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*Short Communication*

# Simultaneous Removal of COD and Ammonia Nitrogen Using a Novel Electro-Oxidation Reactor: A Technical and Economic Feasibility Study

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A novel industrial-scale electro-oxidation device was built for simultaneous removal of Chemical Oxygen Demand (COD) and ammonia nitrogen in wastewater. The specific currents had a strong effect on removal rate and total current efficiency. At a specific current of 1440 A/$m^3$ and electrolysis time of 40min, the concentrations of COD and ammonia nitrogen in effluent decreased from 128.75 mg/L and 69.18 mg/L to 50.0 mg/L and 5.0 mg/L, respectively. The stepping control for the specific current is useful for saving energy, and total current efficiency increased from 57.61% to 69.05% in response to use this stepping control model. The energy consumption was 4.34 kWh/$m^3$, the total operation cost for one ton of effluent was about \$0.574 and the specific capital cost was \$420/$m^3$/d. These findings indicate that the electro-oxidation process is capable of simultaneously decomposing refractory organics and ammonia nitrogen in wastewater.

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**Keywords:** Electro-oxidation; Plunger flow electrochemical reactor; Ammonia nitrogen; Economic feasibility

## 1. INTRODUCTION

Wastewater including pharmaceutical wastewater[1], coking wastewater[2], petrochemical wastewater[3] and landfill leachate[4] usually contains high concentrations of refractory organics and ammonia nitrogen, which will lead to serious pollution of the environment without treatment. Ammonia nitrogen, including free ammonia ($NH_3$) and ammonium ion ($NH_4^+$)[5], is the main nitrogen pollutants in water environment[6]. Conventional physical, chemical and biological processes have been applied in wastewater treatment plants (WWTPs) and efficiently degraded most pollutants. Nitrification and denitrification is the most efficient and widely used process for ammonia nitrogen removal from wastewater[7, 8]. However, in the nitrification process, the oxidation of organics

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consumes oxygen and decreases the concentration of dissolved oxygen, which would limit the metabolism of nitrifiers and then inhibit the converting of ammonium into nitrite. After nitrification process, an amount of refractory organics which are unable to provide energy for the denitrifiers as carbon resource in the denitrification process remain in the effluent, and inhibit the denitrifiers to convert nitrate into nitrite, and then into nitrogen gas[9]. Therefore, there are still an amount of residual refractory organics and ammonia nitrogen in the effluent after bioprocess. Several advanced technologies including reverse osmosis[10], activated carbon adsorption[11], electro-oxidation[12], and ozonation[13, 14], have been studied to remove the recalcitrant COD and ammonia nitrogen from effluent.

Electro-oxidation is an environmental friendly electrochemical technology that is attracting increasing attention for the deep treatment of wastewater worldwide[15, 16]. Many studies have demonstrated that ammonia nitrogen can be eliminated and converted to $N_2$ by electro-oxidation[17-20]. Other pollutants are also decomposed during the electrolysis procedure. The current density, pH value, electrolytes, electrode materials and ionic species present in wastewater have a strong impact on the reaction rate and routes of ammonia nitrogen removal. Zhu et al. found that the removal rate of ammonia nitrogen in coking wastewater was higher at pH 7.72 - 9.98 than pH 3.10 with the same suitable current density of 20 $mA/cm^2$, and the energy consumption for one kilogram COD was 50 kWh[15]. Cabeza et al. indicated that formed active chlorine (hypochlorite ion or hypochlorous acid) could oxidize ammonia nitrogen to $N_2$ with a high removal efficiency of 95.8% after electrolysis for 240 min at a current density of 30 $mA/cm^2$ and an initial chlorite concentration of 8570 mg/L[21]. Ihara et al. investigated that the removal efficiencies of ammonia nitrogen and COD in digested effluent from an anaerobic reactor by $Ti/PbO_2$ as anode within an electrolysis time of 6 hours was 79% and 50%, respectively[22]. However, these studies were all conducted at the laboratory scale, and industrial scale application of electro-oxidation to remove COD and ammonia nitrogen simultaneously has not yet been reported.

Electro-oxidation is a heterogeneous reaction that occurs at the interface between the electrode and electrolyte. In most cases, mass transfer is the controlling factor influencing the removal rate of pollutants. A novel plunger flow electrochemical reactor (PFER) was introduced in our previous study[23]. In this novel reactor, meshed-plate electrodes which offered large surface area for contaminants were arranged perpendicularly to the direction of the flow which moved like piston, higher contaminants removal efficiency and current efficiency were achieved in the electrolysis process. The tested effluent was collected from an industrial park wastewater treatment plant, and the target factor was a residual COD with a low concentration (e.g., 160 mg/L). However, it is still unknown if the novel electro-oxidation reactor efficiently removes COD and ammonia nitrogen simultaneously from wastewater.

This study was conducted to present the technical and economic feasibility of a novel electro-oxidation reactor to remove COD and ammonia nitrogen simultaneously. It is a continuation of previous studies on the removal of COD and ammonia nitrogen by electro-oxidation. Therefore, fundamental investigations of the mechanism, degradation pathway and micro-reaction kinetics were not conducted in this study. Instead we focused on application of the novel electro-oxidation reactor for removal COD and ammonia nitrogen from real effluent. The effects of specific current on removal rate, total current efficiency and economic feasibility were discussed in detail. The information presented herein will be useful for spreading a new ammonia nitrogen removal technology with electro-oxidation.

## 2. EXPERIMENTAL

An industrial-scale set was conducted using a plunger flow electrochemical reactor (PFER) that consisted of an electrolytic tank, electrodes, and a constant current DC power supply. The tank was ditch-shaped and made of polyethylene with dimensions of 10.0m (length) × 1.20m (width) × 1.20m (height) and a total effective volume of 10.0 $m^3$. The electrodes were made up of meshed-plate titanium based lead dioxide electrode ($Ti/PbO_2$) as anode and meshed-plate titanium as cathode. The working area of the meshed-plate electrodes was $96m^2$ with a narrow electrode gap of 1.0 cm. The surface-to-volume ratio, defined as the ratio of the working electrodes area (anodes in this cell) and the effective volume of the electrolytic tank, was $9.6m^2/m^3$.

Effluent was collected from the secondary clarifier of a wastewater treatment system in a pharmaceutical factory and flowed through the electrodes perpendicularly in the ditch-shaped cell. The physicochemical characteristics of effluent were summarized in Table 1. The average COD and ammonia nitrogen of the effluent were 128.75 mg/L, 69.18 mg/L, respectively, which exceeded the emission limits. Therefore, it was imperative to treat the effluent deeply. And the conductivity of 6.21 m*S*/cm was adequate to apply electrochemical processes directly.

**Table 1.** Physicochemical characteristics of effluent used in this study

| Characteristics | Initial value | Emission standards[a] | Units |
|---|---|---|---|
| pH | 7.56 | 6-9 | - |
| COD | 128.75 | 50 | mg/L |
| Ammonia nitrogen | 69.18 | 5.0 | mg/L |
| Chloride | 1083.31 | - | mg/L |
| Conductivity | 6.21 | - | m*S*/cm |

[a] Discharge standard of pollutants for municipal wastewater treatment plant (GB 18918-2002), first level A criteria.

Five current densities ($75A/m^2$, $100\ A/m^2$, $125\ A/m^2$, $150\ A/m^2$, $175\ A/m^2$) were designed according to a previous lab-scale study to expound the effect of current density on removal rates, total current efficiencies of COD and ammonia nitrogen removal, which were directly related to the energy efficiency and operation cost. Accordingly, the specific current (defined as the total amperage divided by the volume of effluent) was 720-1680 $A/m^3$.

COD was determined by the potassium dichromate method (GB11914-89). The ammonia nitrogen concentration was obtained via Nessler' s reagent spectrophotometry. The pH was measured using a 25PHS-3E pH meter. The conductivity was measured using a METTLER TOLEDO Seven

Easy S30K conductivity meter. Chloride concentration was determined by ion chromatography using a Dio-nex ICS-2000, with an Ion Pac AS19-HC Column.

## 3. RESULTS AND DISCUSSION

### *3.1 Effect of current on removal rate*

Current, the electron amount through the wastewater (effluent)[24, 25], is proportional to the electrolysis time. Therefore, the current directly influences the reaction rate, high current meant large electrons and enhanced the reaction rate and vice versa[15]. The influence of current on COD and ammonia nitrogen removal have been assessed by many researchers[26, 27].

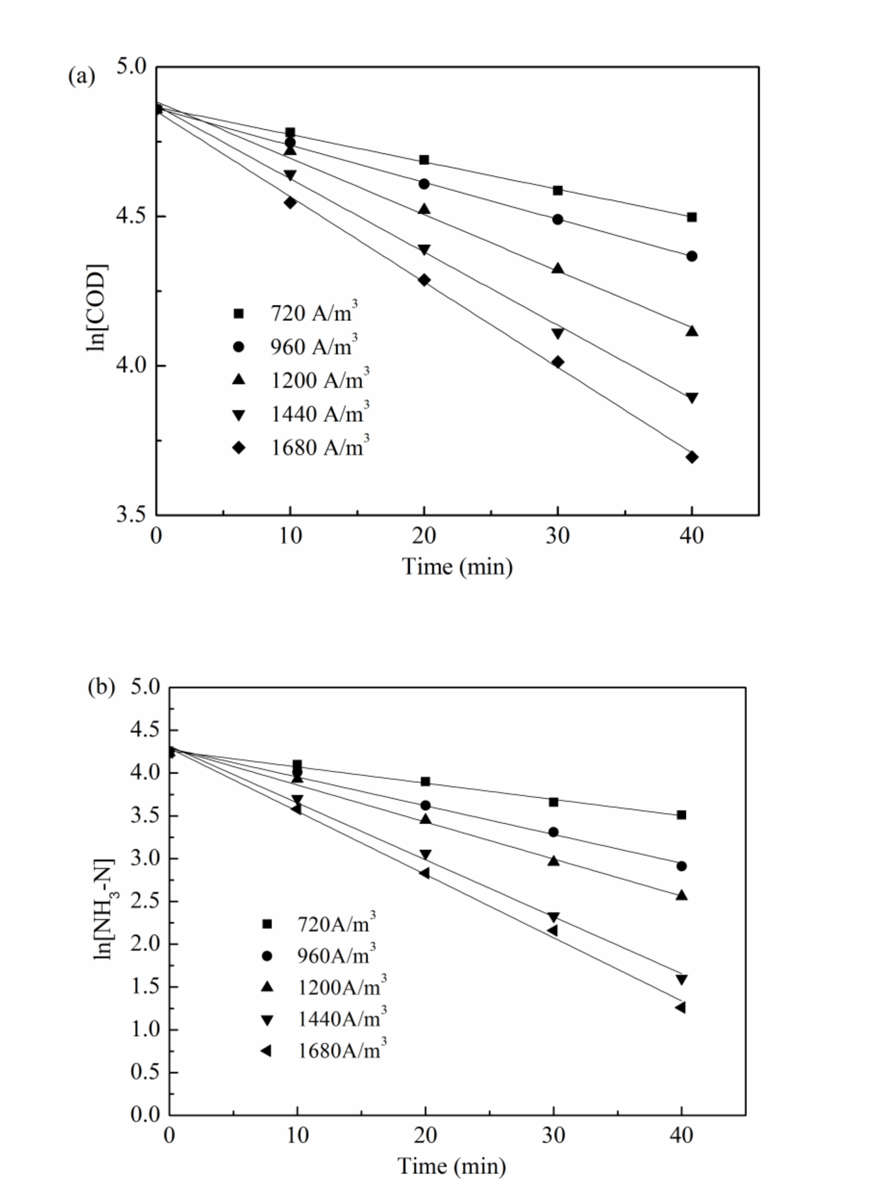

**Figure 1.** Influence of the applied specific current on the evolution of COD (a) and $NH_3$-N (b)

At an initial pH of 7.56, the average COD was 128.75 mg/L and the ammonia nitrogen concentration was 69.18 mg/L. Variations in the concentration of COD and ammonia nitrogen in effluent under different currents are shown in Fig. 1 (a) and (b). The COD and ammonia nitrogen values decreased significantly over the electrolytic time at different specific currents, and the removal rates were higher at higher specific current. Within an electrolysis time of 40 min, the logarithmic values of COD and ammonia nitrogen were linearly related to the electrolytic time. The squared-correlation coefficients ($R^2$) of the five specific currents were 0.997 and 0.990 (720 $A/m^3$), 0.999 and 0.991 (960 $A/m^3$), 0.994 and 0.993 (1200 $A/m^3$), 0.997 and 0.995 (1440 $A/m^3$), and 0.998 and 0.996 (1680 $A/m^3$), indicating a linear relationship between ln[COD], ln[$NH_3$-N] and t, respectively. The apparent reaction rate constants of COD and ammonia nitrogen were calculated easily according to the following formula:

$$\ln[P] = \ln[P]_0 - kt \qquad (1)$$

where, [P] represents the pollutant (COD or ammonia nitrogen) concentration (mg/L), t is the electrolytic time (min), k, the slope of line, is the apparent reaction rate constant ($min^{-1}$).

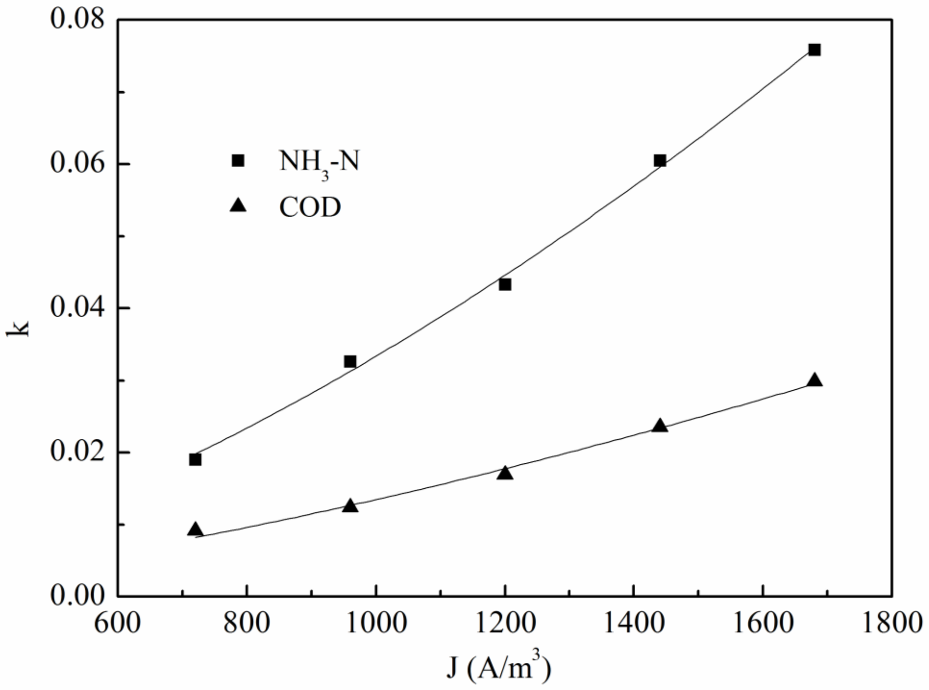

**Figure 2.** Relationship between the apparent reaction rate constant and specific current

The apparent reaction rate constant was affected by many factors, including specific current, flow velocity of wastewater through the electrolytic tank, temperature, pH value, electrodes and electrolyte[28]. With the same wastewater, electrolytic tank, and constant flow velocity, the current density had a strong effect on the apparent reaction rate constant.

The relationship between the specific current and the apparent reaction rate constant using the x-axis for the specific current and y-axis for the apparent reaction rate constant is shown in Fig. 2. The exponential function was suitable for describing the relationship. The formulas describing the COD and ammonia nitrogen removal rate were:

$$k_{COD}=3.88\times10^{-7}\cdot J^{1.51}\quad (R^2=0.991) \tag{2}$$

$$k_{NH_3-N}=5.62\times10^{-7}\cdot J^{1.59}\quad (R^2=0.997) \tag{3}$$

where, J is the applied specific current (A/m$^3$). The $k_{COD}$ and $k_{NH_3\text{-}N}$ in this work was about 2.0 times and 1.5 higher than conventional reactor[29, 30], respectively, and can be attributed to that the meshed-plate electrodes were arranged perpendicularly to the direction of the flow and provided larger acting surfaces.

Substituting (2) and (3) into (1) and integrating it, the final reaction kinetic equations were gotten:

$$\ln[COD]=\ln[COD]_0-3.88\times10^{-7}\cdot J^{1.51}\cdot t \tag{4}$$

$$\ln[NH_3\text{-}N]=\ln[NH_3\text{-}N]_0-5.62\times10^{-7}\cdot J^{1.59}\cdot t \tag{5}$$

Equations (4) and (5) indicated that it was technically feasible to deal with the fluctuations in the quality of effluent by the increase of specific current or extension of electrolytic time.

### *3.2 Total current efficiency*

Electrochemical treatment is undoubtedly an energy-intense process. The energy utilization ratio which can be expressed in terms of current efficiency is usually used to evaluate the performance of electrochemical treatment[31]. Current efficiency is defined as the percentage of the current consumed by the electrode reaction of pollutants divided by the total current passed through the circuit[32]. In electro-oxidation, the total current efficiency for simultaneous COD and ammonia nitrogen removal can be calculated using the following equation:

$$CE\%=\left[\frac{(COD_0-COD_t)}{8It}+\frac{3([NH_4^+]_0-[NH_4^+]_t)}{18It}\right]FV\times100 \tag{6}$$

where, $[COD]_0$, $[NH_4^+]_0$, $[COD]_t$ and $[NH_4^+]_t$ are the COD and ammonia nitrogen values measured at electrolytic times t = 0 and t, respectively (mg/L), V is the volume of solution (L), F is the Faraday constant (96487 C/mol), I is the current (A).

Variations of COD and ammonia nitrogen removal rate and total current efficiency over electrolytic time are illustrated in Fig. 3. As shown in Fig. 3, removal efficiencies of COD and ammonia nitrogen increased and the total current efficiency decreased with retention time during the electrolysis process. And the total current efficiency in this work was about 4 times higher than conventional electrolytic reactor[33], because the plunger flow pattern and meshed-plate electrodes in the novel reactor enhanced contaminant mass transfer and improved current efficiency. Under the specific current of 1440 A/m$^3$, the total current efficiency was 68.03% and the COD and ammonia nitrogen removal rates were 52.55% and 85.13% within an electrolysis time of 30 min, while the total current efficiency decreased to 57.61% with a slight increase in the COD and ammonia nitrogen removal rates after an electrolysis time of 40 min, as shown in line A of Fig. 3. To solve this problem, a stepping control for specific current was presented in industrial-scale application of the electro-oxidation device during wastewater treatment. The ditch-shaped electrolytic cell was divided into three units, each one in series and operated under three different specific currents. The specific currents were selected according to the pollutant concentrations. As shown in line B, the total CE increased by 10%. This operation model improved the total current efficiency and saved energy consumption.

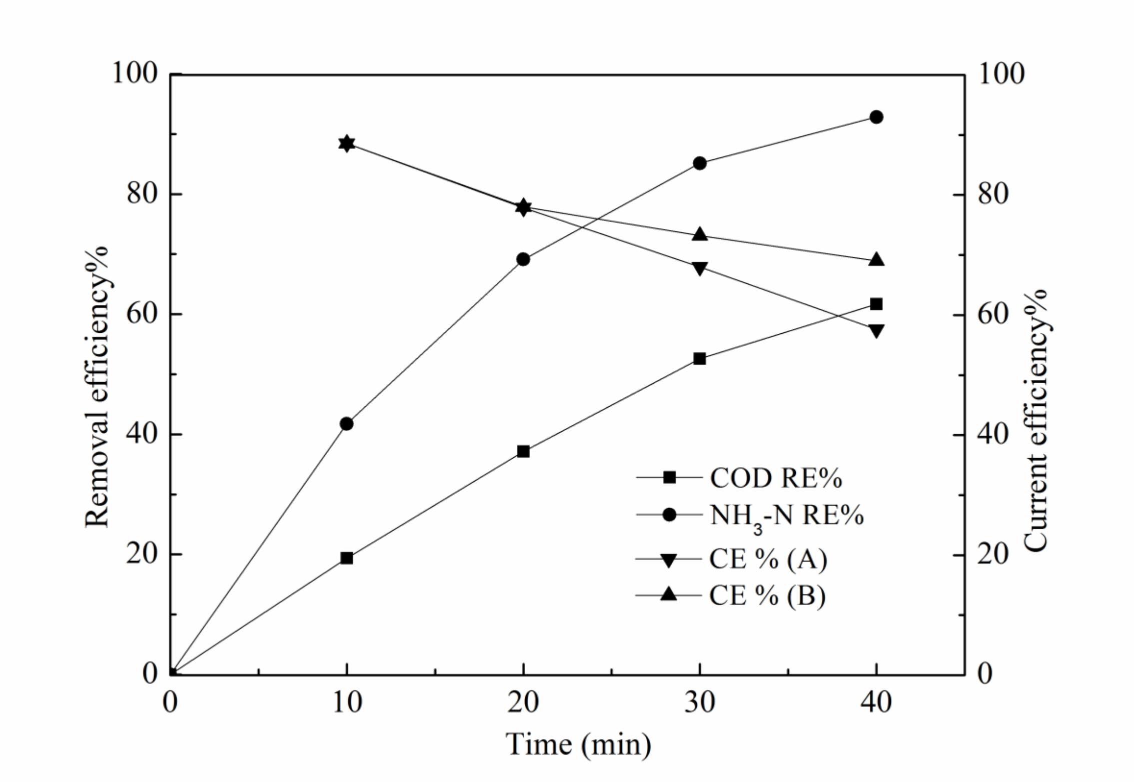

**Figure 3.** Variations in COD and $NH_3$-N removal efficiency and total current efficiency according to retention time. Specific current: 1440 A/$m^3$

### *3.3. Economic feasibility*

The device price and operation cost are the two main factors used to evaluate the economic feasibility of the novel PFER removing COD and ammonia nitrogen simultaneously from wastewater[34]. The device price for the PFER contained electrolysis cell, power supply and auxiliary facilities. The operation cost included electric energy consumption[35], electrode maintenance and staff expenses. According to information regarding an industrial-scale installation capable of treating 300 $m^3$ wastewater per day, the device price and operation cost were estimated in detail. It should be noted that the calculation was based on Chinese Renminbi (RMB) and then converted to United States Dollars ($).The latest average exchange rate of United States Dollars to RMB was around 6.6 according to the State Administration of Foreign Exchange of the People's Republic of China.

As listed in Table 2, the device price was around $126,000 for an industrial-scale installation capable of treating 300 $m^3$ wastewater per day. The specific capital cost was $420 for 1 $m^3$ wastewater per day. With an electrolytic time of 40 min at a specific current of 1440 A/$m^3$, the energy consumption for 1 $m^3$ effluent was 4.34 kWh. The average electric price for utilities in eastern China was $0.11/kWh and the energy cost for 1 $m^3$ effluent was about $0.48. The electrodes used in this process were insoluble, and had an average service lifetime of 3 years. The working electrode costs accounted for 45% of that of the device, and the reprocessing cost of the electrode accounted for 30%

of that of the new one. The cost of the electrode maintenance was about \$0.063/m$^3$. A part-time staff was employed to operate the device with an annual salary \$2810, and approximately \$0.031 for 1m$^3$ effluent. Therefore, the total operating cost for 1 m$^3$ effluent was about \$0.574.

**Table 2.** Cost estimation of the novel electro-oxidation reactor for deep treatment of wastewater

| | |
|---|---|
| Operation conditions | |
| System capacity (m$^3$/d) | 300 |
| Initial COD concentration (mg/L) | 128.75 |
| Initial ammonia nitrogen concentration (mg/L) | 69.18 |
| Emission value of COD (mg/L) | 49.32 |
| Emission value of ammonia nitrogen (mg/L) | 4.95 |
| Fixed capital cost | |
| Electrolysis cell (\$) | 107,000 |
| Power supply (\$) | 9,000 |
| Auxiliary facilities (\$) | 10,000 |
| Total capital cost (\$) | 126,000 |
| Specific capital cost (\$/m$^3$/d) | 420 |
| Operating cost | |
| Electricity charge (\$/kWh) | 0.11 |
| Energy consumption (kWh/m$^3$) | 4.34 |
| Energy cost (\$/m$^3$) | 0.48 |
| Electrode maintenance cost (\$/m$^3$) | 0.063 |
| Staff expense (\$/m$^3$) | 0.031 |
| Total operating cost (\$/m$^3$) | 0.574 |

## 4. CONCLUSIONS

In this paper, we applied a novel plunger flow electrochemical reactor (PFER) in industrial scale to remove the residual COD and ammonia nitrogen in the effluent after biological process. The results indicated that electro-oxidation was available for the simultaneous removal of COD and ammonia nitrogen, and the discharged effluent could reach the discharge standard of pollutants for municipal wastewater treatment plant (GB 18918-2002), first level A criteria. The relationship between COD, ammonia nitrogen concentration and specific current was investigated, and the specific current or electrolytic time could be regulated easily according to the pollutant concentrations during electrolysis. A stepping control model for specific current was presented and suitable for the industrial-scale electro-oxidation device in wastewater treatment, which improved total current efficiency by 10%.

The energy consumption for simultaneous removal of COD and ammonia nitrogen in effluent by the electro-oxidation process was 4.34 kWh per ton, and the operating cost for 1 ton of effluent was about \$0.574. The capital cost of this electro-oxidation device was \$420 for 1 ton of wastewater per day.

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