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# Combination of electrolysis and microalgae cultivation for beneficial reuse of fertilizer wastewater from poultry manure anaerobic digestion effluent

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**ABSTRACT**

Poultry manure anaerobic digestion effluent (PMADE) contained a high content of ammonia nitrogen ($NH_4^+$–N), which should be treated properly before discharge. However, the mechanism of electrolysis in treating high $NH_4^+$–N (over 1,500 mg $L^{-1}$) wastewater has never been studied. In this study, fertilizer wastewater from PMADE with high content of $NH_4^+$–N (over 3,000 mg $L^{-1}$) and low carbon/nitrogen (C/N) ratio was treated via electrolysis and microalgae. Results showed the highest removal of $NH_4^+$–N, total organic carbon (TOC) and inorganic carbon (IC) in electrolysis were 47%, 76%, and 93%, respectively. Quadratic functions are suitable to simulate $NH_4^+$–N removal of FW (coefficient is over 0.95). The removal efficiency of $NH_4^+$–N was 10%–65% during microalgae cultivation. The removal of $NH_4^+$–N, total phosphorus (TP), IC, and TOC in fertilizer wastewater by the combination of electrolysis and microalgae cultivation achieved 96%, 63%, 95%, and 52%, respectively. *Chlorella* sp. used 3.11% carbon, 15.0% nitrogen, and 13.5% phosphorus in the FW as substrates. This study provided an alternative approach to treat and reuse high-ammonia containing wastewater.

*Keywords:* Electrochemical oxidation; Fertilizer wastewater; Microalgae; Ammonia nitrogen

## 1. Introduction

The effluent from anaerobic digestion contains abundant nitrogen, carbon and phosphorous-containing compounds; therefore, it can cause eutrophication if not treated properly before disposal [1]. Owing to high $NH_4^+$–N concentration, poultry manure anaerobic digestion effluent (PMADE) could be used as a kind of nitrogen-enriched liquid fertilizer for crops cultivation [2]. According to China's new water policy known as "The Water Ten Plan" [3], if the wastewater from the animal breeding industry is not to be used as a fertilizer, it needs to be treated before discharge. However, due to the

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short period of crop harvesting/sowing and the shortage of farming land near the anaerobic digestion plant, effluent from anaerobic digestion plant needs to be transported in order to be treated in China [4]. Dewatering of PMADE could save 50% of the energy input transportation and increase the transportation efficiency by up to 34% [5]. Ultrafiltration (UF) membrane has been used to concentrate PMADE to different farmlands and used it as a liquid fertilizer. The permeate of PMADE is regarded as fertilizer wastewater and needs to be further treated prior to discharge into the environment. Due to the high ammonia content and low carbon–nitrogen ratio, the fertilizer wastewater is a challenge to the traditional activated sludge system. Hence, there is an urgent need to develop an effective treatment technology to treat the fertilizer wastewater.

Microalgae cultivation is considered a promising solution for ammonia-containing wastewater treatment. Limited by the ammonia tolerance of microalgae, pretreatment of the wastewater is generally required before being used for microalgae growth. In recent years, the wastewater with a high $NH_4^+$–N content has been pretreated using air stripping [6], struvite precipitation [7], dilution [8], and electrochemical oxidation [9]. Among these methods, electrochemical treatment has proven to be effective to treat high ammonia content wastewater [10,11]. Additionally, the chromaticity of wastewater could be diminished due to the presence of oxidation during electrolysis, contributing to additional light being absorbed by the microalgae [12]. NaCl, common and easy to obtain, added in the electrolysis would accelerate the oxidation process. Lei and Maekawa [9] evaluated electric current, NaCl dosage and initial pH on the oxidization of wastewater with as high as 1,100 mg $L^{-1}$ $NH_4^+$–N, and found out that 1% NaCl dosage was sufficient for ammonia removal. The diluted anaerobic digestion effluent with 500 mg $L^{-1}$ $NH_4^+$–N was treated by electrolysis and achieved about 100% $NH_4^+$–N removal [10]. Even though electrochemical treatment was highly efficient in previous study, the mechanism of electrolysis treating high $NH_4^+$–N (over 1,500 mg $L^{-1}$) wastewater has not been studied. The effect of NaCl addition in the electrolysis process on microalgae cultivation has also not been explored. In this study, fertilizer wastewater from PMADE with a concentration around 3,000 mg $L^{-1}$ $NH_4^+$–N was used to study the mechanism of nutrients removal during electrolysis and the effect of NaCl addition on different species of microalgae cultivation. After electrolysis pretreatment, fertilizer wastewater with different $NH_4^+$–N concentrations was used to cultivate high-growth-rate low-$NH_4^+$–N-tolerance *Spirulina platensis* and low-growth-rate high-$NH_4^+$–N-tolerance *Chlorella* sp., respectively. The objective of this work is to reveal the reaction mechanics and kinetics of high-$NH_4^+$–N removal by electrochemical oxidation and to explore the optimal method to combine wastewater treatment with microalgae cultivation.

## 2. Materials and methods

### 2.1. Tested wastewater

Fertilizer wastewater was obtained from bio-fertilizer production process (Minhe Biotechnology Limited Company, Shandong Province, China), and the production detail of the wastewater could be found in our previous report [13]. The fertilizer wastewater was hereby referred to as FW, containing a high content of $NH_4^+$–N (3,180 mg $L^{-1}$), a low content of TC (1,268 mg $L^{-1}$ total organic carbon [TOC] and 3,078 mg $L^{-1}$ IC), and a low C/N ratio. The TP content of FW was 193 mg $L^{-1}$. The pH value of FW was in the range of 7.9–8.3.

### 2.2. Microalgae cultivation

*S. platensis* (FACHB-350) and *Chlorella* sp. (FACHB-11) were obtained from the Freshwater Algae Culture Collection at the Institute of Hydrobiology, Chinese Academy of Sciences. Microalgae cultivation was conducted in 250 mL flasks containing 160 mL cultivation medium, which was composed of a 1:1 mix ratio of FW and algal inoculums. The control experiments were conducted using the Zarrouk and BG11 culture medium [14,15], respectively. The microalgae were cultivated at the temperature of 28°C and a daily lighting schedule of 12 h on and off, with a light intensity of 170 μmol photons $m^{-2}$ $s^{-1}$. The pH value of the culture medium for *Chlorella* sp. was adjusted to 7.1 ± 0.1 by 1 mol $L^{-1}$ HCl and 1 mol $L^{-1}$ NaOH every day. However, the pH value of culture medium was not adjusted for *S. platensis*.

### 2.3. Experimental setup

#### 2.3.1. Optimal $NH_4^+$–N concentration for microalgae

Based on our previous research [16], two typical species of microalgae, high-growth-rate low-$NH_4^+$–N-tolerance *S. platensis* and low-growth-rate high-$NH_4^+$–N-tolerance *Chlorella* sp., were chosen to treat FW. To determine the optimal $NH_4^+$–N concentration for microalgae growth, FW was diluted to have $NH_4^+$–N concentrations of 250; 580; 800; 1,000; 1,300 mg $L^{-1}$ to cultivate *Chlorella* sp. and 20, 40, 50, 80, 100 mg $L^{-1}$ to cultivate *S. platensis*, respectively. TP, $NH_4^+$–N, TOC, and dry cell weight (DCW) of the microalgal biomass were tested every 3 d.

#### 2.3.2. Electrode equipment and electrochemical treatment

Batch experiments were conducted in a 1,500 mL beaker with a FW volume of 1,000 mL. The electrode boards were made of Pt/Ti-$IrO_2$ and each of them had a size of 15 cm × 9.6 cm. The total effective electrode area was 96 $cm^2$, and the distance between the two electrodes was 6 cm. The electrodes were connected to a direct current (DC) power supply with a voltage of 15 V. NaCl was chosen as an alternative electrolyte in the experiment, making the initial weight ratio of NaCl to $NH_4^+$–N 4:1, which was selected according to previous experiment [11]. FW1 was referred to as FW without NaCl addition, and FW2 was referred to as FW with 15.2 g $L^{-1}$ NaCl addition. During electrolysis, a 10 mL water sample was taken every 30 min to determine the $NH_4^+$–N concentration of the FW.

### 2.4. Analytic method

TP and $NH_4^+$–N were tested by "Water and Wastewater Analyzing Methods" by the State Environmental Protection Administration of China [17]. The DCW of microalgae was evaluated by 0.45 μm pore size glass fiber filter

according to Lee and Shen [18]. TOC and IC were tested by a Total Organic-Carbon Analyzer TOC-VCPN (Shimadzu Corporation Company, Japan). The pH value and light intensity were monitored using a PSH-3 pH meter (Shanghai Precision and Scientific Inc., China) and a LI-250A light meter (LI-COR Inc., Canada), respectively. All experiments were conducted in duplicate, and the results were presented as average values.

The energy needed during the electrolysis process was calculated by Eq (1):

$$E = V \times C \times T \tag{1}$$

where $E$ is the energy (W h) cost during electrolysis, $V$ is voltage (V) of the DC, $C$ is current (A) of the DC, and $T$ is the electrolysis time (h).

The removal quantity is calculated using Eq. (2):

$$\text{Removal quantity}\left(\text{mg L}^{-1}\right) = C_0 - C_i \tag{2}$$

where $C_i$ and $C_0$ are the final and initial concentration, respectively, of $NH_4^+$, TP, IC, and TOC (mg $L^{-1}$). The removal efficiency is calculated using Eq. (3):

$$\text{Removal efficiency}(\%) = \frac{C_0 - C_i}{C_0} \times 100 \tag{3}$$

## 3. Results and discussion

### 3.1. Optimal $NH_4^+$–N concentration for microalgae growth

Different species of microalgae have different $NH_4^+$–N concentration tolerances. Before the electrolysis experiment, microalgae were tested in diluted FW to figure out the optimal $NH_4^+$–N concentration (Fig. 1). The highest DCW (0.26 g $L^{-1}$) of *S. platensis* was obtained at the FW dilution with an $NH_4^+$–N concentration of 20 mg $L^{-1}$. Since *S. platensis* could tolerate wastewater with an $NH_4^+$–N concentration of 40 mg $L^{-1}$, an $NH_4^+$–N concentration below 40 mg $L^{-1}$ was selected for *S. platensis,* and obtained similar result of optimal $NH_4^+$–N concentration as obtained in the study by Chang et al. [19] for *S. platensis*. The highest DCW of *Chlorella* sp. was obtained at the FW dilution with an $NH_4^+$–N concentration of 250 mg $L^{-1}$, followed by an FW dilution with an $NH_4^+$–N concentration of 580; 800; 1,000; and 1,300 mg $L^{-1}$ (Fig. 1b). It was reported that water containing over 250 mg $L^{-1}$ $NH_4^+$–N exceeded the tolerance level for *Chlorella* sp. [20]. In this study, *Chlorella* sp. could still grow in FW with an $NH_4^+$–N concentration over 250 mg $L^{-1}$, which was quite different from that of *Chlorella vulgaris* in 5% volume ratio diluted wastewater [10]. This might be due to FW production process with a membrane which made FW have a shortage of total solid and toxic compounds. Overall, an appropriate $NH_4^+$–N concentration was 250 mg $L^{-1}$ for *Chlorella* sp.

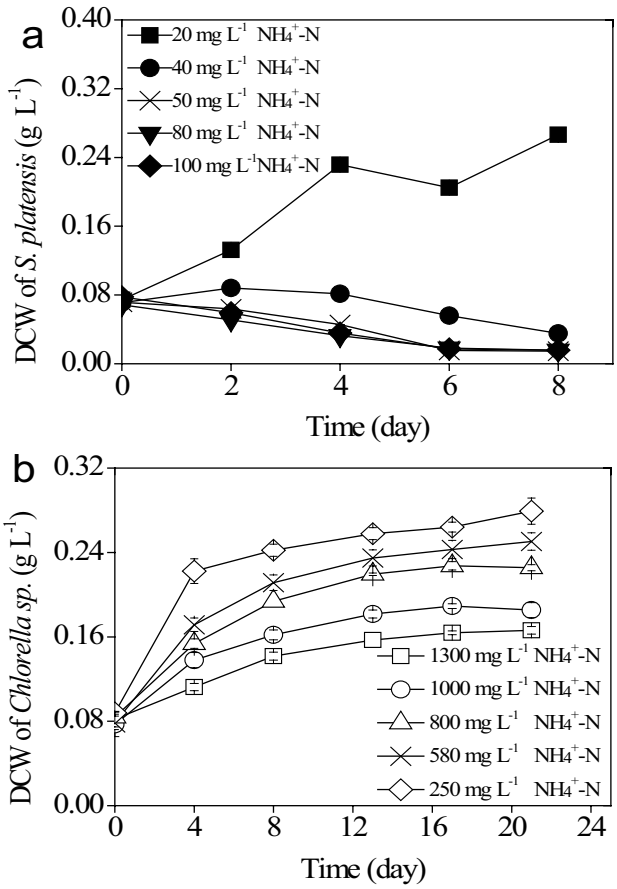


Fig. 1. DCW change of microalgae cultured by FW dilution, (a) *S. platensis*, (b) *Chlorella* sp. The error bar is the standard deviation.

### 3.2. Electrochemical treatment of FW

The initial FW contains 3,180 mg $L^{-1}$ $NH_4^+$–N; 1,268 TOC; 3,078 IC; and 193 TP. After the electrolysis treatment, the water properties of FW are shown in Table 1. Even though the C:$NH_4^+$–N:P ratios of the four kinds of treated FW were lower compared with the C:N:P ratio of Redfield (41.1:7.2:1.0), the concentrations of carbon, nitrogen, and phosphorus appeared to be sufficient for microalgae cultivation. A similar result was previously reported by Farooq et al. [21].

The relationship between the removal of nutrients (TP, $NH_4^+$–N, and TC) by electrolyte dosage was evaluated by adding 0 or 15.2 g $L^{-1}$ NaCl. Based on the study by Lei and Maekawa [9], and Wang et al. [10,11], 15.2 g $L^{-1}$ NaCl was the optimal concentration to improve the electrolysis efficiency, so we selected this concentration to investigate the impact of electrolyte on the microalgae. When the electrolysis process began without NaCl in FW1, bubbles were generated on the surface of the electrodes and these bubbles were bigger than those observed in the research of Ketkar et al. [22]. The results were partly due to TOC and IC turning into carbon dioxide and $NH_4^+$–N turning into nitrogen gas. At the beginning, due to the TOC, IC, and $NH_4^+$–N were electrochemically-oxidized as carbon dioxide and nitrogen gas, the bubbles were generated on the surface of the electrodes and fulfilled the electrolysis reactor. During the first hour, the generation rate of bubbles was faster than that of disappearing rate of bubbles; the longer the electrolysis time, the bigger the shape of the

Table 1
Physical–chemical properties of the electrolysis-treated water

| Treatment | FW1-4 | FW2-3 | FW1-7.5 | FW2-4 |
|---|---|---|---|---|
| Final volume (mL) | 755 | 770 | 630 | 640 |
| TP (mg $L^{-1}$) | 207 | 201 | 241 | 218 |
| $NH_4^+$–N (mg $L^{-1}$) | 528 | 525 | 107 | 91 |
| TOC (mg $L^{-1}$) | 1,863 | 1,374 | 1,723 | 1,399 |
| IC (mg $L^{-1}$) | 959 | 866 | 752 | 731 |
| pH value | 9.15 | 9.12 | 9.85 | 9.48 |
| C:$NH_4^+$–N:P | 13.6:2.6:1.0 | 11.14:2.6:1.0 | 10.3:0.4:1.0 | 9.8:0.4:1.0 |

*Note*: FW1-4 was treated by electrochemical oxidation for 4 h, FW1-7.5 was treated by electrochemical oxidation for 7.5 h, FW2-3 was treated by electrochemical oxidation for 3 h, FW2-4 was treated by electrochemical oxidation for 4 h.

bubbles. After 1.5 h, the presence of bubbles began to decline. When NaCl was added in FW2 during the electrolysis process, the $Cl^-$ concentration of FW2 was higher than that of FW1 with no NaCl addition. More $Cl^-$ existing in the wastewater could accelerate the oxidation reaction and produce more bubbles. Moreover, it took 0.5 and 1.5 h for the biggest bubbles to appear in FW2 and FW1, respectively. Electroflotation was the main mechanism for TOC and IC removal [9]. The formation and size of the bubbles is an evidence for NaCl addition accelerating the electrolysis.

The temperature of the electrolyte solution increased along with the electrolysis process and reached 78°C. The heat generated during the electrolysis could be used for maintaining the temperature for microalgae growth. The electrolysis resulted in a 30% decrease in volume of the FW. This was mainly due to the high temperature vaporizing part of $H_2O$ during electrolysis.

TP of the FW in the reactor had a small decrease after electrolysis which is in agreement with Wang et al. [11]. The decreased TP was mainly due to electro-flotation and electro-coagulation [23]. The decrease of the volume could be the reason for the increase in the TP for both FW1 and FW2. This could be explained by the fact that the TP amount in the electrolysis cell was a constant value, but the decrease of the water volume led to an increase in the TP concentration of per unit water increasing.

When the electrolysis process ended, the pH value of the FW increased to 9.15–9.85, which was higher than the initial pH value. One reason for the pH value increasing was that $H_2O$ was consumed and $OH^-$ was produced by the electrolysis anode. During the electrolysis process, the $H_2O$ was oxidized into $O_2$ and $O_3$ [24]. In this study, the main oxidation reactions are listed in Eq. (4). Another reason for pH value increase might be due to $CO_2$ stripping from the FW which caused a shift of pH to the alkaline side (Eq. (6)).

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$$
(In alkaline solution, main reaction) (4)

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \text{ (In acidic solution)} \quad (5)$$

$$HCO_3^- \rightarrow CO_2 + OH^- \quad (6)$$

Two forms of ammonia, $NH_3$ and $NH_4^+$, established an equilibrium as shown in Eq. (7). The percentage of ammonia existing in its un-ionized form ($NH_3$) had a positive correlation with both pH and temperature [25]. Of these two forms of ammonia, the $NH_3$ was much easier to oxidize [26]. In this study, the pH value was in the range of 9–10, so the ammonia nitrogen mainly existed as $NH_3$ and was oxidized by $OH^-$ and generated $N_2$ (Eq. (8)) [27]. In addition, ammonia can be removed by air stripping when pH is between 9.0 and 11.6.

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (7)$$

$$2NH_3 + 6OH^- \rightarrow N_2 + 6H_2O + 6e^-$$
(In alkaline solution, main reaction) (8)

$$2NH_4^+ + 3HClO + 5OH^- \rightarrow N_2 + 8H_2O + 3Cl^-$$
(In alkaline solution, main reaction) (9)

$$NH_4^+ + 2H_2O + OH^- \rightarrow NO_3^- + 9H^+ + 8e^- \quad (10)$$

$$2Cl^- + H_2O - 2e^- \rightarrow Cl_2 + H_2O \rightarrow ClO^- + Cl^- - e^-$$
(minor reaction) (11)

$$2NH_4^+ + 3HClO \rightarrow N_2 + 3H_2O + 5H^+ + 3Cl^- \text{ (minor reaction)} \quad (12)$$

Approximately 88% of $NH_4^+$–N was removed during the electrolysis process (Fig. 2). The main products of $NH_4^+$–N were nitrogen gas and nitrate (Eqs. (9) and (10)) [28]. Moreover, the solubility of $NH_4^+$–N and $Cl_2$ decreased as the FW temperature increased. The elimination of $NH_4^+$–N could be mainly attributed to the electrochemical oxidation process [29]. The presence of additional NaCl could accelerate $NH_4^+$–N removal. The $Cl^-$ can be oxidized into $ClO^-$ by electrolysis first and then reacted with $NH_4^+$–N (Eqs. (11) and (12)) [30]. Since there were $Cl^-$ ions already existed in FW, NaCl addition did not accelerate the $NH_4^+$–N oxidation reaction at the beginning. After 2.5 h, the additional NaCl dosage had an obvious effect on the $NH_4^+$–N removal (Fig. 2). The removal of $NH_4^+$–N was in the range of 83.5%–97.1% during electrolysis. The linear equation of

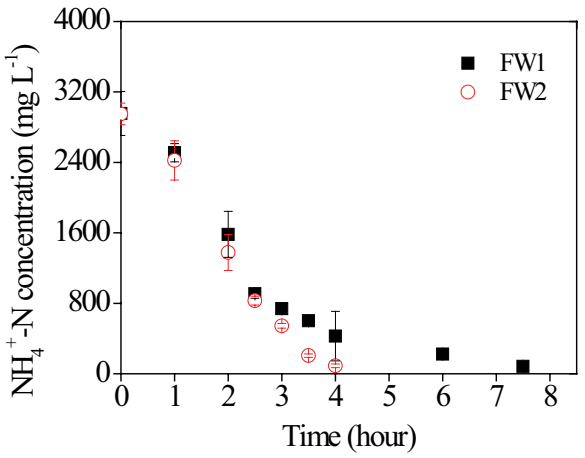


Fig. 2. $NH_4^+$–N removal and simulation of wastewater during electrolysis. The error bar is standard deviation.

$NH_4^+$–N removal during the electrolysis process is simulated in Table 2. During the first 3 h, there was no substantial difference between $NH_4^+$–N concentrations between FW1 and FW2 ($p > 0.05$). It took 7.5 h for the $NH_4^+$–N concentration of FW1 and 3.5 h for FW2 to fall below 100 mg $L^{-1}$. The $NH_4^+$–N removal of FW1 (0–3 h) and FW2 (0–4 h) fitted a first-order kinetic well with insufficient $Cl^-$, which agreed with the findings of Wang et al. [11]. For FW1, $NH_4^+$–N removal decreased between an electrolysis time of 3–7.5 h, which might have been caused by an insufficient $Cl^-$ concentration. When it comes to electrolysis of FW1 (3–7 h), the $NH_4^+$–N removal fitted a second-order kinetics better than that of a first-order kinetics. For both FW1 (0–7.5 h) and FW2 (0–4 h), the $NH_4^+$–N removal fitted a second-order kinetic. As shown in Eqs. (11) and (12), the $Cl^-$ could be oxidized to produce HClO, and then the HClO could oxidize $NH_4^+$–N and produce $N_2$.

Through literature review [11], the $NH_4^+$–N removal followed the zero-order kinetics with sufficient $Cl^-$ and the first-order kinetics with insufficient $Cl^-$. NaCl dosage addition could affect the simulation of $NH_4^+$–N removal. Hence, both linear function and quadratic function were used to simulate the $NH_4^+$–N concentration change of FW1 and FW2 during the electrolysis. The detail of the equations is listed in Table 2.

Logarithm function and exponential function have also been used to simulate the $NH_4^+$–N change during the electrolysis. However, the logarithm function could not meet the requirement for the electrolysis period being 0 hour at the beginning. For the FW1 and FW2, the logarithm function would work unless the $x \neq 0$. Since the electrolysis periods of FW1 and FW2 were 7.5 and 4 h, respectively. It is estimated that the $NH_4^+$–N concentration is 0 mg $L^{-1}$ when the electrolysis period was over 8–10 h. Thus, the exponential function is also not suitable for the simulation of $NH_4^+$–N change.

As mentioned above, the linear and quadratic functions are much more suitable in this case.

The IC concentration of FW decreased dramatically during electrolysis and the removal efficiency of IC was in the range of 69%–76%. The removal of IC was mainly because of $CO_2$ stripping from the FW (Eq. (13)). By contrast, the change of the TOC content was small, and the removal efficiency of TOC was 28%–47%. The removal of TOC was caused by the low $Cl_2$ in the free chlorine in the pH range of 8.08–9.48 (Eqs. (14)–(16)) [31]. The results were comparable with that obtained by Lei and Maekawa [9].

$$CO_3^{2-} + 2H^+ \rightarrow HCO_3^- + H^+ \rightarrow CO_2 + H_2O \text{ (IC removal)} \quad (13)$$

$$(CHO) + MO_X[OH] \rightarrow MO_X + CO_2 + H^+ + e^- \text{ (TOC removal)} \quad (14)$$

$$(CHO) + O_2 \rightarrow CO_2 + H_2O \text{ (TOC removal)} \quad (15)$$

$$(CHO) + HOCl \rightarrow Cl^- + \text{product (TOC removal)} \quad (16)$$

### 3.3. Pretreated water for microalgae cultivation

The biomass growth and the nutrients concentration change in the culture media for *S. platensis* is shown in Fig. 3. During cultivation, the pH and DCW of the Zarrouk culture medium increased from 10.0 to 10.8 and 0.5 to 1.5 g $L^{-1}$, respectively. The pH value of FW2-4-S increased slightly, and the DCW increased from 0.5 to 0.8 g $L^{-1}$ (Fig. 3). For *S. platensis*, the DCW of FW2-4-S was significantly higher than that of FW1-7.5-S ($p < 0.01$). This result might be caused by the addition of NaCl, which not only enhances oxidation reaction to degrade the materials in the effluent but also provides a more suitable osmotic pressure for *S. platensis* to grow. Therefore, proper salinity for a suitable osmotic pressure (0.5–2.0 g $L^{-1}$ salt) is needed to cultivate *S. platensis* [32].

$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_2 + H_2O \rightarrow (CH_2O) + O_2 \quad (17)$$

Table 2
Correlation equations and coefficients of $NH_4^+$–N removal with different reaction times

| Item | FW1 | | | FW2 |
|---|---|---|---|---|
| Time (h) | 0–3 | 3–7.5 | 0–7.5 | 0–4 |
| First order equation | $y = -812x + 3{,}106$ | $y = -155x + 1{,}183$ | $y = -384x + 2{,}375$ | $y = -778x + 2{,}981$ |
| $R^2$ of first order equation | 0.9576 | 0.9228 | 0.7813 | 0.9788 |
| Second order equation | $y = 56x^2 - 917x + 3{,}094$ | $y = 27x^2 - 419x + 1{,}732$ | $y = 79x^2 - 984x + 3{,}106$ | $y = 42x^2 - 947x + 3{,}074$ |
| $R^2$ second order equation | 0.9682 | 0.9802 | 0.9707 | 0.9829 |

$y$, the concentration of $NH_4^+$–N (mg $L^{-1}$); $x$, the time (h).

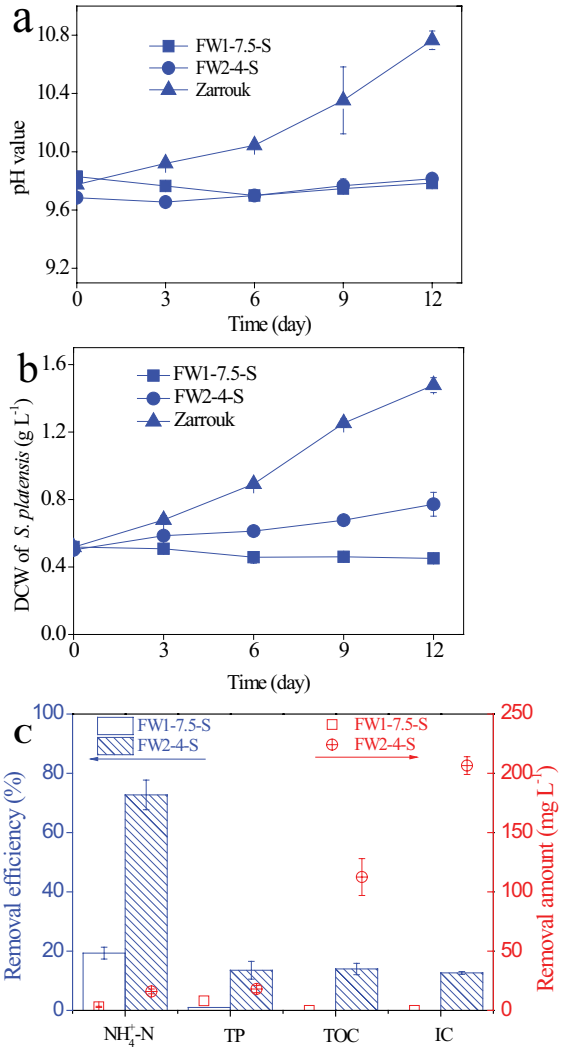


Fig. 3. Characteristics of electrolysis pretreated wastewater for *S. platensis* cultivation, (a) pH value, (b) biomass growth, (c) nutrients removal.
*Note*: FW1-7.5-S, *S. platensis* was cultivated in FW1-7.5; FW2-4-S, *S. platensis* was cultivated in FW2-4. The error bar is the standard deviation.

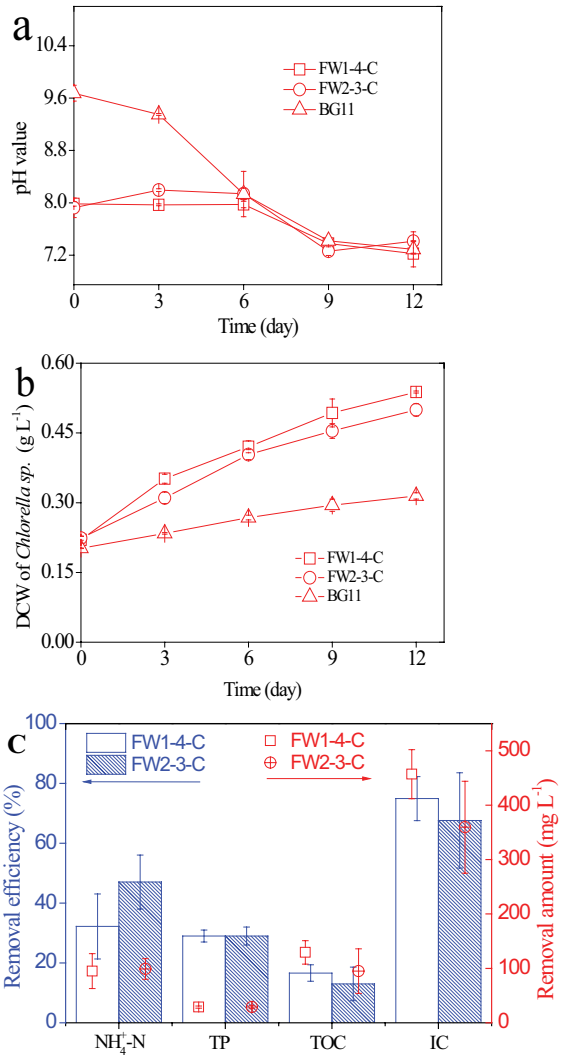


Fig. 4. Characteristics of electrolysis pretreated wastewater for *Chlorella* sp. cultivation, (a) pH value, (b) biomass growth, (c) nutrients removal.
*Note*: FW1-4-C, *Chlorella* sp. was cultivated in FW1-4; FW2-3-C, *Chlorella* sp. was cultivated in FW2-3. The error bar is the standard deviation.

With the growth of *S. platensis*, IC was consumed, which might follow the trend expressed by Eq. (17) [33]. As $CO_3^{2-}$ and $HCO_3^-$ were consumed, the concentration of $H^+$ decreased and the pH value of the water increased, which led to an increase of the DCW. The IC and TOC in FW2-4-S decreased during the microalgae cultivation, this was due to the *S. platensis* in FW2-4-S growing mixotrophically. The removal efficiencies of $NH_4^+$–N and TP for FW2-4-S were 50% and 10% higher than that of FW1-7.5-S. The concentrations of IC, TOC and TP in FW1-7.5-S only changed slightly, which corresponded to the steady state of the DCW for *S. platensis*. Therefore, FW treated by electrolysis with NaCl was more suitable for the growth of *S. platensis* than growth without the addition of NaCl.

The biomass growth and pH value change in the culture media for *Chlorella* sp. is shown in Fig. 4. With the addition of 1 mol $L^{-1}$ HCl, the BG11 culture medium was easier than FW2-3-C and FW1-4-C to adjust to a neutral state. While $NH_3$ existed in FW2-3-C and FW1-4-C, ammonium chloride was formed when $H^+$ was added. The DCWs of FW2-3-C and FW1-4-C increased throughout the entirety of the experimental period. For *Chlorella* sp., there was no difference between the DCWs of FW1-4 and FW2-3 ($p > 0.05$). The growth rates of FW2-3-C and FW1-4-C were 0.023 and 0.021 g $L^{-1}$ $d^{-1}$, respectively, which were higher than that of BG11 with a growth rate of 0.012 g $L^{-1}$ $d^{-1}$. The removal efficiency of $NH_4^+$–N of FW2-3-C was 15% higher than that of FW1-4-C. There was no difference between the removal amount of TP and $NH_4^+$–N between FW2-3-C and FW1-4-C ($p > 0.05$). Both the DCWs of *Chlorella* sp. from FW with electrolysis were higher than that of the BG11 culture medium and FW dilution. Electrolysis pretreatment converted the FW into a more suitable culture

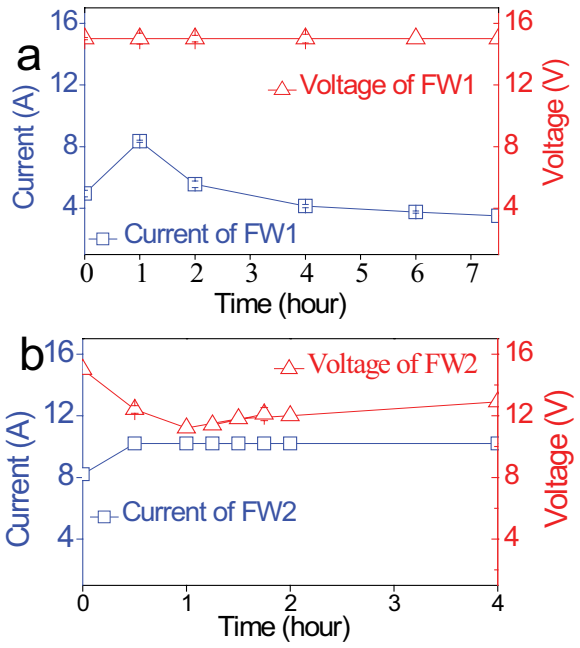


Fig. 5. Current and voltage change of DC power supply during electrolysis treatment. (a) Current and voltage of FW1, (b) current and voltage of FW2.

medium for the growth of *Chlorella* sp. Based on the results above, NaCl addition during electrolysis not only shortened the duration period but also improved the microalgae production.

For both *Chlorella* sp. and *S. platensis*, the DCWs of microalgae from diluted FW and electrolysis-pretreated FW showed a significant difference ($p < 0.01$). In this case, the DCW of *Chlorella* sp. is 0.15 g $L^{-1}$ $d^{-1}$ higher than that of *S. platensis*. Compared with the culture medium (BG11 and Zarrouk), the electrolysis-pretreated FW was superior for the growth of *Chlorella* sp., while it was not suitable for *S. platensis*. Compared with no electrolyte addition, NaCl addition during electrolysis for FW could enhance microalgae production for both *Chlorella* sp. and *S. platensis*. This is due to the addition of NaCl increased the conductivity of the solution and supplied a more suitable osmotic pressure for the cells of *Chlorella* sp. and *S. platensis*. Since salt is one of the major problems in water treatment, brackish water, seawater or salinity wastewater could be used as the alternative option instead of salt in the aim of wastewater treatment and nutrient recovery.

### 3.4. Energy consumption during the electrolysis

Energy consumption is the main drawback of electrolysis. Based on Eq. (1) and Fig. 5, for a certain period, the energy needed to conduct electrolysis was calculated based on Eqs. (18) and (19):

$$E \approx 60 + 60 \times T \quad (18)$$

$$E_2 \approx 120 \times T \quad (19)$$

*Note*: $E$ is the energy (W h) cost for electrolysis of FW without of NaCl, $E_2$ is the energy for electrolysis of FW with of NaCl, $T$ is the electrolysis time (h).

When the electrolysis time was 1 h, the electricity consumption was 120 Wh regardless of NaCl addition. It would take electrolysis over an hour when treating wastewater with high $NH_4^+$–N concentration (over 1,000 mg $L^{-1}$). Based on Fig. 2, there was no difference between $NH_4^+$–N removal between FW1 and FW2 in the first 3 h during electrolysis ($p > 0.05$). After 3 h, addition of NaCl could have an obvious influence on electrolysis and accelerate the efficiency of $NH_4^+$–N removal. The process of electrolysis treatment cost around 500 and 330 Wh electricity for *S. platensis* and *Chlorella* sp., respectively. So, *Chlorella* sp. was a better option for being used in electrolysis-treated wastewater comparing with *S. platensis*. Electrolysis is an energy consuming process, which would increase the cost for wastewater treatment. Thus, if solar panels, wind energy, or cogeneration of heat and power could be used for the system, electrolysis would be more promising.

### 3.5. Evaluation of whole system

Results of this study are compared with literature in Table 3. The removal of $NH_4^+$–N, TP, IC, and TOC in fertilizer wastewater by the combination of electrolysis and microalgae cultivation achieved 96%, 63%, 95%, and 52%, respectively.

Single method including membrane and microalgae was used to treat animal wastewater. Microalgae have the potential to recover the TOC (or COD) and IC due to microalgae maintaining mixotrophic growth in wastewater. Unless the $NH_4^+$–N of the wastewater was suitable for microalgae growth, dilution was required before being used for microalgae cultivation. The working periods of biological method for most cases are days or weeks. Air stripping, struvite precipitation, and electrolysis belong to popular physical and chemical methods to remove $NH_4^+$–N from wastewater. They are very efficient, and the working periods are customarily few hours. Electrolysis and air stripping have higher removal (over 90%) for wastewater with a high $NH_4^+$–N content. However, the air stripping and electrolysis converted $NH_4^+$–N into $N_2$ or $NH_3$, which caused nutrients loss. For further utilization of the nutrients, microalgae always combined the physical and chemical methods to recover the nutrients in the wastewater. A complex technologic combination is always chosen to treat wastewater with over 1,000 mg $L^{-1}$ $NH_4^+$–N. Thus, the combination of microalgae cultivation and electrolysis has the potential to recover nutrients rather than remove nutrients during wastewater treatment. Compared with dilution experiment in section 3.1, the electrolysis saved 11 and 80 L fresh water for utilizing 1-L wastewater to cultivate *Chlorella* sp. and *S. platensis*, respectively. According to the chemical characteristics of *Chlorella* sp. in our previous study [34], *Chlorella* sp. utilized 3.11% carbon, 15.03% nitrogen, and 13.48% phosphorus in the FW as substrates in this study.

## 4. Conclusion

Electrolysis coupled with microalgae cultivation to treat fertilizer wastewater was an effective and water-saving

Table 3
Comparison of different methods to treat wastewater

| Method category | Wastewater and treatment | Initial concentration (mg $L^{-1}$) | | | | Nutrient removal (%) | | | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $NH_4^+$–N | TP | IC | TOC(COD) | $NH_4^+$–N | TP | IC | TOC(COD) | |
| Physical | Anaerobically digested swine and UF membrane | 1,413 | 203 | – | (9,433) | – | – | – | (90) | [35] |
| Biological | Fertilizer wastewater and dilution, microalgae | 2,990 | 179 | 3,039 | 1,563 | 17 | 19 | 58 | 55 | [13] |
| Biological | Wastewater from membrane bioreactor and Microalgae ($CO_2$ supply) | 80 | 11 | – | – | 67 | 97 | – | – | [33] |
| Biological | Effluent from poultry litter anaerobic digestion and dilution, microalgae | 1,787 | 214 | – | 891 | 60 | 80 | – | – | [36] |
| Biological | Piggery digestate and dilution, microalgae | 2,050 | 318.5 | – | (17,600) | 90 | 90 | – | – | [37] |
| Physical and biological | Ultra-filtered permeate of dairy cattle manure and ultra-filtered, dilution, microalgae | 1,130 | 17 | – | – | 100 | – | – | – | [8] |
| Physical and biological | Swine wastewater and biological conversion, filtration, reverse osmosis | 503 | – | – | (24,300) | 91 | – | – | 91 | [38] |
| Physical and chemical | Digested pig manure and struvite precipitation | 2,498 | 551 | 1,600 | – | 68 | 61 | 63 | – | [7] |
| Physical and chemical | Anaerobic digester effluent and struvite precipitation | 643 | 235 | – | – | 96 | 99 | – | – | [12] |
| Physical and chemical | Anaerobic digester supernatant and struvite crystallization | 742 | 41 | – | – | 10 | 90 | – | – | [39] |
| Physical and chemical | Anaerobic digestion effluent from pig farm and air stripping | 2,200 | – | – | 5,400 | 93 | – | – | – | [40] |
| Physical and chemical | Food anaerobic digestion effluent and air stripping | 4,860 | – | – | – | 85 | – | – | – | [41] |
| Physical and chemical | Anaerobic digestion effluent using pig excreta and kitchen garbage and electrochemical treatment | 1,124 | | 1,122 | 2,549 | 100 | | 73 | 51 | [9] |
| Physical, chemical and biological | Piggery wastewater and anaerobic digestion, coagulation, microfiltration, air stripping, algae, ozone | 2,945 | 142 | - | (21,600) | 88 | 60 | - | 89 | [42] |
| Physical, chemical and biological | PMADE after membrane and air stripping, microalgae ($CO_2$ supply) | 2,500 | 30 | – | 1,000 | 97 | – | – | – | [6] |
| Physical, chemical and biological | PMADE and dilution, electrolysis/centrifugation/ autoclave, microalgae | 5,202 | 308 | 4,742 | 3,887 | 100/100/99 | 99/92/99 | – | – | [10] |
| Physical, chemical and biological | PMADE and dilution, electrochemical oxidation, microalgae | 4,870 | 307 | 4,042 | 5,270 | 99 | 92 | 100 | 11 | [11] |
| Physical, chemical and biological | Fertilizer wastewater and electrolysis, microalgae | 3,180 | 193 | 3,078 | 1,268 | 96 | 63 | 95 | 52 | This study |

approach to promote production of biomass. Electrolysis is an energy intensive process which might need renewable energy such as solar panels as power supply. NaCl addition had a significant effect on the removal of $NH_4^+$–N in fertilizer wastewater when the electrolysis period was over 3 h. NaCl addition had a positive effect on the microalgae growth. The $NH_4^+$–N removal efficiencies of the wastewater during electrolysis and microalgae cultivation achieved 93% and 65%, respectively. Quadratic functions are suitable to simulate $NH_4^+$–N removal of FW (coefficient is over 0.95). *Chlorella* sp. used 3.11% carbon, 15.0% nitrogen, and 13.5% phosphorus in the FW as substrates. Compared with the culture medium (BG11 and Zarrouk), the electrolysis-pretreated FW was superior for the growth of *Chlorella* sp., while it was not suitable for *S. platensis*. NaCl addition during electrolysis for FW could enhance microalgae production for both *Chlorella* sp. and *S. platensis*. As for nutrients recovery, the complex technologic combination is a promising method to treat and reuse high $NH_4^+$–N contained in wastewater.

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