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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 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.

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 μmol m^{-2} 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 80*i* 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 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 × 10 cm × 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 × 10 cm × 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 × 10 cm × 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 ($Al_2(SO_4)24H_2O$) 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 ± 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:

$$\text{Microalgal recovery efficiency } \mu_a = [(OD_i - OD_f)/OD_i] \times 100 \quad (1)$$

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

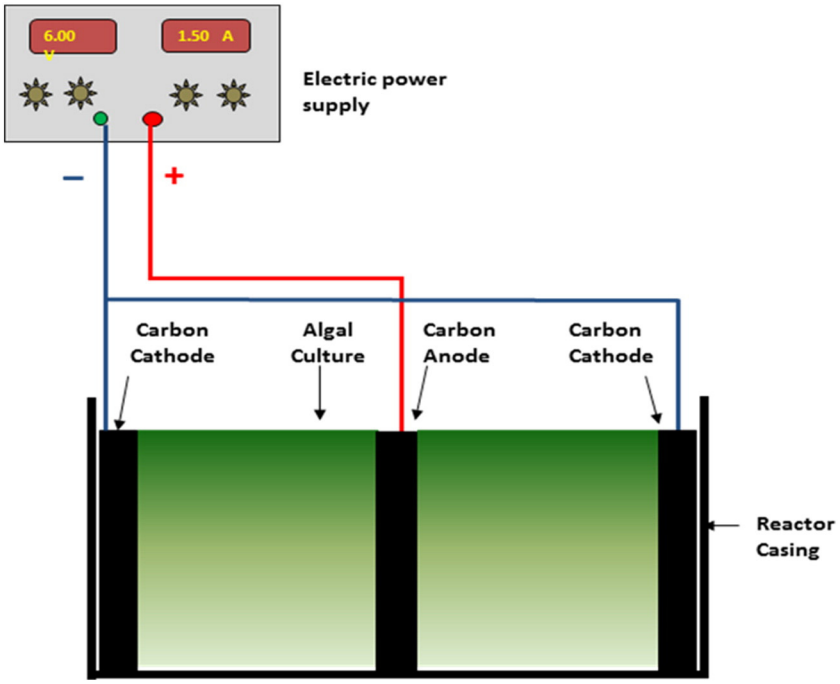

Fig. 1. Schematic representation of electrochemical harvesting reactor.

2.4. Power consumption of various processes

The power consumption E (in kWh/kg of recovered microalgae) was calculated as:

$$E = (P \times t)/(1000 \times V \times \mu_a \times C_i) \quad (2)$$

where P is the power (W), t the time of the ECH treatment (h), V the volume of the microalgal solution treated (m^3), μ_a the microalgae recovery efficiency, and C_i the initial microalgae biomass concentration (kg/m^3).

2.5. Biochemical composition analysis

2.5.1. Lipids and fatty acid analysis

Lipids were extracted from the biomass using microwave assisted solvent extraction to calculate the lipid content and lipid productivity. Dried biomass was mixed with chloroform and methanol (2:1 *v*/*v*) and then subjected to microwave treatment (100 °C for 10 min at 1000 watt) for cell disruption [19]. The treated samples were then filtered to remove the biomass residues. The organic layer was collected and oven dried at 70 °C for lipid recovery. The lipids obtained were measured gravimetrically and the percentage lipid content was determined based on lipid recovered from known weight of dry biomass.

The lipids extracted were subjected to the simultaneous esterification and transesterification processes employing sulphuric acid as a catalyst and methanol as an acyl acceptor. The reaction conditions for FAME production were 30:1 methanol to oil molar ratio; temperature: 60 °C; catalyst concentration: 10% *w*/*w* of oil; time: 4 h; hexane: 1 ml [19]. The stirring rate was kept constant at 200 rpm in orbital shaker incubator (Model TU-454, mrc Ltd., Israel). The fatty acid methyl esters (FAMEs) were then analysed by gas chromatography (Shimadzu GC-2014, Japan) with a flame ionization detector and a capillary column (SP2380, Supelco Analytical, USA). The oven temperature was programmed to start at 60 °C and kept at hold for 2 min, thereafter increased the temperature to 160 °C at a ramp rate of 10 °C·min^{-1} and then to 240 °C at a ramp rate of 7 °C·min^{-1} and again kept at hold for 1 min at 240 °C. The injector and detector temperature was 250 °C and nitrogen was used as carrier gas. A 37 component FAME standard was used to identify peaks.

2.5.2. Determination of total carbohydrate

Microalgal biomass was hydrolyzed by mixing 100 mg of biomass in 10 mL of 2% H_2SO_4 and autoclaved at 121 °C for 20 min. After hydrolysis sample was diluted up to 100 mL with distilled water and centrifuged at 2683 *g* for 10 min. Supernatant was used to determine sugar content by using Anthrone method and glucose was used as the standard [20]. Anthrone reagent was prepared by dissolving 100 mg of Anthrone (9, 10-dihydro-9- oxoanthacene) in 50 mL of ice cold 95% sulphuric acid (H_2SO_4). 4 mL of Anthrone reagent was added against 1 mL of glucose standard solutions and sample. The solution was kept in a boiling water bath for 10 min. Green colour of the resultant solution was observed by taking optical density at 630 nm [20]. Carbohydrate content was determined by the calibration curve prepared using glucose standards.

2.5.3. Determination of protein content

Protein content was determined by Bradford method. 100 μL of 1 M NaOH was added to 10 mg of dried microalgae powder and incubated in water bath at 80 °C for 10 min. 900 μL of H_2O was added to the hydrolyzed sample to bring volume upto 1 mL then the mixture was centrifuged at 12,000 *g* for 10 min. The supernatant was used to determine the protein concentration by the Bradford method. Different concentration of bovine serum albumin was used to prepare the calibration curve [21].

3. Result and discussion

3.1. Effect of applied current on the microalgal recovery efficiency and power consumption by ECH process

The applied current is an important factor in electrochemical harvesting of microalgae as it influences electrolysis efficiency, time and process economics. Fig. 2A shows the effect of applied current on the microalgal recovery efficiency by electrochemical harvesting process for *A. falcatus*. Microalgal recovery efficiency increases with the increase in the applied current. The recovery efficiencies found at 0.5, 1 and 1.5 A were 82.89 ± 0.82, 91.63 ± 0.23 and 92.24 ± 0.21% respectively at the end of 45 min of the ECH processes. Production of charged particles is directly proportional to the applied current in the ECH process. The applied current also has great influence on the generation of flocs and bubbles in the ECH process [14,22]. Increased generation of charged particles, bubbles and flocs due to increase in applied current eventually reflects in the enhanced recovery efficiency. The initial recovery rate of the ECH process with 1 and 1.5 A applied current was high upto 30 min and subsequently slowed. This is because of the change in ratio of charge on microalgal cell surface and charge particles generated at various applied currents. The recovery efficiencies achieved after 30 min of ECH process were 91.26 ± 0.29% at 1 A and 91.7 ± 0.5% at 1.5 A applied current respectively (Fig. 2A). Thus the optimum time

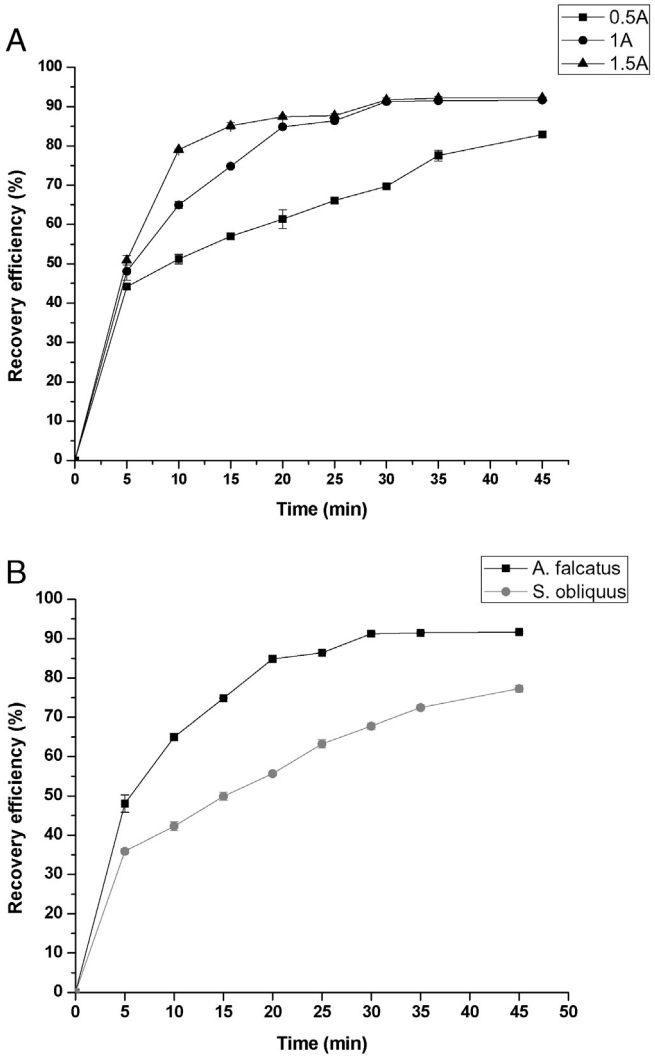

Fig. 2. A: Effect of applied current on the ECH process for *A. falcatus*. B: Harvesting efficiency of ECH for *A. falcatus* and *S. obliquus*.

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for harvesting of *A. falcatus* by ECH process was found to be 30 min. For ECH process with 0.5 A the reaction rate gradually increased even after 30 min. The recovery efficiency was much lower (69.71 ± 0.57%) after 30 min at 0.5 A applied current. In ECH process the recovery efficiency of 67.73 ± 0.8% after 30 min was observed for harvesting of *S. obliquus* which is comparatively bigger in size than *A. falcatus* (Fig. 2B). In ECH process with carbon electrodes, charge neutralization of microalgal cells takes place near the anode [17]. The charge neutralization causes floc formation of microalgal cells due to reduced repulsive forces [23]. H_2 and O_2 gas bubbles are generated due to the electrolysis of water at the electrodes during ECH process. The bubbles trapped in the microalgal flocs help for electroflotation [17,23]. It is clearly evident from the results that the smaller size of *A. falcatus* aids in rapid electroflotation of flocs to the surface. Thus it can be concluded that ECH process is more efficient for the harvesting of small size microalgae like *A. falcatus*.

The energy consumption of the process is crucial parameter for the development of an economically viable and sustainable harvesting process [24]. The energy consumptions for the 30 min ECH processes with 0.5, 1 and 1.5 A were 0.84, 1.76 and 3.62 kWh kg^{-1} respectively. Increase in applied current increases the applied potential which results in greater power consumption. Vandamme et al. [14] proved that electricity is the driving force for the reactions occurring at the anode and cathode, thus applied current is an important variable in the ECH process. Applied current is thus the most significant aspect for ECH process, which needs to be optimized for maximum recovery efficiency at minimum power consumption. In this study, even though 1.5 A applied current showed maximum recovery efficiency the power consumption was double compared to 1 A applied current with comparable recovery efficiency (Table 1). Thus the 1 A applied current was chosen as the optimum for the harvesting of *A. falcatus* using ECH process.

3.2. Centrifugation

Centrifugation is the most widely used technique for harvesting of microalgae in laboratory and industrial scale [13]. Harvesting by centrifugation of *A. falcatus*, achieved 93.41 ± 0.35% recovery efficiency in 20 min, after which there was no significant increase (Fig. 3A). Recovery efficiency of 92.02 ± 0.2% for *S. obliquus* using centrifugation was achieved in 15 min (Fig. 3A). Thus it is observed that the size of microalgal cells determines the efficiency and processing time required for effective harvesting by centrifugation. Centrifugation is a rapid harvesting technique; however the high energy consumption and damage of microalgal cells due to mechanical and shear stress are the drawbacks of this technique [14,25].

3.3. Flocculation

Alum as chemical flocculant and chitosan as biological flocculant are widely used for microalgal harvesting [10,26]. A gradual increase in recovery efficiency was observed with increasing time for both flocculation processes with alum and chitosan. The flocculation process for harvesting of *A. falcatus* with alum showed recovery efficiency of 86.09 ± 0.09%, while chitosan showed recovery efficiency of 55.22 ± 0.54% at 60 min (Fig. 3B and C). Harvesting using flocculation works in two stages; the first stage generates the microalgal flocs and in second stage flocs are settled at the bottom of the reactor by gravitational settling [7]. In this study when flocculation process was applied for *S. obliquus*, recovery efficiency of 91.35 ± 0.29% was observed with alum and recovery efficiency of 76.98 ± 0.5% was observed with

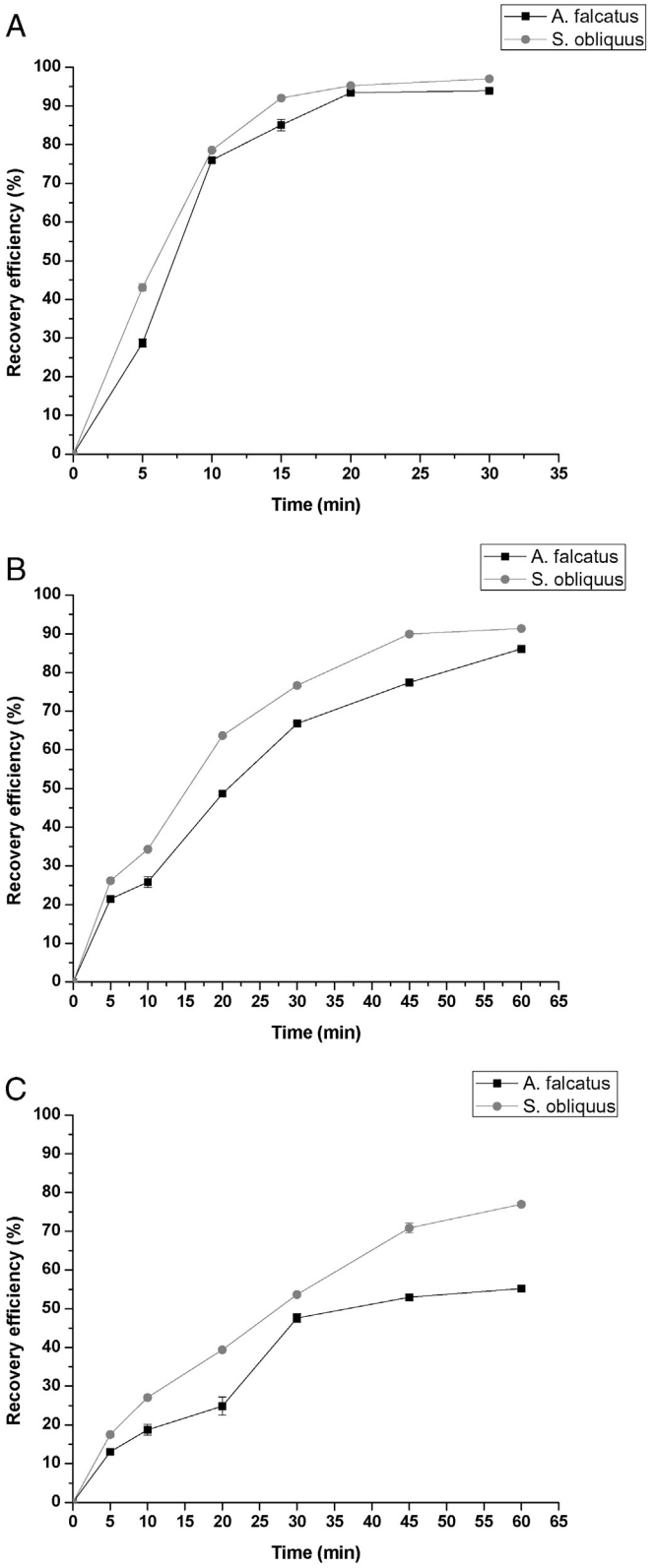

Fig. 3. A: Harvesting efficiency of centrifugation for *A. falcatus* and *S. obliquus*. B: Harvesting efficiency of alum flocculation for *A. falcatus* and *S. obliquus*. C: Harvesting efficiency of chitosan flocculation for *A. falcatus* and *S. obliquus*.

Table 1
Recovery efficiency and energy consumption of the ECH process for *A. falcatus* at different applied current.

Harvesting method	Applied current (A)	Recovery efficiency (%)	Time (min)	Power consumption (kWh kg^{-1})
ECH	0.5	69.71 ± 0.57	30	0.84
ECH	1	91.26 ± 0.29	30	1.76
ECH	1.5	91.71 ± 0.5	30	3.62

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chitosan at 60 min process (Fig. 3A and B). *S. obliquus* is comparatively bigger in size than the *A. falcatus* and thus showed higher recovery efficiency with same processing time. Bigger size of *S. obliquus* aids in rapid gravitational settling of the flocs. Flocculation processes are used at industrial scale in wastewater treatment and mining; however in these cases the final product is liquid after separation of solid impurities [8]. In microalgal harvesting by flocculation the end product is biomass and thus needs an additional dewatering step. Contamination of microalgal biomass by chemical additives is the major concern for flocculation technique [7].

3.4. Comparison of ECH with other harvesting techniques

Centrifugation achieved the highest microalgal recovery efficiency of 93.41 ± 0.35% at 20 min followed by ECH process which showed recovery efficiency of 91.26 ± 0.29% in 30 min. The flocculation processes showed much lower recovery efficiencies (86.09 ± 0.09% for alum and 55.22 ± 0.54% for chitosan) compared to ECH process (Table 2). For harvesting of small microalgae like *A. falcatus* flocculation processes required much longer time periods than the ECH and centrifugation processes. To achieve the comparable recovery efficiencies and processing time by flocculation the possible solution is to use higher dosage of flocculants. However higher dosage of chemicals like alum could hamper the downstream processing of biomass for extraction and conversion of lipid and could also deteriorate the quality of harvested biomass. Higher dosage of flocculants like alum and chitosan will also add to the processing cost. Chitosan flocculation is reported to be pH dependant and therefore needs a pH adjustment for efficient harvesting [26]. In terms of recovery efficiency and process time centrifugation was found to be the best harvesting method followed by the ECH process. Vandamme et al. [27] reported that the organic matter secreted by the microalgae interferes with the flocculation process and requires the higher dosage depending upon the amount of organic matter present in the medium. Generally when microalgae are used for biofuel production various stress factors are applied to induce the lipid and carbohydrate accumulation. Thus the harvesting of the microalgae with higher organic content may require the higher dosage of the flocculants adding extra cost.

Centrifugation and ECH harvesting processes achieved over 90% recovery efficiencies in relatively short time periods. Energy consumption of the process is an important criterion for the economical and sustainable large scale application of any process [24]. The power consumption for 20 min centrifugation process with 93% recovery efficiency was 65.34 kWh kg^{-1} (Table 2). Whilst the 30 min ECH process with 91% recovery efficiency consumed 1.76 kWh kg^{-1} of energy (Table 2). Similarly Vandamme et al. [14] reported the power consumption of 16 kWh kg^{-1} for harvesting of *Chlorella vulgaris* by centrifugation and 2 kWh kg^{-1} by electro-coagulation–flocculation process. Uduman et al. [23] investigated the electrocoagulation process for harvesting and observed that, to achieve maximum recovery efficiency in 15 min process the energy consumptions were 9.16 kWh kg^{-1} for *Tetraselmis* sp. and 4.44 kWh kg^{-1} for *Chlorococcum* sp.

The ECH process with low energy input and high recovery efficiency could be successfully applied as a sustainable harvesting step for the production of bulk commodities like microalgal biofuels, feed and other low value products. Furthermore ECH process with non-sacrificial electrodes avoids the metal contamination of biomass. Thus this technique can also be applied for the production of high value products such as pigments and long chain fatty acids which are used in nutraceuticals and pharmaceutical industry.

3.5. Effect of harvesting processes on biochemical composition of microalgae

The ideal harvesting technique should not have the deteriorating effect on the microalgal biomass quality. Furthermore the harvesting technique should not interfere with the extraction processes. In this study lipids, carbohydrate and protein contents of the *A. falcatus* does not show any significant modification due to the various harvesting techniques investigated (Table 3). The content of these primary metabolites is strain specific and primarily dictated by the cultivation conditions The lipid recovered from *A. falcatus* was slightly higher in biomass harvested by ECH (26.37 ± 0.47%) as compare to other process such as centrifugation (24.03 ± 0.53%), chitosan (24.02 ± 0.51%) and alum (24.05 ± 0.24%). Carbohydrate content of *A. falcatus* biomass harvested by centrifugation was 15.59 ± 0.27%, ECH was 15.98 ± 0.08%, chitosan was 15.84 ± 0.21% and alum 15.69 ± 0.12% respectively. Lipids and carbohydrates produced by microalgae are mostly utilized as feedstock for the production of biofuels such as biodiesel, bio-oil, and biomethane. *A. falcatus* showed high protein content of approximately 45%, which highlights its potential application as an animal and aquaculture feed supplement. Highest protein content (45.02 ± 0.17%) was observed in biomass harvested from ECH process (Table 3). The higher lipid and protein yields by ECH process found in this study could be attributed to the formation of irreversible pores in the membrane of microalgal cell due to the electrical field and charge particles generated in the process [28,29]. This porosity in the microalgal cell wall not only facilitates discharge of intracellular compounds but also allows solvents to access the lipids [29,30]. Daghrir et al. [28] investigated the electrochemical process for the extraction of lipid and protein from *C. vulgaris*. In their study they found that electrochemical process efficiently extracted lipids and proteins by disrupting the cell wall. Even though there are slight changes in biochemical composition of *A. falcatus* using different harvesting technique, none of the technique showed any severe deteriorating influence.

Fatty acid composition of the lipids extracted from *A. falcatus* biomass harvested by different techniques did not show any significant difference. However the *A. falcatus* biomass harvested by alum showed slight increase in saturated fatty acids and decrease in unsaturated fatty acids compared to other harvesting techniques (Fig. 4). This could be possible because polyunsaturated fatty acids are prone to oxidative cleavage caused by number of factors such as nutritional stress, free radicals etc. [16,31]. C16:0, C18:0, C18:1, C18:2 and C18:3 were found to be major contributing fatty acids in lipid composition of *A. falcatus*. These results show that the selection of harvesting method is also based on the degree of saturation required for the end product. Higher saturated fatty acids are required for production of biodiesel with high oxidation stability [31]. Long chain polyunsaturated fatty acids are important for pharmaceutical and nutraceuticals applications of microalgae [32].

Chemical flocculants such as alum can cause the metal contamination of biomass and residual water which can restrict its use in feed and food industry. Chitosan requires lower pH for efficient harvesting, which can damage the cells and reduce the life of harvested biomass.

Table 2
Summary of harvesting of *A. falcatus* using various harvesting techniques.

Harvesting method	Recovery efficiency (%)	Time (min)	Power consumption (kWh kg^{-1})
Centrifugation	93.41 ± 0.35	20	65.34
ECH	91.26 ± 0.29	30	1.76
Chitosan	55.22 ± 0.54	60	–
Alum	86.09 ± 0.09	60	–

Table 3
Biochemical composition of *A. falcatus* using different harvesting techniques.

Method	Lipid (%)	Carbohydrate (%)	Protein (%)
Centrifugation	24.03 ± 0.53	15.59 ± 0.27	44.17 ± 0.38
ECH	26.37 ± 0.47	15.98 ± 0.08	45.02 ± 0.17
Chitosan	24.02 ± 0.51	15.84 ± 0.21	44.04 ± 0.02
Alum	24.05 ± 0.24	15.69 ± 0.12	43.61 ± 0.62

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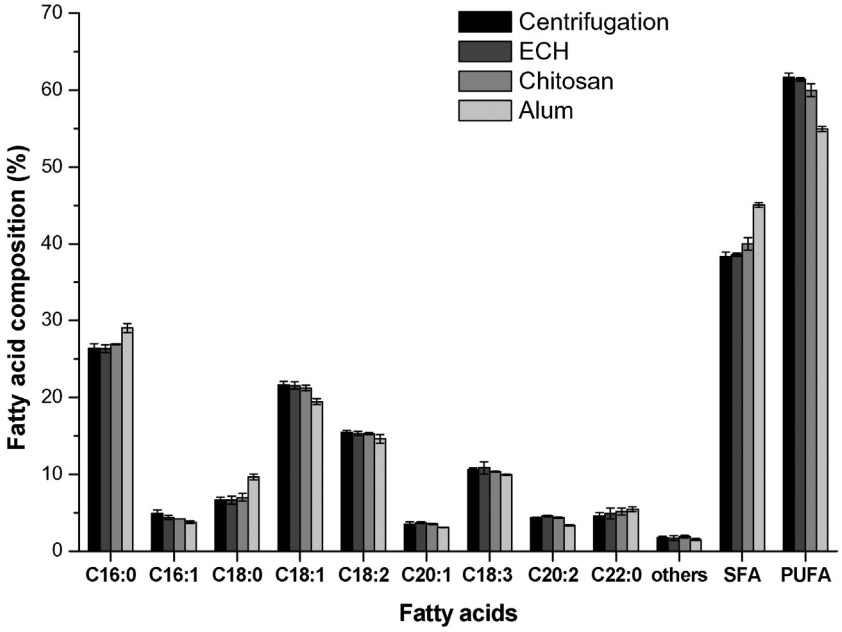

Fig. 4. Fatty acid composition of *A. falcatus* biomass harvested by various techniques.

These flocculants may also affect the composition and quality of the metabolites which needs to be further investigated depending on the final application of the biomass. Similarly centrifugation can also damage the cells and reduce the shelf life of harvested biomass. The ECH process was carried out without adjusting the culture pH. Non sacrificial electrodes used in this ECH process avoid the metal contamination of biomass. Thus the electrochemical harvesting could be the best suited technique for biofuels, feed, and food application of microalgae as well as for production of high value products from microalgae.

4. Conclusion

Electrochemical harvesting technique was found to be efficient for the harvesting of small sized microalgae *A. falcatus* with recovery efficiency of 91.26% in 30 min. ECH process showed comparable recovery efficiency with centrifugation process and higher recovery efficiency compared to alum and chitosan flocculation. The energy consumption of ECH process was much less than the centrifugation process. Non-sacrificial electrodes do not require frequent replacement unlike metal electrodes and also avoids contamination of biomass. ECH process does not affect the lipid, carbohydrate and protein content and fatty acid composition of *A. falcatus* biomass. These results underline the potential of ECH process for sustainable and economical microalgal biomass harvesting for various applications.

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