# Synergy of flocculation and flotation for microalgae harvesting using aluminium electrolysis

Wenqing Shi[1, †], Lin Zhu[2,†], Qiuwen Chen[1,*], Ji Lu[3], Gang Pan[4], Liuming Hu[1], Qitao Yi[1]

1. CEER, Nanjing Hydraulics Research Institute, Guangzhoulu 223, Nanjing 210029, China
2. NIGLAS, Chinese Academy of Sciences, Beijingdonglu 73, Nanjing 210008, China
3. Huaneng Lancang River Hydropower Co., Ltd., Shijichengzhonglu 1, Kunming 650214, China
4. RCEES, Chinese Academy of Sciences, Shuangqinglu 18, Beijing 100085, China

[†] These authors contributed equally to this work.

[*]Corresponding author: Tel./Fax: +86 2585829765; E-mail: qwchen@nhri.cn

**Abstract**

Microalgae are often used as feedstock for renewable biofuel production and as pollutant up-takers for wastewater treatment; however, biomass harvesting still remains a challenge in field applications. In this study, electro-flocculation using aluminium electrolysis was tested as a method to collect *Chlorella vulgaris*. The electrolysis products were positively charged over a wide pH range below 9.5, which gave them a flocculation potential for negatively charged microalgae. As flocculants were in-situ generated and gradually released, microalgae flocs formed in a snowballing mode, resulting in the compaction of large flocs. When higher current density was applied, microalgae could be harvested more rapidly, although there was a trade-off between a higher energy use and more residual aluminium in the culture medium. Benefits of this flocculation method are two-fold: the phosphate decrease in post-harvesting could improve nutrient removal in microalgae based wastewater treatment, while the ammonium increase may favor microalgae recovery for medium recycling.

**Keywords**: Microalgae harvesting; Electro-flocculation; Current density; Energy consumption; Phosphate.

# 1. Introduction

In recent years, the use of microalgae has attracted great interest as a means to produce biofuels and treat wastewater (Baeyens et al., 2015; Kang et al., 2010; Sulzacova et al., 2015). The biofuel yield from microalgae was estimated to be 10 ~ 20 times higher than those from oleaginous seeds and vegetable oils (Chisti, 2007). In microalgae based wastewater treatment, pollutants can be ecologically and safely removed through microalgae assimilation, with the added benefit of biofuel production (Mehrabadi et al., 2016; Tan et al., 2016). However, microalgae harvesting still remains a challenge due to the small cell size, electrical stability and low density in growth media (Cerff et al., 2012). The cost of microalgae harvesting can represent about 60% of the total cost of the final products (Grima et al., 2003).

Several methods have been tested to harvest microalgae, including gravity sedimentation (Depraetere et al., 2015), centrifugation (Chen et al., 2015), filtration (Nurra et al., 2014) and chemical flocculation (Reyes and Labra, 2016). Gravity settling is simple but only suitable to harvest microalgae with large size (Park and Craggs, 2010). Centrifugation and filtration are rapid and reliable, but require high energy input and large capital investment, making the large-scale implementation economically unfeasible (Kim et al., 2015). Chemical flocculation requires minimal equipment to effectively harvest microalgae; however, the addition of chemical flocculants inevitably introduces large amounts of other undesired anions such as sulfates and chlorides, and thereby leads to operation cost increase and potential negative impacts (Pan et al., 2011).

So far, there are few cost-effective and efficient technologies for microalgae harvesting, which limits large-scale applications of microalgae in biofuel production and wastewater treatment.

Electro-flocculation is an electrochemical technique for pollutant removal, which is based on the in-situ generation of flocculants during metal electrolysis (Vasudevan et al., 2008). Owning to the advantages of low cost, high efficiency and easy operation, electro-flocculation has been widely applied in wastewater treatment to remove phosphorus (Mores et al., 2016), dyes (Mollah et al., 2010), fluoride (Hu et al., 2005), organic matter (Asselin et al., 2008) and heavy metals (Hanay and Hasar, 2011). Charge neutralization is identified as the main mechanism of electro-flocculation, which creates the sorption affinity for negatively charged pollutants (Vasudevan et al., 2008). Electro-flocculation may act as a potential solution for microalgae harvesting, due to the net negative surface charges on the cells. Dassey and Theegala (2014) observed the limited efficacy of electro-flocculation on the harvesting of *Dunaliella* sp. and *Nannochloris* sp. Xiong et al. (2015) tested the synergy of electro-flocculation and sand particles on the removal of *Dunaliella salina*. In spite of the recent advances, knowledge gaps still exist with respect to the technique's efficacy, especially the mechanisms responsible for flocculation remain poorly understood.

This study explored aluminium (Al) based electro-flocculation to harvest microalgae. The electrolysis products were characterized, and the relationship among harvesting efficiency, surface charge, floc size and floc structure were investigated to reveal the mechanisms. The energy input, Al consumption and culture medium responses were studied for field applications. After microalgae harvesting, the residual Al in the culture medium was also assessed with respect to potential risk.

## 2. Experimental section

### *2.1 Microalgae species and culture*

Freshwater *Chlorella vulgaris* (*C. vulgaris*), a commonly used species in biofuel production and microalgae based wastewater treatment (Arbib et al., 2014; de-Bashan et al., 2004), was used in this study. The *C. vulgaris* cells (FACHB-24) were obtained from the Institute of Hydrobiology, Chinese Academy of Sciences, and cultured in BG11 medium according to the instructions. The BG11 medium was composed of 500 mg $L^{-1}$ Bicin, 100 mg $L^{-1}$ $KNO_3$, 100 mg $L^{-1}$ b-$C_3H_7O_6PNa_2$, 50 mg $L^{-1}$ $NaNO_3$, 50 mg $L^{-1}$ $Ca(NO_3)_2$•$4H_2O$, 50 mg $L^{-1}$ $MgCl_2$•$6H_2O$, 40 mg $L^{-1}$ $Na_2SO_4$, 20 mg $L^{-1}$ $H_3BO_3$, 5 mg $L^{-1}$ $Na_2EDTA$, 5 mg $L^{-1}$ $MnCl_2$•$4H_2O$, 5 mg $L^{-1}$ $CoCl_2$•$6H_2O$ and 0.8 mg $L^{-1}$ $Na_2MoO_4$•$2H_2O$, 0.5 mg $L^{-1}$ $FeCl_3$•$6H_2O$ and 0.5 mg $L^{-1}$ $ZnCl_2$. Microalgae batch cultures (10 L) were maintained at 30 ± 1°C under continuous cool white fluorescent light of 2000 ~ 3000 lux on a 12 h light and 12 h darkness regimen in an illuminating incubator (LRH-250-G, Guangdong Medical Apparatus Co., Ltd., China). The culture was continuously aerated with air at a flow rate of 5 L $min^{-1}$ using a pump (AC0-001, Sensen Group Co., Ltd., China), and microalgae growth was monitored by counting the cell numbers. The dry cell weight was measured by filtering an aliquot of the culture suspension through pre-weighed GF/C filters (Whatman, England). After rinsed with deionized water, the filters were dried at 105°C for 24 h and re-weighed.

*2.2 Electro-flocculation system*

The electro-flocculation unit consisted of two Al electrode plates (Jinjia Metal Co., Ltd., China) and a flat stir paddle (Zhongrun Water Industry Technology Development Co., Ltd., China) for mixing in a 500-ml beaker. The Al electrode plates had a surface area of 3 × 10 cm and a thickness of 1 cm, and were vertically installed with a gap of 3 cm. During electro-flocculation, the electrode plates were partially immersed in the microalgae solution, such that the effective surface area was 22.5 $cm^2$. The electric current was supplied by a direct current power supply (DF1730SL5A, Ningbo Zhongce Dftek Electronics Co., Ltd., China). The experimental set-up was schematically presented in Fig. S1 in the supporting information (SI).

*2.3 Microalgae electro-flocculation*

The exponential growth phase of *C. vulgaris* culture was used in the electro-flocculation experiment. The initial cell concentration was set to $3.63 \times 10^{10}$ cells $L^{-1}$. 0.4 L of readily prepared *C. vulgaris* solution was transferred to the electro-flocculation cell, and then stirred at 200 rpm after electric current was supplied. The control was run in the above-mentioned *C. vulgaris* solution, but without electric current. Prior to each run, the electrodes were immersed in 5% $HNO_3$ solution, and lightly wiped with abrasive paper, and then rinsed with deionized water to remove barrier oxide film on the electrode surface. The flocculation experiments were conducted at raw microalgae solution pH of 8.6. All the flocculation experiments were conducted in triplicates.

*2.4 Analytical methods*

After 10 min of microalgae electro-flocculation, samples were collected from 5 cm above the bottom to enumerate the cell number using an Axioskop 2 mot plus microscope (Carl ZEISS, Germany). The microalgae harvesting efficiency was calculated as:

$$\text{Harvesting efficiency} = (IC\text{-}SC)/IC \times 100\% \quad (1)$$

where *IC* and *SC* are the initial and sample cell concentration, respectively.

The surface charge of microalgae cells was characterized using a Zetasizer 2000 (Malvern Co. United Kingdom). Dynamic size growth of microalgae flocs during electro-flocculation was analyzed using a laser particle size analyzer (Mastersizer 2000, Malvern Co., United Kingdom). The apparatus set-up was described in Fig. S2 in the SI, and the size was denoted by the measured mean diameter ($d_{0.5}$). For the floc image study, the flocs were carefully transferred onto a glass slide and then photographed by an electromotive microscope (ST-CV320, Chongqing UOP Photoelectric Technology Co., Ltd., China). After microalgae harvesting, phosphate and ammonium in the culture medium were measured according to the Monitoring Analysis Method of Water and Wastewater (Ministry of Environmental Protection of China, 2002). The medium pH and temperature were measured using a Yellow Springs Instruments (Yellow Springs, Ohio, USA). The energy consumption was calculated as:

$$\text{Energy consumption (kWh L}^{-1}\text{)} = UIt/\,v \quad (2)$$

$$\text{Energy consumption (kWh g}^{-1}\text{ microalgae)} = UIt/v\beta\theta\sigma \quad (3)$$

where $U$ is cell voltage (V), $I$ is current intensity (A), $t$ is electrolysis time (s), and $v$ is the volume of microalgae solution (L), $\beta$ is the initial microalgae concentration, $\theta$ is the microalgae harvesting efficiency (%), and $\sigma$ is the microalgae weight ($32 \times 10^{-12}$ g cell$^{-1}$).

The Al consumption and charge loading were calculated using the Eq. (4) and Eq. (5) according to Faraday's law (Zaied and Bellakhal, 2009),

$$\text{Al consumption} = ItM/zFv \quad (4)$$

$$\text{Charge loading} = It/Fv \quad (5)$$

where $M$ is the molecular mass of Al (26.98 g mol$^{-1}$); $z$ is the number of electrons transferred ($z$ = 3); $F$ is Faraday's constant (96487 C mol$^{-1}$). After electro-flocculation, the residual Al in the medium was analyzed using an Inductively Coupled Plasma Optical Emission Spectrometer (Optima 8300, PerkinElmer, USA).

## 3. Results

### *3.1 Surface charge of Al electrolysis products*

During Al electrolysis, amorphous-like products were observed. Analysis on surface charge indicated that the products were positively charged. At the current density of 22.2, 44.4 and 66.7 A m$^{-2}$, the zeta potential of Al electrolysis products (AEP) ranged between +6.5 and +15.2 mV within the electrolysis time of 8 min (Fig. 1a). The surface charge of AEP maintained positive in a wide pH range below 9.5, and reached the highest value of +27.2 mV under near-neutral pH conditions. In contrast, the zeta potential of *C. vulgaris* cells gradually decreased from -0.2 to -21.8 mV in the pH range of 1.8 ~ 10.5 (Fig. 1b).

*3.2 Microalgae floc formation*

After Al electrolysis was initiated, microalgae aggregation occurred, thus flocs became larger and more compact along time. At the current density of 44.4 A $m^{-2}$, the floc size ranged between 2.5 and 316.2 μm with the mean diameter ($d_{0.5}$) of 99.3 μm at the electrolysis time of 2 min, and ranged between 70.8 and 562.3 μm with the mean diameter of 262.3 μm at 4 min, and ranged between 89.1 and 794.3μm with the mean diameter of 298.1 μm at 6 min, and ranged between 125.9 and 891.3μm with the mean diameter of 367.6 μm at 8 min (Fig. 2a). The floc fractal dimension was 1.29, 1.71, 1.96 and 2.01 at the electrolysis time of 2, 4, 6, 8 min, respectively (Fig. 2b). Large amounts of tiny gas bubbles were observed on microalgae flocs (Fig. S3 in the SI.). These bubbles carried the flocs to water surface and then broke up.

*3.3 Effect of current density on microalgae harvesting*

Using Al electrolysis, a maximum microalgae harvesting efficiency of about 98% was achieved, although different electrolysis time was needed, depending on the current density applied. In general, the higher current density, the shorter electrolysis time is needed to reach the maximum microalgae harvesting. When 22.2, 44.4 and 66.7 A $m^{-2}$ was applied, it took 7, 6 and 4 min to achieve the maximum microalgae harvesting, respectively (Fig. 3a). However, the charge loading holds a similar shape at different current densities. To remove 98% of microalgae cells, the charge loading was about

0.75 Faradays $m^{-3}$ (Fig. 3b). The surface charge of microalgae cells as a function of electrolysis time was also investigated during microalgae harvesting. As the electrolysis time increased, an increase was obtained in the cell surface charge, which was enhanced by the higher current density. When 22.2, 44.4 and 66.7 A $m^{-2}$ was applied, the zeta potential of microalgae cells was gradually increased from -14.0 mV to -12.7, -6.2 and -3.9 mV at the electrolysis time of 8 min, respectively (Fig. 3b).

*3.4 Energy consumption*

When higher current density was applied, more energy consumption was needed to achieve the same microalgae harvesting rate. At the current density of 22.2, 44.4 and 66.7 A $m^{-2}$, the energy consumption was $0.99 \times 10^{-4}$, $2.53 \times 10^{-4}$ and $3.35 \times 10^{-4}$ kWh $L^{-1}$, respectively (Fig. 4a). Energy consumption per gram microalgae biomass was calculated and presented in Fig. 4b. It indicated that the energy consumption was the highest at the low microalgae harvesting efficiency. As the harvesting efficiency increased, the energy consumption decreased and kept stable at the harvesting efficiency of > 80%. However, the use of lower charge density generally yielded lower energy consumption per gram biomass for effective microalgae harvesting (> 80%). The energy consumption was $0.87 \times 10^{-4}$, $2.22 \times 10^{-4}$ and $2.94 \times 10^{-4}$ kWh $g^{-1}$ biomass at the current density of 22.2, 44.4 and 66.7 A $m^{-2}$, respectively.

*3.5 Al consumption and charge loading*

Al consumption is calculated and plotted against microalgae harvesting efficiency in Fig. 5a. The data sets take on a similar shape at different current densities. To harvest

98% of *C. vulgaris*, 7.23 mg $L^{-1}$ of Al was consumed from the culture medium. However, the residual Al in the culture medium varied with the current density. The use of higher current density led to higher residual Al. When 22.2, 44.4 and 66.7 A $m^{-2}$ was applied, the residual Al was 1.6, 4.2 and 4.9 mg $L^{-1}$ at the harvesting efficiency of 98% (Fig. 5b).

*3.6 Microalgae culture medium responses*

After microalgae harvesting, there were no significant changes in the medium temperature and pH. When 44.4 A $m^{-2}$ was applied, the temperature and pH kept stable throughout the experiments at 21.8°C and 8.6, respectively (Fig. 6a). However, electro-flocculation did lead to chemical changes in the culture medium. Phosphate decrease and ammonium increase were observed during microalgae harvesting. At the current density of 44.4 A $m^{-2}$, the phosphate decreased from 3.9 to 3.7 mg $L^{-1}$ within the initial 1 min, and quickly decreased to 1.8 mg $L^{-1}$ at 4 min, and then slowly decreased to 0.6 mg $L^{-1}$ at 8 min; while the ammonium gradually increased from 0.34 to 1.22 mg $L^{-1}$ within the 8 min of electrolysis (Fig. 6b).

## 4. Discussion

*4.1 Charge neutralization, bridging and bubble flotation*

Charge neutralization is an essential step in microalgae flocculation, which decreases energy barrier for microalgae aggregation (Hjorth and Jorgensen, 2012). The AEPs were positively charged over a wide pH range below 9.5, which gave them the flocculation potential for negatively charged microalgae cells (Fig. 1b). With the neutralization, the surface charge of microalgae cells was gradually increased, indicating that positive charge plays a key role in microalgae harvesting using electro-flocculation. It is further supported by the fact that microalgae harvesting efficiency as a function of charge loading holds a similar shape at different current densities (Fig. 3b). However, the higher current density could shorten the electrolysis time of microalgae harvesting (Fig. 3a), due to the higher rate of charge loading (Fig. S4 in the SI).

With the operation of charge neutralization mechanism alone, the optimum flocculation often occurs at the point of total charge neutralization (Shi et al., 2016). However, in this study, the zeta potential of microalgae cells was negative at the optimum microalgae harvesting (Fig. 3c), which indicated that the optimum flocculation was already achieved before the cell surface charge was totally neutralized. The operation of a potential "bridging mechanism" may favor microalgae flocculation. During Al electrolysis, the generated $Al^{3+}$ and $OH^-$ react spontaneously to produce various monomeric species such as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(OH)_4^-$, and polymeric species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}(OH)_{34}^{5+}$ (Ghosh et al., 2008). These freshly amorphous AEPs (Fig. S5 in the SI) have the potential to trap small microalgae flocs and bridge them into large ones (Fig. 2a). Then, $H_2$ bubbles generated at the cathode entrap into these microalgae flocs (Fig. S3 in the SI), causing them to float to the water surface where they can be easily collected. This "charge neutralization-bridging-flotation" mechanism is illustrated in Fig. S6 in the SI.

The floc structure has great influence on flocculation kinetics (Shi et al., 2016; Wyatt et al., 2013). The compact flocs are resistant to breakage and beneficial to the solid-liquid separation. Previous studies reported that large flocs are often fragile (Gibbs, 1982); however, in this study, microalgae flocs became not only larger but also denser (Fig. 2a and 3b) as the electrolysis time increased, which may be attributed to the snowballing-mode floc formation. During electro-flocculation, flocculants were in-situ generated and gradually released to form flocs. This layer-by-layer assembly could cause the flocs to become progressively more compact with the continuous addition of flocculants.

### *4.2 Energy and Al consumption*

Economic cost is often a major concern for the practical application of a method, largely driven by energy and material costs (Dassey and Theegala, 2014). In this study, the use of higher current density resulted in quicker microalgae harvesting (Fig. 3a). However, the application of higher current density in an attempt to speed up microalgae harvesting may not be economically efficient, due to the greater energy consumption. To harvest 98% of *C. vulgaris,* the energy consumption at 66.7 A $m^{-2}$ was approximately 1.32 and 3.38 times higher than those at 44.4 and 22.2 A $m^{-2}$, respectively (Fig. 4), which may be attributed to the production of more waste heat at the higher current density (Kobya and Delipinar, 2008). During electro-flocculation, energy consumption per microalgae biomass exhibited a decreasing trend. It was the most energy-efficient at the harvesting efficiency of > 80% (Fig. 4b). Thus, it is not necessary to collect all the biomass in some fields, such as microalgae based wastewater treatment. The remaining cells may benefit microalgae recovery, possibly aiding further treatment of wastewater. Previous studies demonstrated that electrode distribution and water conductivity may have great influence on energy consumption (Chen, 2004). It was concluded that energy consumption could be minimized by using high conductivity electrolytes (i.e. high salt content) with narrow electrode spacing in a low electric current (Emamjomeh and Sivakumar, 2009). Further studies are needed to optimize the energy efficiency of microalgae harvesting.

Charge loading was identified as the key factor of microalgae electro-flocculation (Fig. 3b), leading to the similar Al consumption at different charge densities (Fig. 5a). This is because that the amount of electrochemically dissolved Al is proportional to charge loading according to Faraday’s law (Zuo et al., 2008). However, the residual Al in the culture medium varied with the current density. The use of high charge density led to high residual Al in the culture medium (Fig. 5b), which may cause negative impacts due to its potentially toxic nature (Sinha and Mathur, 2016).

*4.3 Water quality changes*

In the electrolysis process, water pH and temperature are often increased because of the hydroxyl formation and waste heat production (Harif and Adin, 2007). However, due to the low electric power input in this study, there were no significant changes in water pH and temperature in the culture medium after microalgae harvesting (Fig. 6a). Hence, it is possible to balance microalgae harvesting and maintaining acceptable levels of water quality by carefully operating electrolysis, which makes the method sustainable. In the microalgae biofuel industry, medium reuse offers a promising strategy for saving water and nutrients (Castrillo et al., 2013; González-López et al., 2013).

In addition to biofuel production, microalgae are also widely used in wastewater treatment (Sulzacova et al., 2015; Tan et al., 2016). In microalgae based wastewater treatment, phosphorus and nitrogen are assimilated by microalgae as nutrients for growth, and are subsequently removed through biomass harvesting (Tan et al., 2016). Following microalgae collection using electro-flocculation in this study, residual phosphate in the medium was significantly decreased (Fig. 6b), which potentially enhanced nutrient removal in wastewater treatment. Ammonium as a nitrogen source is generally favored by microalgae (Kim et al., 2013); as seen in this study, a post-harvesting increase in ammonium may benefit microalgae recovery for future medium recycling. During electrolysis, nitrate reduction ($NO_3^- + 10\ H^+ + 8\ e^- = NH_4^+ + 3H_2O$) can occur at the cathode, which potentially contributes to the ammonium increase in the culture medium (Peel et al., 2003).

### *4.4 Recommendations for future applications*

Microalgae harvesting is a crucial step but still remains a challenge for biomass engineering or environmental applications. In this study, electro-flocculation proved to be a rapid and efficient way to harvest microalgae. The in-situ generation of flocculants can be easily controlled by an electrical switch, which offers the prospect of applications in continuous systems (Fig. S7 in the SI). Many studies have conducted the life cycle assessment (LCA) of biofuel production from microalgae and confirmed the potential of microalgae as an energy source (Lardon et al., 2009; Yang et al., 2011). In this study, the cost of microalgae harvesting using Al electrolysis was estimated to be 1.47 × $10^{-3}$ US\$ $g^{-1}$ biomass, most of which was born on the material use (Table S1). Further studies are needed to optimize operation conditions to increase the electrode utilization efficiency.

Despite the fact that Al electrolysis is an effective microalgae harvesting technique for most engineering applications, it is not recommended for cases where the biomass is to be used for food or animal feed. The excess Al could enter the food chain and induce bond and brain diseases in human beings (Douichene et al., 2016). The synergy of edible macromolecular flocculants (flocculation) and insert electrodes (flotation) may provide a promising strategy to harvesting microalgae for food use.

## 5. Conclusions

The use of Al electrolysis allowed feasible microalgae harvesting (~ 98%) with the operation of charge neutralization, bridging and bubble flotation mechanisms. Microalgae floc formation followed a snowballing mode, with the flocs becoming larger and more compact through time. When the higher current density of 66.7 A $m^{-2}$ was applied, microalgae harvesting was achieved in a shorter time of 4 min, but at the cost of higher energy consumption of 3.35 × $10^{-4}$ kWh $L^{-1}$ and more residual Al of 4.9 mg $L^{-1}$. Using electro-flocculation, the phosphate removal can be a side benefit for microalgae based wastewater treatment.

## Acknowledgments

This work is supported by the National Nature Science Foundation of China (No. 91547206, 51425902) and Jiangsu Water Resources Department (No. 2015005). We thank Bryce Van Dam for proofreading the English.

## References


1. Arbib, Z., Ruiz, J., Alvarez-Diaz, P., Garrido-Perez, C., Perales, J.A., 2014. Capability of different microalgae species for phytoremediation processes: Wastewater tertiary treatment, $CO_2$ bio-fixation and low cost biofuels production. Water Res. 49, 465-474.

2. Asselin, M., Drogui, P., Brar, S.K., Benmoussa, H., Blais, J.F., 2008. Organics removal in oily bilgewater by electrocoagulation process. J. Hazard. Mater. 151(2-3), 446-455.

3. Baeyens, J., Kang, Q., Appels, L., Dewil, R., Lv, Y., Tan, T., 2015. Challenges and opportunities in improving the production of bioethanol. Prog. Energy Combust. Sci. 47, 60-88.

4. Castrillo, M., Lucas-Salas, L.M., Rodríguez-Gil, C., Martínez, D., 2013. High pH-induced flocculation-sedimentation and effect of supernatant reuse on growth rate and lipid productivity of *Scenedesmus obliquus* and *Chlorella vulgaris*. Bioresource Technol. 128, 324-329.

5. Cerff, M., Morweiser, M., Dillschneider, R., Michel, A., Menzel, K., Posten, C., 2012. Harvesting fresh water and marine algae by magnetic separation: Screening of separation parameters and high gradient magnetic filtration. Bioresource Technol. 118, 289-295.

6. Chen, C.L., Huang, C.C., Ho, K.C., Hsiao, P.X., Wu, M.S., Chang, J.S., 2015. Biodiesel production from wet microalgae feedstock using sequential wet

extraction/transesterification and direct transesterification processes. Bioresource Technol. 194, 179-186.

7. Chen, G.H., 2004. Electrochemical technologies in wastewater treatment. Sep. Purif. Technol. 38(1), 11-41.

8. Chisti, Y., 2007. Biodiesel from microalgae. Biotechnol. Adv. 25(3), 294-306.

9. Dassey, A.J., Theegala, C.S., 2014. Reducing electrocoagulation harvesting costs for practical microalgal biodiesel production. Environ. Technol. 35(6), 691-697.

10. de-Bashan, L.E., Hernandez, J.P., Morey, T., Bashan, Y., 2004. Microalgae growth-promoting bacteria as "helpers" for microalgae: a novel approach for removing ammonium and phosphorus from municipal wastewater. Water Res. 38(2), 466-474.

11. Depraetere, O., Pierre, G., Deschoenmaeker, F., Badri, H., Foubert, I., Leys, N., Markou, G., Wattiez, R., Michaud, P., Muylaert, K., 2015. Harvesting carbohydrate-rich Arthrospira platensis by spontaneous settling. Bioresource Technol. 180, 16-21.

12. Douichene, S., Hammadi, K., Djebli, N., 2016. Neuroprotective effect of hypericum thymopsis against chronic exposure to aluminum chloride and Alzheimer’s disease. J. Pharm. Pharm. 3(3), 20-28.

13. Emamjomeh, M.M., Sivakumar, M., 2009. Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes. J. Environ. Manage. 90(5), 1663-1679.

14. Ghosh, D., Solanki, H., Purkait, M.K., 2008. Removal of Fe(II) from tap water by

electrocoagulation technique. J. Hazard. Mater. 155(1-2), 135-143.

15. Gibbs, R.J., 1982. Floc Stability during Coulter-Counter Size Analysis. J. Sediment. Res. 52(2), 657-660.

16. González-López, C.V., Cerón-García, M.C., Fernández-Sevilla, J.M., González-Céspedes, A.M., Camacho-Rodríguez, J., Molina-Grima, E., 2013. Medium recycling for *Nannochloropsis gaditana* cultures for aquaculture. Bioresource Technol. 129, 430-438.

17. Grima, E.M., Belarbi, E.H., Fernandez, F.G.A., Medina, A.R., Chisti, Y., 2003. Recovery of microalgal biomass and metabolites: process options and economics. Biotechnol. Adv. 20(7-8), 491-515.

18. Hanay, O., Hasar, H., 2011. Effect of anions on removing $Cu^{2+}$, $Mn^{2+}$ and $Zn^{2+}$ in electrocoagulation process using aluminum electrodes. J. Hazard. Mater. 189(1-2), 572-576.

19. Harif, T., Adin, A., 2007. Characteristics of aggregates formed by electroflocculation of a colloidal suspension. Water Res. 41(13), 2951-2961.

20. Hjorth, M., Jorgensen, B.U., 2012. Polymer flocculation mechanism in animal slurry established by charge neutralization. Water Res. 46(4), 1045-1051.

21. Hu, C.Y., Lo, S.L., Kuan, W.H., Lee, Y.D., 2005. Removal of fluoride from semiconductor wastewater by electrocoagulation-flotation. Water Res. 39(5), 895-901.

22. Kang, D.H., Lee, H.Y., Han, J.G., Park, H.S., Lee, H.S., Kang, R.S., 2010. Liquefied extract of marine algae for producing bio-ethanol under high pressure and

method for producing the same. United States Patent. 7763724.

23. Kim, K., Shin, H., Moon, M., Ryu, B.G., Han, J.I., Yang, J.W., Chang, Y.K., 2015. Evaluation of various harvesting methods for high-density microalgae, *Aurantiochytrium* sp KRS101. Bioresource Technol. 198, 828-835.

24. Kim, S., Lee, Y., Hwang, S.J., 2013. Removal of nitrogen and phosphorus by *Chlorella sorokiniana* cultured heterotrophically in ammonia and nitrate. Int. Biodeter. Biodegr. 85, 511-516.

25. Kobya, M., Delipinar, S., 2008. Treatment of the baker's yeast wastewater by electrocoagulation. J. Hazard. Mater.154(1-3), 1133-1140.

26. Lardon, L., Helias, A., Sialve, B., Steyer, J.P., Bernard O., 2009. Life-cycle assessment of biodiesel production from microalgae. Environ. Sci. Technol. 43(17), 6475-6481.

27. Mehrabadi, A., Craggs, R., Farid, M.M., 2016. Biodiesel production potential of wastewater treatment high rate algal pond biomass. Bioresource Technol. 221, 222-233.

28. Ministry of Environmental Protection of China, 2002. The Monitoring Analysis Method of Water and Waste Water. China Environmental Science Press, Beijing.

29. Mollah, M.Y.A., Gomes, J.A.G., Das, K.K., Cocke, D.L., 2010. Electrochemical treatment of Orange II dye solution-Use of aluminum sacrificial electrodes and floc characterization. J. Hazard. Mater. 174(1-3), 851-858.

30. Mores, R., Treichel, H., Zakrzevski, C.A., Kunz, A., Steffens, J., Dallago, R.M.,

2016. Remove of phosphorous and turbidity of swine wastewater using electrocoagulation under continuous flow. Sep. Purif. Technol. 171, 112-117.

31. Nurra, C., Torras, C., Clavero, E., Rios, S., Rey, M., Lorente, E., Farriol, X., Salvado, J., 2014. Biorefinery concept in a microalgae pilot plant. Culturing, dynamic filtration and steam explosion fractionation. Bioresource Technol. 163, 136-142.

32. Pan, G., Chen, J., Anderson, D.M., 2011. Modified local sands for the mitigation of harmful algal blooms. Harmful Algae, 10(4), 381-387.

33. Park, J.B.K., Craggs, R.J., 2010. Wastewater treatment and algal production in high rate algal ponds with carbon dioxide addition. Water Sci. Technol. 61(3), 633-639.

34. Peel, J.W., Reddy, K.J., Sullivan, B.P., Bowen, J.M., 2003 Electrocatalytic reduction of nitrate in water. Water Res. 37(10), 2512-2519

35. Reyes, J.F., Labra, C., 2016. Biomass harvesting and concentration of microalgae *scenedesmus sp* cultivated in a pilot phobioreactor. Biomass Bioenerg. 87, 78-83.

36. Shi, W.Q., Tan, W.Q., Wang, L.J., Pan, G., 2016. Removal of *Microcystis aeruginosa* using cationic starch modified soils. Water Res. 97, 19-25.

37. Shi, W.Q., Bi, L., Pan, G., 2016. Effect of algal flocculation on dissolved organic matters using cationic starch modified soils. J. Environ. Sci. 45, 177-184.

38. Sinha, R., Mathur, S., 2016. Use of activated silica sol as a coagulant aid to remove aluminium from water defluoridated by electrocoagulation. Desalin. Water Treat. 57(36), 16790-16799.

39. Sulzacova, K., Trtilek, M., Rataj, T., 2015. Phosphorus removal using a microalgal

biofilm in a new biofilm photobioreactor for tertiary wastewater treatment. Water Res. 71, 55-63.

40. Tan, F., Wang, Z., Zhouyang, S.Y., Li, H., Xie, Y.P., Wang, Y.P., Zheng, Y.M., Li, Q.B., 2016. Nitrogen and phosphorus removal coupled with carbohydrate production by five microalgae cultures cultivated in biogas slurry. Bioresource Technol. 221, 385-393.

41. Tripathy, T., De B.R., 2006. Flocculation: A new way to treat the waste water. J. Physical Sci. 10, 93-27.

42. Vasudevan, S., Sozhan, G., Ravichandran, S., Jayaraj, J., Lakshmi, J., Sheela, S.M., 2008. Studies on the removal of phosphate from drinking water by electrocoagulation process. Ind. Eng. Chem. Res. 47(6), 2018-2023.

43. Wyatt, N.B., O'Hern, T.J., Shelden, B., Hughes, L.G., Mondy, L.A., 2013. Size and structure of *Chlorella zofingiensis*/FeCl(3) flocs in a shear flow. Biotechnol. Bioeng. 110(12), 3156-63.

44. Xiong, Q., Pang, Q., Pan, X.W., Chika, A.O., Wang, L.Q., Shi, J., Jia, L.S., Chen, C.P., Gao, Y.H., 2015. Facile sand enhanced electro-flocculation for cost-efficient harvesting of *Dunaliella salina*. Bioresource Technol. 187, 326-330.

45. Yang, J., Xu, M., Zhang, X.Z., Hu, Q., Sommerfeld, M., Chen, Y.S., 2011. Life-cycle analysis on biodiesel production from microalgae: water footprint and nutrients balance. Bioresource Technol.102, 159-165.

46. Zaied, M., Bellakhal, N., 2009. Electrocoagulation treatment of black liquor from

paper industry. J. Hazard. Mater. 163(2-3), 995-1000.

47. Zuo, Q.H., Chen, X.M., Li, W., Chen, G.H., 2008. Combined electrocoagulation and electroflotation for removal of fluoride from drinking water. J. Hazard. Mater. 159(2-3), 452-457.

## Figure Captions

**Fig.1.** The surface charge properties of AEP. (a) Effect of electrolysis time; (b) Effect of pH. Error bars indicate standard deviations.

**Fig. 2.** The microalgae floc formation during electro-flocculation. (a) The floc size distribution at different electrolysis time; (b) The floc fractal dimension at different electrolysis time. The current density was set to 44.4 A $m^{-2}$. Error bars indicate standard deviations.

**Fig. 3.** The microalgae harvesting efficiency (a), charge loading (b) and cell surface charge (c) at different current densities. Error bars indicate standard deviations.

**Fig. 4.** The energy consumption during microalgae harvesting using electro-flocculation. (a) Energy consumption per liter; (b) Energy consumption per gram microalgae biomass. Error bars indicate standard deviations.

**Fig. 5.** The Al consumption (a) and residual Al (b) at different current densities. Error bars indicate standard deviations.

**Fig. 6.** The responses of microalgae culture medium to electro-flocculation using Al electrodes. (a) Temperature and pH, (b) Phosphate and ammonium. The current density was set to 44.4 A $m^{-2}$. Error bars indicate standard deviations.

**Fig.1**

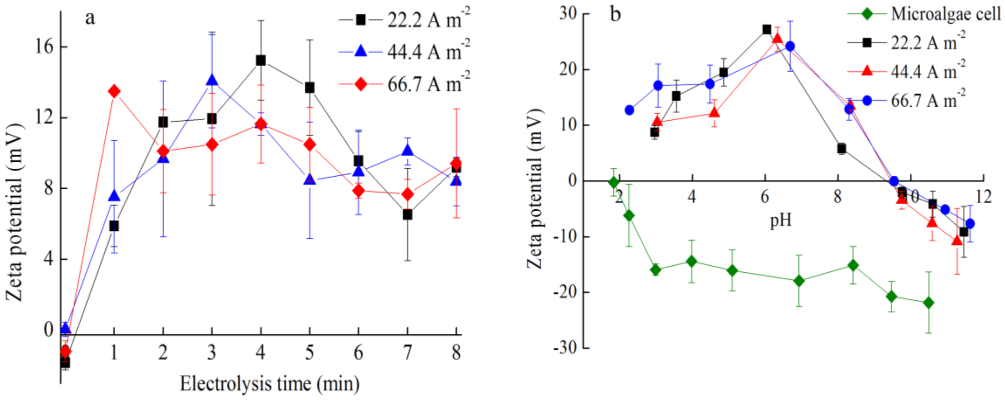

a
22.2 A m-2
44.4 A m-2
66.7 A m-2
Zeta potential (m V)
Electrolysis time (min)
b
Microalgae cell
22.2 A m-2
44.4 A m-2
66.7 A m-2
Zeta potential (m V)
pH

**Fig. 2**

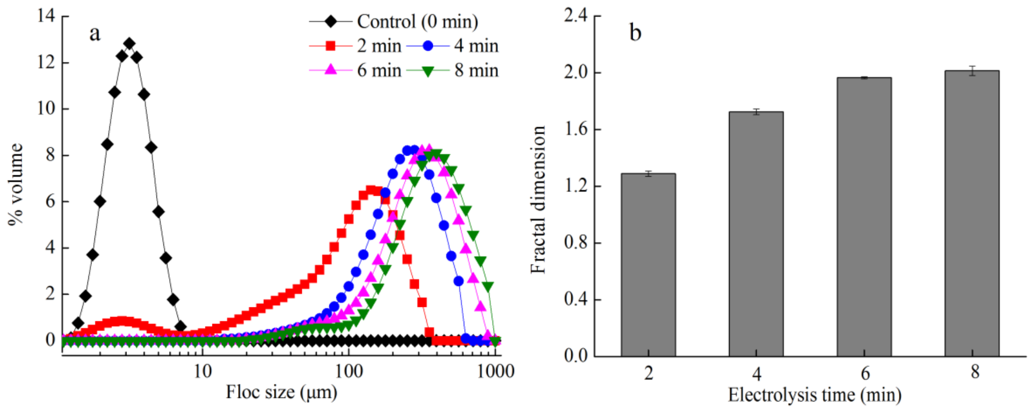
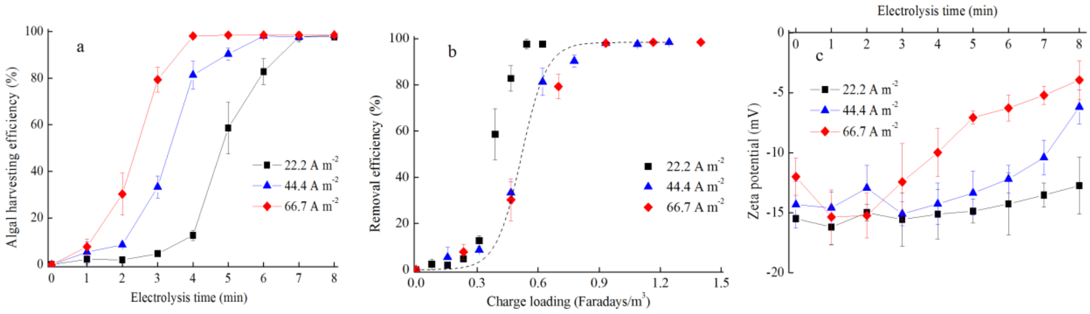
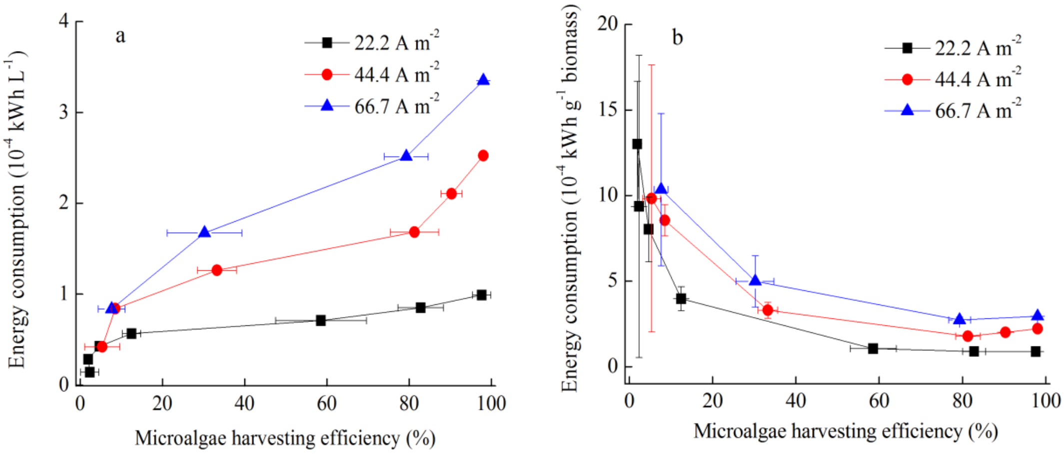

a
Control (0 min)
2 min
4 min
6 min
8 min
% volume
Floc size (μm)
b
Fractal dimension
Electrolysis time (min)

**Fig. 3**



a
Algal harvesting efficiency (%)
Electrolysis time (min)
22.2 A m-2
44.4 A m-2
66.7 A m-2
b
Removal efficiency (%)
Charge loading (Faradays/m3)
22.2 A m-2
44.4 A m-2
66.7 A m-2
c
Electrolysis time (min)
Zeta potential (mV)
22.2 A m-2
44.4 A m-2
66.7 A m-2

**Fig. 4**



a
22.2 A m-2
44.4 A m-2
66.7 A m-2
Energy consumption (10-4 kWh L-1)
Microalgae harvesting efficiency (%)
b
22.2 A m-2
44.4 A m-2
66.7 A m-2
Energy consumption (10-4 kWh g-1 biomass)
Microalgae harvesting efficiency (%)

**Fig. 5**

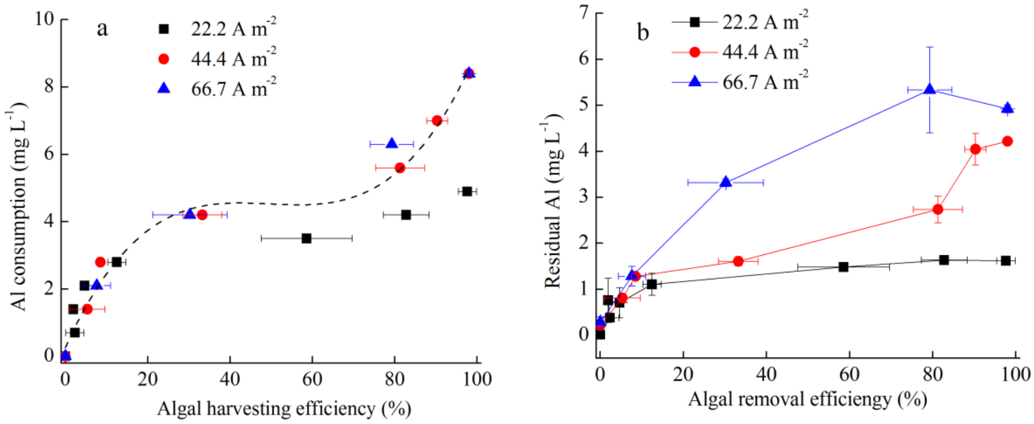
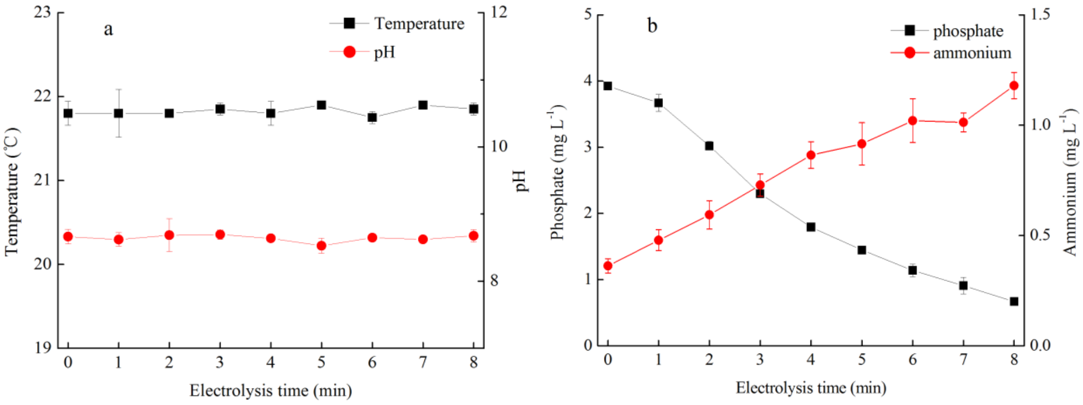

a
22.2 A m-2
44.4 A m-2
66.7 A m-2
Al consumption (mg L-1)
Algal harvesting efficiency (%)
b
Residual Al (mg L-1)
Algal removal efficiengy (%)

**Fig. 6**


a
Temperature
pH
Temperature (℃)
pH
Electrolysis time (min)
b
phosphate
ammonium
Phosphate (mg L$^{-1}$)
Ammonium (mg L$^{-1}$)
Electrolysis time (min)