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Harvesting of *Scenedesmus obliquus* cultivated in seawater using electro-flotation

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Abstract−Seawater, when supplemented to a growth medium, appears to stimulate auto-flocculation of a certain microalgae species like *Scenedesmus obliquus* and thus renders its harvesting easy. To make use of this unique response for the purpose of biomass harvesting, *S. obliquus* was grown in a seawater-added medium and then collected in electrochemically-mediated ways. Significantly higher harvesting efficiency and energy saving were observed with electro-flotation (EF) than with electro-coagulation-flotation (ECF) and the standard BG11 medium. An optimal EF condition, the highest recovery rate with least energy use, was found with a supply of 0.5 A. Seawater amendment was most beneficial in a level of 10%. All this clearly showed that applying EF to cells cultivated in the seawater-supplemented medium is a promising harvesting means that enables one to obtain algae biomass without interfering with the downstream process of biodiesel production.

Keywords: *Scenedesmus obliquus*, Harvest, Seawater, Electro-flotation (EF), Electro-coagulation-flotation (ECF)

INTRODUCTION

The demand for the renewable energy source has been rising at an unprecedented rate on account of the CO_2-causing climate change and eventually-depleting fossil fuel. Among a good many potential sources, microalgae are viewed as the feedstock of choice, in particular for biofuel production: they grow surprisingly fast and do so only with sunlight and CO_2, and possibly with nutrients found in wastewater [1-4]. In addition to transportation fuels, microalgae are also an excellent way of producing a variety of functional bioproducts such as food supplements, natural pigments, and polyunsaturated fatty acids [5-7]. Though the entire production process is far from being optimal, the concentration of biomass, namely, harvesting and dewatering, is especially energy-intensive [8,9], due to small cell size, cell density similar to water, and charged cell surface [10-12].

Among a large number of harvesting means developed thus far, flocculation, combined with either flotation or sedimentation, stands out for its effectiveness, maturity, and energy-efficiency [13]. This ever-promising approach can further be facilitated by an electrochemical reaction, termed electro-coagulation-flotation (ECF) [14, 15]. In the process of ECF, positively charged aluminum or iron ions are produced from the sacrificial anode electrode and electrostatically attached to the negatively charged surface of microalgae, resulting in the destabilization and coagulation of the cells. Concomitantly generated hydrogen microbubbles from the cathode electrode make the coagulated microalgae float [5]. ECF, though exceeding the chemical counterpart, still has an issue of coagulant residual, which may deteriorate biodiesel quality and medium recyclability [16]. In this sense, electro-flotation (EF) is a hassle-free alternative and in certain circumstances is particularly suited [17].

In a previous study, *Scenedesmus obliquus*, especially when cultivated in a seawater-supplemented medium, showed a strong tendency of auto-flocculation, much greater than cells grown in the standard medium [18]. It was speculated to be attributable to a change in zeta potential and an increase in extracellular polymeric substance (EPS) production, all of which were caused by high salt content. This finding led to a hypothesis that *S. obliquus*, in particular when grown in the seawater-added medium, can be efficiently harvested simply with EF, which enables one to obtain biomass without any coagulant-associated complication. The objective of this study, therefore, was to explore the possibility.

MATERIALS AND METHODS

1. Preparation of Microalgae

Scenedesmus obliquus UTEX 393 was obtained from Culture Collection of Algae at the University of Texas at Austin, USA. Cells were cultivated in two conditions: BG11 medium ($NaNO_3$, 1.5 g/L; KH_2PO_4, 40 mg/L; $MgSO_4 \cdot 7H_2O$, 75 mg/L; $CaCl_2 \cdot 2H_2O$, 36 mg/L; citric acid, 6 mg/L; ferric ammonium citrate, 6 mg/L; NA_2-$EDTA_2 \cdot H_2O$, 1 mg/L; Na_2CO_3, 20 mg/L; H_3BO_3, 2.86 mg/L; $MnCl_2 \cdot 4H_2O$, 1.81 mg/L; $ZnSO_4 \cdot 7H_2O$, 222 μg/L; $Na_2MoO_4 \cdot 2H_2O$, 390 μg/L; $CuSO_4 \cdot 5H_2O$, 79 μg/L; and $Co(NO_3)_2 \cdot 6H_2O$, 49.4 μg/L) as a control and

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SBG11 medium (seawater-supplemented BG11) as an experimental group. Seawater was obtained from Ulsan province in South Korea and its salinity was 3.47% (34.7 gram per kilogram). The seawater was filtered using a 0.45 μm syringe filter. SBG11 media with different volume percentages of seawater were prepared: S1: 10%, and S2: 20%. *S. obliquus* was grown in 2 L culture bottles for each medium (BG11, S1, and S2). A constant 3% CO_2 (v/v) enriched air flow (250 mL/min) at 25 °C was supplied along with a light intensity of 100 μmol photons m^{-2} s^{-1}. A change in pH was checked with a pH meter (Horiba Co. Ltd., Kyoto, Japan). Initial concentrations of cells were 1.17±0.01, 1.05±0.02, and 0.76±0.01 g/L in BG11, S1, and S2, respectively. Experiments were performed with the same concentrations.

2. Electrolytic Microalgae Harvesting

An ECF experiment was performed using a 70 mm×170 mm×70 mm (width×height×thickness) chamber installed with two perforated plate-type electrodes in 57 mm×115 mm×2 mm (width×height×thickness): aluminum (Mg, 2.2-2.8%; Cr, 0.15-0.35%) as the sacrificial anode and a dimensionally stable anode (DSA®, Ti/IrO_2) as the cathode. The anode was connected to the positive outlet, and the cathode was connected to the negative outlet using a DC power supply (S-3005Q, Fine-Power Korea). The voltage was measured with a voltage meter (GDM-8261, Good Will Instrument, Taiwan) during the electrolytic harvest at a supply of 0.25, 0.5, and 0.75 A. At each experiment, 400 mL of the microalgae suspension was used. A magnetic stirring bar was placed on the floor of the chamber and rotated at 350 rpm. Harvesting efficiency was measured using optical density of 680 nm. Every 5 minutes, 3 ml of the sample was obtained using a 5 ml syringe connected with a 15 cm needle at 8.5 cm below the suspension surface. Apart from using a non-sacrificial electrode, instead of the sacrificial one, the same methods were applied to EF. All experiments were performed in duplicate. The harvesting efficiency was calculated using the following equation:

$$\text{Harvesting Efficiency (\%)} = \frac{OD_i - OD_f}{OD_i} \times 100 \tag{1}$$

where OD_i represents the initial optical density of the sample, and OD_f is the final optical density of the sample.

3. Electrical Power Consumption

Electrical power consumption was calculated as:

$$E = \frac{UIt}{1000V\eta_a c_i} \tag{2}$$

where U represents the voltage (V), I the current (A), t the time of the EF treatment (h), V the volume of the microalgal solution used in the experiment (m^3), η_a the harvesting efficiency, and c_i the initial microalgae biomass concentration (kgm^{-3}).

RESULTS AND DISCUSSION

1. Different Harvesting of *S. obliquus* Grown in BG11 and SBG11

Because of the nature of the process, electrochemistry-based harvesting is bound to be affected by salt concentration. To see if that was also the case with *S. obliquus*, the cells grew in a seawater-supplemented medium and the harvesting efficiency compared with those grown in the regular BG11 medium. The cells cultivated in BG11 responded rather poorly to the electrochemical treatments, yielding less than 60% of harvesting efficiency after 10 min of both EF and ECF; the cells grown in S1 and S2, on the other hand, reached almost 95% even in EF (Fig. 1). Generally, cells are removed at a faster rate with ECF, because it leads to the formation of large cell flocs via flocculation process and more efficiently entrapping gas bubbles [19]. It is this reason that the exceedingly high harvesting efficiency of S1 and S2 with EF was substantial. This rather surprising result might have something to do with the increased production of EPS in a high-salinity condition, which was known to lead to the auto-flocculation of some microbial species including *S. obliquus* [18]. It was speculated that cells grown in S1 and S2, which naturally formed large enough flocs due to the auto-flocculation, were able to entrap gas bubbles generated through the EF, and as a result be efficiently and rapidly removed even without the

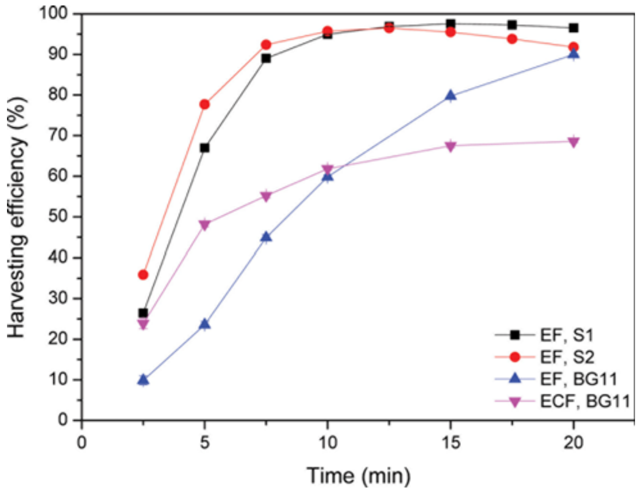

Fig. 1. Harvesting efficiency of EF and ECF for *S. obliquus* cultivated in BG11 (control), S1 (BG11 with 10% seawater), and S2 (BG11 with 20% seawater).

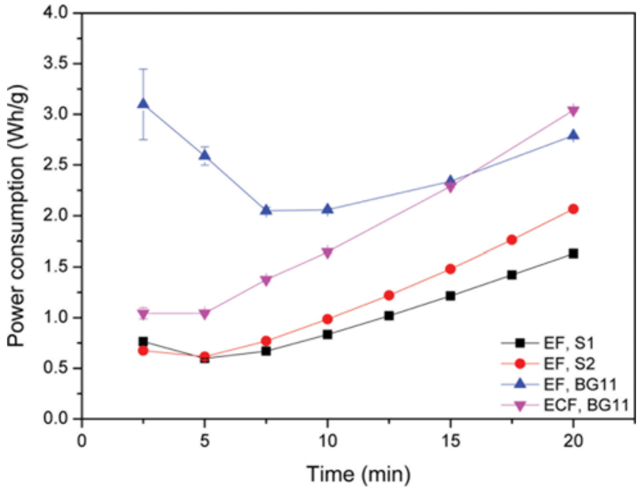

Fig. 2. Power consumption of EF and ECF for *S. obliquus* cultivated in BG11, S1, and S2.

help of coagulant. Besides, the high conductivity nature of the seawater in connection with salts such as $MgSO_4$, $CaCl_2$, and Na_2CO_3 must give rise to the improved production of gas bubbles from the cathode electrode. It is also plausible that divalent cations, especially Ca^{2+}, acted as a potent ligand that played a role in forming flocs and entrapping gas bubbles in them [20].

In addition to the high harvesting efficiency, the seawater-based cultivation offered another merit of the lowered consumption of electrical energy (Fig. 2). This advantageous trait also was attributable to the heightened conductivity by sea salts in SBG11. In fact, Misra et al. [17] even deliberately used NaCl for the purpose of harvesting *Chlorella sorokiniana* by means of enhancing electrochemical reaction rate; they obtained impressive harvesting with less power consumption. With the addition of 6 g/L NaCl, harvesting efficiency was increased to 95% using 1.6 Wh/g only, compared to 66% without NaCl using 4 Wh/g.

2. Effects of Current and Seawater Content on Harvesting

To see how much applied current and added seawater had effects on harvesting *S. obliquus*, harvesting rates of the S1 and S2 samples were measured, in terms of removal rate using EF at 0.25, 0.5, and 0.75 A. Fig. 3 shows that the harvesting efficiency gradually increased in accordance with supplied currents in both S1 and S2. At 0.25 A, the harvesting efficiency reached about 80% while the removal rate went over 95% at 0.5 and 0.75 A in 10 min. In the electrophoretic harvesting process, current is a determining factor for the electrochemical reaction rate, and it is so because electricity acts as a driving force for it. Accordingly, as applied current increases, the mass transport of ions between the electrodes increases, resulting in high harvesting efficiency.

It was found that the amount of current input was closely related to the amount of power consumption (Fig. 4), which was in fact expected. At 0.5 A, to reach the harvesting efficiency of more than 95%, 0.834 and 0.985 Wh/g were used in S1 and S2, respectively, whereas 1.516 and 1.736 Wh/g were required at 0.75 A. With the similar harvesting efficiency, twice less power was consumed at 0.5 A than 0.75 A. It was possible that the amount of produced gas bubbles was just right at 0.5 A for the optimal and highly efficient harvesting; a larger current supply would end up consuming greater power without apparent benefit. Likewise, the amount of seawater seemed to have an optimal value in relation to harvesting efficiency and power use, and in our experimental condition it was found to be 10% of seawater.

3. Comparison of Energy Consumption

Among many harvesting techniques, filtration methods, especially based on pressure filters, have been known to consume the

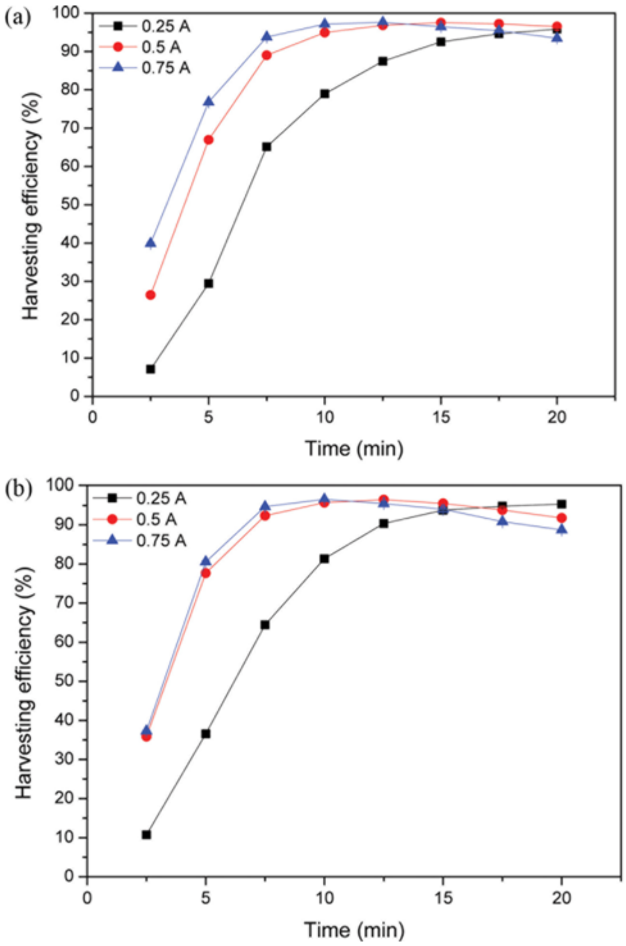

Fig. 3. Harvesting efficiency of EF using different currents for *S. obliquus* cultivated in (a) S1 and (b) S2.

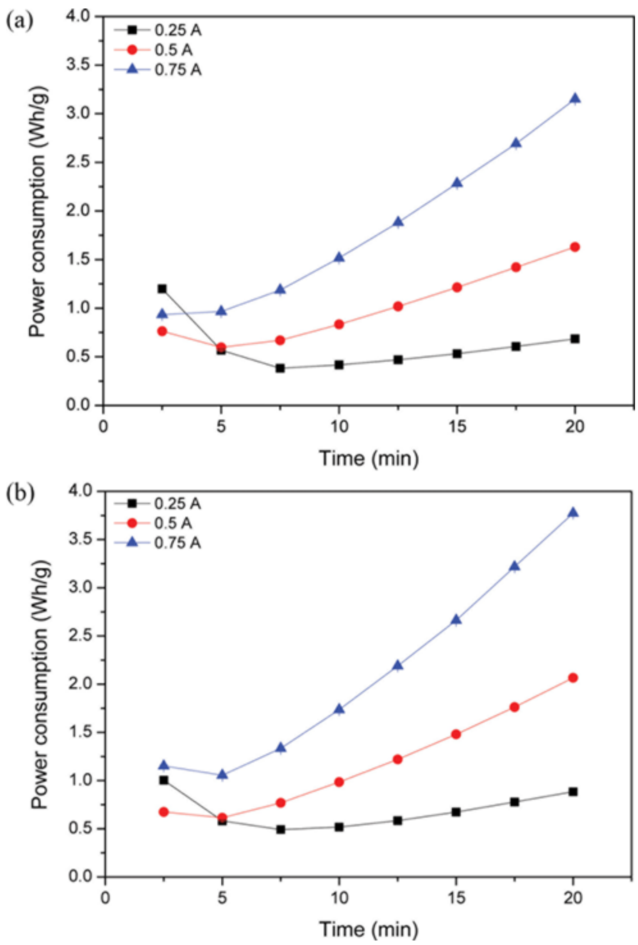

Fig. 4. Power consumption of EF using different currents for *S. obliquus* cultivated in (a) S1 and (b) S2.

Table 1. Electrical energy consumption of electro-flotation with the seawater-supplemented medium and other microalgae harvesting methods [8,22,23]

Harvest method	Electrical energy consumption (Wh/g)
Electro-flotation with S1	0.68
Electro-flotation with S2	0.88
Polarity exchange with Al-Pt	1.19
Polarity exchange with Al-DSA	1.23
Tangential flow filtration	3.47
Polymer flocculation	35.62
Pressure filters	0.18
Vacuum filters	1.19
Centrifugation	1.67

least energy (Table 1); considering a total cost including investment and maintenance, however, the electrolytic process seems to be winning: US$0.11/m^3 versus pressure filtration of US$0.21/m^3 [21,22]. This cost-competitiveness could be reinforced when accompanied by a smart operation. For instance, Kim et al. [23] implemented polarity exchange, and by doing so reduced the overall cost to a significant degree. Our approach went even further: In EF applied in S1 and S2, merely half of the power used in polarity exchange methods was needed, making the electrochemical method even more competitive.

CONCLUSION

Scenedesmus obliquus can readily be harvested when grown in a seawater-supplemented medium; effective harvesting is possible with electro-flotation even in the absence of coagulant. The added sea salts induce self-destabilization of the cells, leading to faster process time during electro-harvesting. The increased salts raise electric conductivity in the culture medium, which in turn reduces energy consumption. Considering both harvesting efficiency and energy expenditure, *S. obliquus* grown in the seawater-added medium could be best harvested by EF only at 0.5 A of current and it is particularly so when the growth medium contained 10% of seawater. All this was done without coagulant added, making it possible to more easily recycle medium and obtain high quality biomass in an energy-efficient manner.

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