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An innovative electrochemical process to alleviate the challenges for harvesting of small size microalgae by using non-sacrificial carbon electrodes

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ABSTRACT

Harvesting of microalgal biomass is still a bottleneck to its commercial scale application, due to small cell size, low culture densities, colloidal stability and thus unfavourable economics. Centrifugation is an efficient technique but the high energy consumption makes it unsuitable for low value microalgal products. Chemical flocculation and filtration are inefficient and time consuming methods for harvesting of small size microalgae. In this study, an electrochemical harvesting (ECH) process was assessed for the harvesting of a small size microalga *Ankistrodesmus falcatus* by using non-sacrificial carbon electrodes. Harvesting efficiency of ECH was compared to centrifugation and flocculation using alum and chitosan. The highest recovery efficiency was obtained by centrifugation (93% after 15 min) followed by ECH process (91% after 30 min), alum (86% after 60 min) and chitosan (55% after 60 min). However, the energy consumption of ECH process (1.76 kWh kg^{-1}) was much lower than the centrifugation process ($65.34 \text{ kWh kg}^{-1}$). The biochemical composition of harvested biomass was also assessed, and it was found that the ECH process has no deteriorating effect on the quality of biomass. High recovery efficiency, low energy consumption and the use of non-sacrificial electrodes make ECH a sustainable harvesting technique for small size microalgae.

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1. Introduction

Microalgae have garnered the interest of researchers, industry and governmental organizations for production of various commercial products and its environmental benefits. Simple structure, high growth rates, environmental benefits and metabolites which can be exploited for various commercial products are the principal reasons for heightened interest in microalgae. Microalgae have been shown to have potential to produce biofuels, supplements for animal and aquaculture feed, pigments and high nutritional value long chain fatty acids, gelling and colouring agents for the food industry etc. Environmental benefits of microalgae include their ability to sequester CO_2 and use waste substrates for growth. Mass cultivation of microalgae does not compete with the food crops for agricultural land [1,2]. Despite of the benefits and applications, generation of microalgal biomass faces challenges of large scale cultivation and high production cost which needs to be addressed for its sustainable commercial scale application [3–5].

Harvesting of the microalgal biomass from the culture suspension is a critical step in various microalgal biomass applications. The small size of microalgal cells (1–30 μm), similar density of the algal cells to the

growth medium, the negative charge on the microalgae surface keeps them dispersed in stable suspensions especially during the growth phase and high growth rates which require frequent harvesting compared to terrestrial plants are the major bottlenecks of microalgae harvesting [6–8]. Harvesting and dewatering steps are major contributors towards the microalgal biomass production cost. Microalgae can be harvested by a number of methods such as sedimentation, flocculation, flotation, centrifugation and filtration or a combination of any of these [9,10]. The selection of harvesting technique is dependent on density and size of the microalgae as well as the value and nature of the desired products. The efficiencies of most harvesting techniques are hampered when applied for small size microalgae. Significantly longer processing times are also required for harvesting of small size microalgae especially using techniques which rely on the gravitational settling. Centrifugation is most widely used harvesting technique. However, for low value products like biodiesel and feed, conventional centrifugation and filtration methods are considered to be energy intensive and expensive.

Electrochemical technologies are already proven technologies for several environmental and industrial applications [11,12]. Electrochemical harvesting (ECH) techniques work on the principle of electrocoagulation and electroflotation, and thus offer the possibility of an innovative, cheap, and effective method of microalgae harvesting that requires little or no addition of chemicals [13,14]. Electrocoagulation forms the microalgal

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flocs by charge neutralization, while bubbles generated during the electrochemical process aids in these flocs rising to the surface via electroflotation. Microalgal biomass can thereafter be easily skimmed from the surface of culture medium potentially making this technique efficient for harvesting small size microalgae. During the process of electrocoagulation (EC), metal ions are disseminated from the oxidizing metal electrodes. This process involves oxidation of anode which causes the electrode depletion and thus the electrode requires periodic replacement. Metal electrodes can cause also contamination of harvested biomass; therefore in this study non-sacrificial carbon electrodes were substituted for metallic electrodes.

The focus of the present study is to develop an electrochemical process for harvesting of small size microalgae and compare its efficiency to other common harvesting techniques. *Ankistrodesmus falcatus* is small size microalgae and is reported to be a potential feedstock for biodiesel production and also has application in wastewater remediation [15,16]. The electrochemical method is compared with conventional centrifugation and flocculation using chemical (Alum) and biological (Chitosan) flocculants. Efficiencies and processing time of ECH and other selected harvesting techniques for *A. falcatus* were compared to those achieved for *Scenedesmus obliquus* due to its larger size. Effect of different harvesting techniques on biochemical composition of *A. falcatus* was also investigated.

2. Material and methods

2.1. Cultivation of microalgae

A. falcatus and *S. obliquus* were cultivated in BG11 medium at 25 °C, at a photon flux of approximately $120 \mu\text{mol m}^{-2} \text{s}^{-1}$, with a 16:8 light-dark cycle on an orbital shaker (110 rpm). Microphotography and measurement of cell size was done using Nikon eclipse 80i microscope. For the harvesting experiments mass culture for selected microalgal strains was done in 5000 mL flasks with culture volume of 3000 mL for 14 days. Biomass (g/L) was estimated gravimetrically. *A. falcatus* is smaller in size (3.39 μm length and 0.94 μm width) compared to *S. obliquus* (4.54 μm lengths and 3.54 μm).

2.2. Harvesting of microalgae

All the ECH experiments were carried out at room temperature in a batch reactor (Fig. 1) of 14 cm \times 10 cm \times 14 cm filled with 1 L of microalgal culture (Biomass for *A. falcatus* was 2.88 g L^{-1} and *S. obliquus* was 2.76 g L^{-1}) as described in our previous work [17]. Two carbon Plates (12 cm \times 10 cm \times 2 cm) were used as cathodes kept 6 cm apart on opposite sides and fixed to the reactor casing, and a third carbon plate (12 cm \times 10 cm \times 2 cm) was used as the anode was placed in the middle of the reactor. Both carbon plate cathodes were connected to negative pole and carbon anode was connected to positive pole of the Manson (HCS-3302) DC power supply. Effect of 0.5, 1 and 1.5 A applied current on harvesting efficiency was determined in separate experiments. Centrifugation was done using centrifuge (Heraeus multifuge 4KR, USA) at 2683 g for both microalgal species at varying time. Culture volume used for each centrifugation experiment was 1 L. Harvesting using alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$) and chitosan was conducted as per Gupta et al. [18] using 100 mL culture in glass cylinders. All the experiments were carried out in triplicates. Data is represented as mean value \pm SD (Standard deviation).

2.3. Efficiency analysis of various harvesting processes

To determine the microalgal recovery efficiency of microalgal biomass, samples were collected at different time points (t) during the ECH process. Ten millilitre samples were collected at 5 cm below the water surface in the ECH reactor. For flocculation and centrifugation experiments samples were collected from the centre of the cylinder and centrifugation bottles at different time points. The microalgal recovery efficiency was determined based upon the decrease in optical density of the microalgal suspension (measured at 680 nm with a UV-VIS spectrometer, SpectroquantPharo 300, Merck). The recovery efficiency was subsequently calculated as:

$$\text{Microalgal recovery efficiency } \mu_a = \left[\frac{(\text{OD}_i - \text{OD}_t)}{\text{OD}_i} \right] \times 100 \quad (1)$$

where OD_i is the optical density of the suspension prior to the start of the ECH process, and OD_t is the optical density of the suspension at time t.

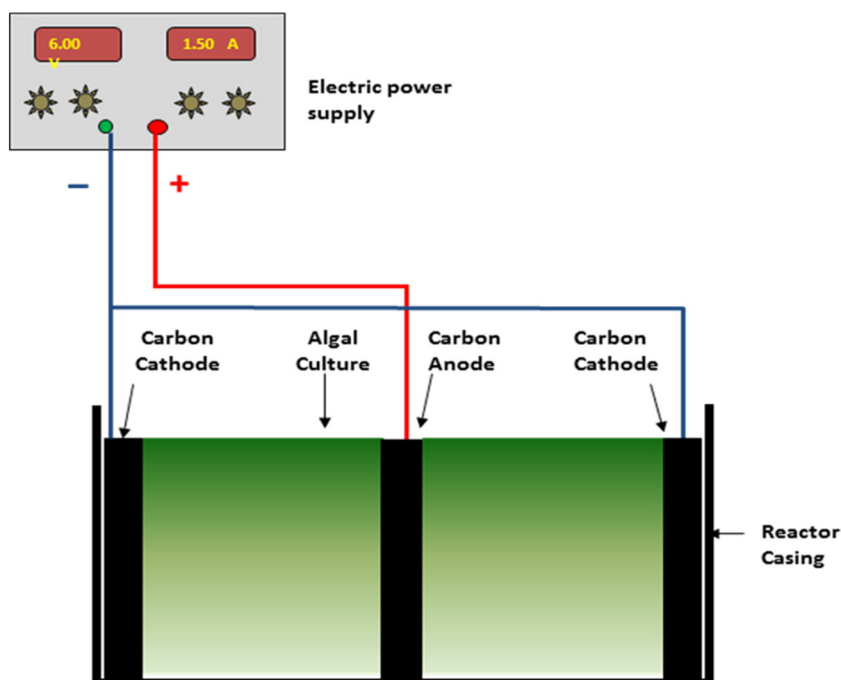


Fig. 1. Schematic representation of electrochemical harvesting reactor.

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