providing the lifting force required for transportation and separation. Flotation separation efficiency is inversely related to bubble size [12,13]. Modern flotation technology utilises efficient ways of enabling bubble–particle interactions in the liquid medium. Effective flotation requires high bubble–particle collision, attachment and stability efficiencies before reaching the pulp-froth interface [14]. Small bubbles have a higher surface area to volume ratio. One of the most efficient ways of achieving maximum attachment is by generating as many small bubbles as possible [20]. Ahmed and Jameson [1] estimate a 100-fold enhancement in separation performance for fine particles with bubble size reduction from approximately 700–70 μm. Furthermore, small bubbles have low rise velocity [34] enabling them to remain in liquid medium for longer time thereby increasing the attachment efficiency. It has been reported that smaller bubbles employed in some flotation machines such as flotation column with oscillatory air supply and Jameson flotation cell could lead to improved microalgae flotation efficiency [20,19].

In the present work, dispersed-air flotation was used to harvest marine microalgae. The study was focused on elucidating the influence of the surfactant head group on the flotation efficiency of marine microalgae at various pHs. The surfactants include three cationic surfactants and one anionic surfactant, with equal carbon chain length. Important factors affecting microalgae flotation were identified, including the affinity of collectors to algal surface, the solubility of collectors, and froth stability. Pilot-scale Jameson flotation tests with small air bubbles were also carried out. The important role of collector chemistry and hydrodynamics in microalgae flotation was discussed.

2. Materials and methods

The surfactants tested included dodecyl pyridinium chloride (DPC, 99% pure, Sigma Aldrich), sodium dodecyl sulphate (SDS, 98.5% pure, Sigma Aldrich), and dodecyl amine hydrochloride (DAH, 97% pure, Alfa Aesar), which were used without further purification. N-dodecylpropane-1,3-diamine hydrochloride (DN_2) solution was prepared by dissolving N-dodecylpropane-1,3-diamine (97% pure, Nanjin Chemlin Chemical Industry) in hydrochloric acid at a 1:1 mol ratio. Fig. 1 shows the chemical structure of these surfactants. Artificial sea salt was purchased from Aquasonic (Wauchope, New South Wales, Australia). f/2 medium was purchased from Algaboost (Wallaroo, South Australia, Australia). HCl was used to adjust the pH.

2.1. Cultivation of algae

The 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) [26]. Microalgae 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 25 L polyethylene bags 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 [21] and _ENREF_20then collected for flotation experiments. The natural pH of the culture samples prior to flotation was 9.5.

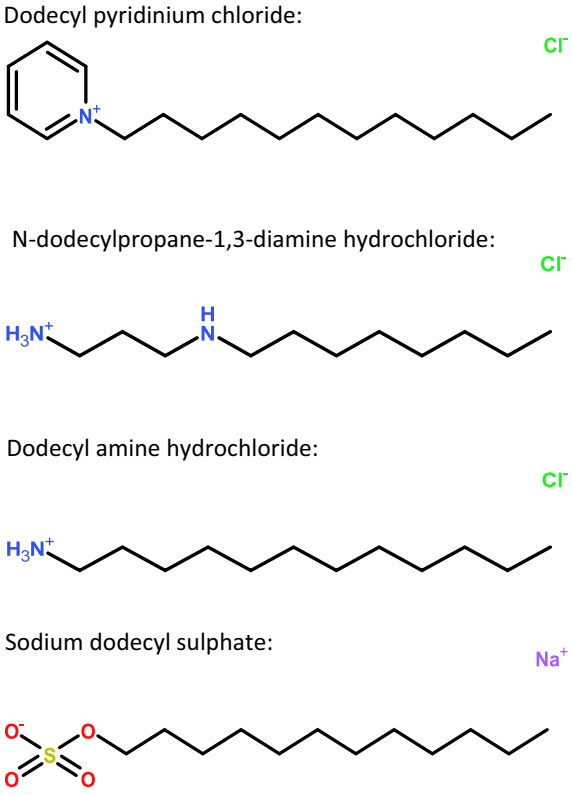

Fig. 1. Chemical structures of surfactants tested for froth flotation.

2.2. Hydrophobicity test

The hydrophobicity of microalgae was measured by using the modified adherence-to-hydrocarbon method [31]. 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 20 s. Then, 1 mL liquid from the bottom layer was carefully obtained from the bottom aqueous layer of the test tube and its absorbance (A) 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:

$$H = \left(\frac{A_o - A_w}{A_o}\right) \times 100\% \quad (1)$$

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 20 s.

2.3. Dispersed air flotation

Mechanical cell: Flotation experiments were carried out using a 1.5-litre 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, microalgal cultures were stirred for 1 min. Then each culture was subdivided into aliquots of 1.3 l, weighed and transferred into the flotation cell. The pH of the flotation

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