



Ammonia removal in electrochemical oxidation: Mechanism and pseudo-kinetics

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ABSTRACT

This paper investigated the mechanism and pseudo-kinetics for removal of ammonia by electrochemical oxidation with RuO₂/Ti anode using batch tests. The results show that the ammonia oxidation rates resulted from direct oxidation at electrode–liquid interfaces of the anode by stepwise dehydrogenation, and from indirect oxidation by hydroxyl radicals were so slow that their contribution to ammonia removal was negligible under the condition with Cl⁻. The oxidation rates of ammonia ranged from 1.0 to 12.3 mg NL⁻¹ h⁻¹ and efficiency reached nearly 100%, primarily due to the indirect oxidation of HOCl, and followed pseudo zero-order kinetics in electrochemical oxidation with Cl⁻. About 88% ammonia was removed from the solution. The removed one was subsequently found in the form of N₂ in the produced gas. The rate at which Cl⁻ lost electrons at the anode was a major factor in the overall ammonia oxidation. Current density and Cl⁻ concentration affected the constant of the pseudo zero-order kinetics, expressed by $k = 0.0024[\text{Cl}^-] \times j$. The ammonia was reduced to less than 0.5 mg NL⁻¹ after 2 h of electrochemical oxidation for the effluent from aerobic or anaerobic reactors which treated municipal wastewater. This result was in line with the strict discharge requirements.

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1. Introduction

Ammonia removal has attracted much attention in the past due to the need for the control of nitrogen nutrient to prevent eutrophication in a variety of water bodies. However, present technologies, such as biological nitrogen removal, air stripping and ion exchange have several constraints, including their inability to reduce ammonia to much lower levels, pollutant transfer into other media and higher cost, among others. Therefore, it is important to develop a technology for treating ammonia-containing wastewaters to lower levels (e.g. <1 mg NL⁻¹) for eventual discharge to critical receiving water bodies, such as Dianchi Lake (6th largest fresh water lake in China). The electrochemical process seems to be a promising method.

Monica et al. [1] in 1980 reported that, by means of electrochemical process, ammonia could be effectively removed along with organic pollutants from the domestic wastewater mixed with seawater. Since then, electrochemical process has been successfully used for the removal of ammonia in wastewaters from tannery [2,3], power plants [4], municipal areas [5], and landfills [6,7]. A unique characteristic of these successful applications

is that the wastewater itself contained high concentration of Cl⁻, ranging from 2000 to 18,500 mg L⁻¹ [3,6], or extra amount of 4800–6600 mg L⁻¹ [4,5] was added to take advantage of the formation of oxidizing agent (HOCl) through electrochemical reaction of Cl⁻. Further, ammonia concentrations were relatively high, ranging from 150 [5] to 3000 mg NL⁻¹ [6]. Only a few reported the removal of low concentration of ammonia (less than 30 mg NL⁻¹) using electrochemical treatment of aquaculture waters [8].

The removal mechanism of ammonia in the electrochemical process is poorly understood in terms of the oxidation route and reaction kinetics. A direct oxidation of ammonia at electrode–liquid interfaces of the anode was observed with the assistance of differential electrochemical mass spectrometry [9–11]. However, the removal of ammonia also takes place through an indirect oxidation route by both hydroxyl radicals and HOCl formed in electrochemical processes [3,5]. Chiang et al. [6] proposed that ammonia in landfill leachate could only be removed by indirect oxidation of chlorine/hypochlorite. Still, others [2,12] postulated that both direct and indirect oxidation might occur. Consequently, the exact role of direct and/or indirect oxidation for ammonia needs better quantified [12].

As for reaction kinetics, there appear some contradictions. Pseudo first-order rate was reported for ammonia removal [2] whereas Vanlangendonck et al. [4] proposed that the ammonia

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oxidation rate was constant in pseudo zero-kinetics due to the regeneration of Cl^- during electrolysis.

Ammonia removal efficiency and rate are affected by several factors, such as current density [4,6,7], Cl^- concentration [3–7], pH [4,6,7,13], etc. However, previous studies have shown different results. In addition, the effects of these factors on low concentration of both ammonia and Cl^- have not been reported.

The present study, therefore, attempts to better understand the above phenomena, particularly the contribution of direct and indirect oxidation of ammonia. Specifically, the contribution of hydroxyl radicals and HOCl to indirect oxidation of ammonia was determined. Ammonia solution with Cl^- was used to observe the pseudo-kinetics and factors affecting ammonia removal, including ammonia concentrations, current density, initial Cl^- and pH. In addition, effluents from a local biological municipal wastewater treatment plant and anaerobic reactor were treated by the electrochemical process in order that its effectiveness in ammonia removal can be observed.

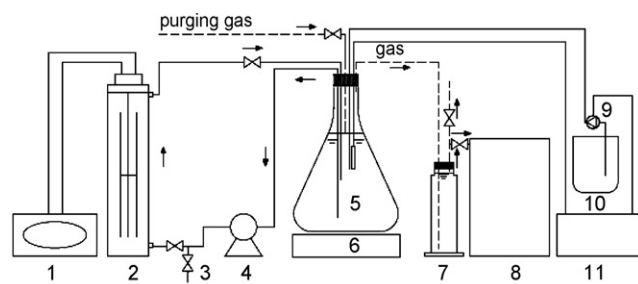
2. Materials and methods

2.1. Setup

Batch experiments were conducted in an apparatus shown in Fig. 1 at ambient temperature (about 20–23 °C). Direct current power source (1) supplied the voltage of 0–10 V at a constant current (0–2 A) by varying the resistance to a 1-L electrolysis cell (2) equipped with pairs of RuO_2/Ti anode and stainless steel cathode. The size of both anode and cathode was 172 mm × 38 mm × 1 mm, and the distance between them was 10 mm. Approximately 4.0 L of ammonia solution was added into the electrolysis cell (2) and the holding bottle (5). Ammonia solution was recycled at 150 mL min⁻¹ rate via a pump (4) from the holding tank (5) to the electrolysis cell (2) during electrochemical treatment. Hydraulic retention time in the electrolysis cell and holding bottle was 6.7 and 20 min in every cycle, respectively. Periodically, samples were taken from a sampling port (3) for subsequent analysis of different parameters. The pH of the solution in holding bottle was monitored and maintained to its initial value by a MP-113 Meller pH/ORP controller (11) which drove a Longer pump (YZ2515x) (9) connecting 1 M NaOH solution (10). Gas produced during the experiment was absorbed into 20 g L⁻¹ boric acid solution (50 mL) in the gas washer (7) and then entered the gas collector (8). The gas phase of the system was purged by the helium about 5 min before every batch experiment.

2.2. Experimental methods

Mechanism, pseudo-kinetics, and influencing factors of ammonia removal in the electrochemical process were investigated



1. direct current power source, 2. electrolysis cell, 3. sampling port, 4. recycling pump, 5. holding bottle, 6. magnetic stirrer, 7. gas washer, 8. gas collector, 9. pump, 10. 1 M NaOH solution, 11. pH controller

Fig. 1. Schematic experimental layout.

using ammonia solution without any organic matter. Chloride-free ammonia solution was prepared by dissolving $(\text{NH}_4)_2\text{SO}_4$ and Na_2SO_4 in deionized water. NaCl besides above chemicals was added for ammonia solution with chloride. $(\text{NH}_4)_2\text{SO}_4$ and NaCl were used to control ammonia and Cl^- concentration, respectively. Either 1 M NaOH or 1 M H_2SO_4 was used to adjust initial pH, and Na_2SO_4 to ensure electro-conductivity at about 1500 $\mu\text{S cm}^{-1}$. All chemicals used were analytical reagents. Note that the effect of SO_4^{2-} was assumed to be insignificant in ammonia removal due to their low concentrations ranging 348–709 mg L⁻¹ (as mg $\text{SO}_4^{2-} \text{L}^{-1}$) and hence not evaluated in the present study.

The removal mechanism of ammonia in the electrochemical process was evaluated under two conditions: ammonia solution with or without Cl^- addition. Chloride-free electrolysis experiments were conducted at different initial pHs (7.0 and 9.2) and ammonia concentrations (32 and 1053 mg NL⁻¹). Experiments with chloride ion addition were conducted at 300 mg L⁻¹ of initial Cl^- and 32 mg NL⁻¹ of ammonia at pH 7.0. Concentrations of ammonia, nitrite, nitrate, total nitrogen, Cl^- , free chlorine, and chloramines in wastewater were analyzed with time. Absorbed ammonia concentration in the gas washer was measured at the end of experiment. The volume of the gas collector was also measured and the concentrations of nitrogen and NO_x in gas collector were analyzed at the end of batch test.

Both integral and differential methods were used to study the pseudo-kinetics of ammonia removal in the electrochemical oxidation process with Cl^- . Four batch tests with 10, 32, 51, and 103 mg NL⁻¹ of initial ammonia were conducted to determine pseudo-kinetics by differential method. A pseudo-kinetic relationship was also determined for every batch test by integration.

Three major factors (current density, initial Cl^- concentration and pH) were investigated for individual effect on ammonia removal under the condition of initial 32 mg NL⁻¹ of ammonia with Cl^- . One parameter of these three factors was varied while the other two kept constant: the current density was 15.4 mA cm⁻², Cl^- concentration 300 mg L⁻¹, and pH 7.0. The variable parameter ranges were: current density was varied from 3.8 to 15.4 mA cm⁻², Cl^- concentration from 30 to 300 mg L⁻¹, and pH 3.0–9.3.

Two kinds of actual wastewater were used to investigate the effectiveness of ammonia removal in the present electrochemical setup. The effluent with approximate 293 mg L⁻¹ of Cl^- and 1420 $\mu\text{S cm}^{-1}$ from the secondary settler in Shanghai Quyang Municipal Wastewater Treatment Plant with traditional activated sludge technology was treated in the electrochemical setup at a constant current 15.4 mA cm⁻² without both the addition of extra Cl^- and the control of pH for the system. Similar conditions were used for the other effluent with 302 mg L⁻¹ of Cl^- and 1315 $\mu\text{S cm}^{-1}$ of electro-conductivity from an anaerobic reactor of enhanced granular sludge bed (EGSB) which treated the influent of the same plant.

2.3. Analytical methods

The concentration of ammonia, nitrite, nitrate, total nitrogen, Cl^- , free chlorine (including Cl_2 , HOCl, and OCl^-), chloramines (monochloramine, dichloramine, and trichloramine), and chemical oxygen demand (COD), and alkalinity in solution were measured according to *Standard Methods* [14,15]. Initial pH was determined by a pH meter (PHS-2C, Tianda Company, Shanghai, China). Measurement of conductivity was made with a conductivity meter (DDS-307, Leici Company, Shanghai, China). The produced gas volume was determined by a replacement method. NO_x concentration in produced gas was measured by Chemiluminescence NO/NO_x Analyzer—Model 200E (Teledyne Technologies Company). N_2 content in produced gas was analyzed by a gas chromatograph (GC)

(Hewlett-Packard, Model 5890 Series II) equipped with a thermal conductivity detector and a 10-m stainless steel column packed with HayeSepQ (80/100 mesh). Helium was used as the carrier gas at a flow rate of 22 ml min⁻¹, followed by a 2-min heating at 110 °C. The temperatures of the injector and detector were 130 and 200 °C, respectively.

3. Results and discussion

3.1. Mechanism of ammonia removal

3.1.1. Chloride-free ammonia solution

Results of batch test ammonia removal by 24 h electrochemical oxidation without Cl⁻ are listed in Table 1. Ammonia concentration did not change significantly (less than 0.06%) under the conditions of low initial ammonia (32 mg NL⁻¹) and at pH 7.0 or 9.2. Both nitrite (as nitrite nitrogen) and nitrate (as nitrate nitrogen) were less than their detecting limit values of 0.005 and 0.08 mg NL⁻¹, respectively. Ammonia in the gas washer at the end of the experiment was less than the detecting limit of 0.02 mg NL⁻¹. Similar results were observed at 1053 mg NL⁻¹ for initial ammonia at pH 7.0. Therefore, the ammonia removal rate resulted from both direct oxidation at the anode and indirect oxidation by hydroxyl radical was too slow to be detected at pH 7.0 with a wide range of initial ammonia, from 32 to 1053 mg NL⁻¹, as well as at pH 9.2 with low initial ammonia (about 32 mg NL⁻¹), during 24 h of electrochemical oxidation. However, a slight decrease of ammonia and little production of nitrite were observed at pH 9.2 and 1053 mg NL⁻¹ of initial ammonia, as shown in Table 1. Both concentrations of nitrate and nitrite were low, the former less than the detecting limit, and the latter ranging from 0.000 to 0.049 mg NL⁻¹ throughout the 24 h of electrochemical oxidation. The concentration of ammonia decreased from 1053 to 1037 mg NL⁻¹. Since the volume of the solution was 4 L, 64 mg ammonia was removed from the wastewater during the electrolysis process. Ammonia absorbed by the gas washer was 5 mg. Therefore, only 59 mg ammonia or 1.5% of ammonia was removed by both direct oxidation at the anode and indirect oxidation by hydroxyl radical within 24 h since there was no Cl⁻ in the solution. Alkaline pH and high ammonia resulted in the increase of NH₃ concentration, which was beneficial for the oxidation of ammonia by either direct oxidation at the anode or indirect oxidation by hydroxyl radical. However, even under optimal conditions, at alkaline (pH 9.2) and high initial ammonia (1053 mg NL⁻¹), the removal rate by these two oxidation ways was considerably slow.

3.1.2. Ammonia solution with chloride

Fig. 2 shows the results of electrochemical oxidation of ammonia under the same experimental conditions as the previous batch tests except for the external addition of 300 mg L⁻¹ Cl⁻: initial ammonia concentration 32 mg NL⁻¹, pH 7.0 and current density 15.4 mA cm⁻². The experimental results with Cl⁻ addition completely differed from those without Cl⁻. Fig. 2a illustrates that ammonia decreased rapidly and linearly with time, from an initial

32 to 1.3 mg NL⁻¹ in 2.5 h. Concurrently, the corresponding total nitrogen also decreased from an initial 32 to 2.8 mg NL⁻¹ at 2.5 h. During 2.5 h of electrochemical oxidation, nitrate was low, ranging from 0 to 0.9 mg NL⁻¹, and nitrite was maintained below detecting limit. In addition, the concentration of produced chloramines, including monochloramine, dichloramine, and trichloramine, was less than 3.0 mg Cl₂ L⁻¹. The nitrogen in the forms of chloramines was 0.74 mg NL⁻¹ at 2.5 h if measured chloramines was considered as monochloramine. Ammonia in the gas washer at the end of the experiment was less than the detecting limit of 0.02 mg NL⁻¹. The NO, NO₂ and N₂ in produced gas with a total volume of 2.5 L were 11 × 10⁻⁶, 37 × 10⁻⁶ and 43 mg L⁻¹, respectively. Consequently, about 88% of the removed ammonia was found in form of N₂ in produced gas. Similar results were reported by other researchers using IrO₂ anode [16]. The produced nitrate could have come from the indirect oxidation of ammonia by HOCl, as suggested by Chad and Valentine [17] or by hydroxyl radicals.

Thus, the results clearly demonstrate that with the external addition of 300 mg L⁻¹ Cl⁻, up to 32 mg NL⁻¹ of ammonia could be completely oxidized and most of it was converted into N₂. More likely, the reactions result from the indirect oxidation by HOCl as shown in the following equations [3,5,6,17–19]. Both direct oxidation at electrode–liquid interfaces of the anode by a stepwise dehydrogenation of NH₃ [9–11], and indirect oxidation by hydroxyl radicals [2,12], could be neglected.

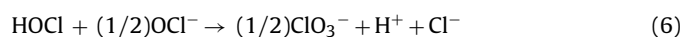
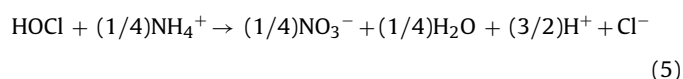
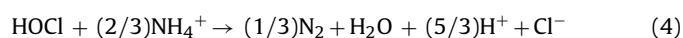
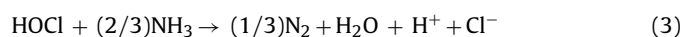
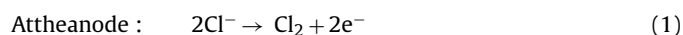


Fig. 2b shows the variety of Cl⁻, free chlorine (including Cl₂, HOCl, and OCl⁻), and chloramines (including monochloramine, dichloramine, and trichloramine) in solution with time during electrochemical oxidation. The concentrations of both free chlorine and chloramines were low. The former was less than 2.1 mg Cl₂ L⁻¹, and the latter was less than 3.0 mg Cl₂ L⁻¹. Cl⁻ decreased from initial 304 to 285 mg L⁻¹ Cl⁻ lost electrons to turn into Cl₂ at the anode, and then formed Cl₂ hydrolyzed and reacted with NH₃ or NH₄⁺ through breakpoint chlorination to regenerate Cl⁻, as shown in Eqs. (1)–(5) [3,5,6,17–19]. Therefore, in theory, the Cl⁻ quantity remained unchanged after reactions, only serving as a catalyst. Experimental results illustrate that the total quantity of Cl element (including Cl⁻ and other forms of chlorine) in solution during the process was less than the original quantity of Cl element (only in

Table 1
Concentration profiles of ammonia, nitrite and nitrate during the electrolysis experiment of chloride-free ammonia solution (mg NL⁻¹)

Time (h)	Initial pH 7.0			Initial pH 9.2			Initial pH 7.0			Initial pH 9.2		
	Ammonia	Nitrite	Nitrate	Ammonia	Nitrite	Nitrate	Ammonia	Nitrite	Nitrate	Ammonia	Nitrite	Nitrate
0	31.9	BD	BD	1053	BD	BD	31.7	BD	BD	1053	ND	BD
3	31.9	BD	BD	1053	BD	BD	31.4	BD	BD	1037	0.034	BD
6	31.9	BD	BD	1053	BD	BD	31.5	BD	BD	1037	0.036	BD
11	31.9	BD	BD	1053	BD	BD	31.4	BD	BD	1037	0.038	BD
24	31.9	BD	BD	1053	BD	BD	31.4	BD	BD	1037	0.049	BD

BD: below detection limit.

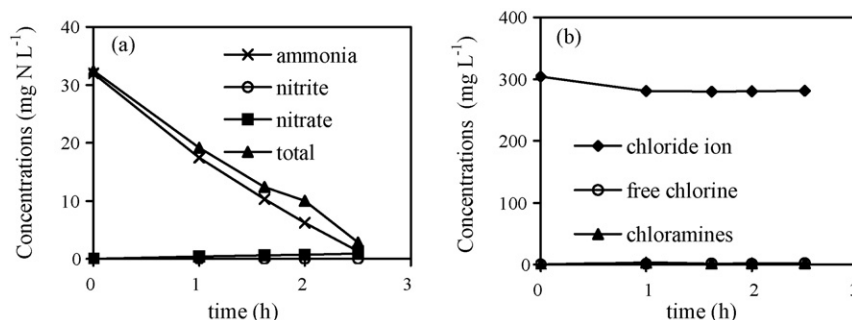


Fig. 2. Concentration profiles during the electrolysis process of ammonia solution with $300 \text{ mg L}^{-1} \text{ Cl}^{-}$ at pH 7.0 and current density 15.4 mA cm^{-2} : (a) different nitrogens and (b) chloro species.

Cl^{-} form). One explanation for this phenomenon could be that part of formed Cl_2 escaped from the solution with gas.

3.2. Pseudo-kinetics of ammonia removal with Cl^{-}

Fig. 3a shows that ammonia concentration decreased linearly with time for all four different initial ammonia concentrations (10, 32, 50, 103 mg N L^{-1}) in the electrochemical oxidation process with 300 mg L^{-1} of initial Cl^{-} , pH 7.0, and 15.4 mA cm^{-2} of current density. Slopes of lines were -11.4 , -12.3 , -11.7 , -11.5 with correlation coefficients of 0.996, 0.992, 0.991 and 0.995, respectively. Correspondingly, ammonia oxidation rates were 11.4, 12.3, 11.7 and $11.5 \text{ mg N L}^{-1} \text{ h}^{-1}$ with an average of $11.7 \pm 0.6 \text{ mg N L}^{-1} \text{ h}^{-1}$, as shown in Fig. 3b. The ammonia oxidation rate was found to be independent of the concentration of ammonia. Therefore, simulation results by either integral method as shown in Fig. 3a, or differential method as illustrated in Fig. 3b, show that ammonia oxidation rates could be described by pseudo zero-order kinetics:

$$\frac{-d[\text{NH}_3\text{-N}]}{dt} = k \quad (7)$$

where $d[\text{NH}_3\text{-N}]/dt$ is the ammonia oxidation rate ($\text{mg N L}^{-1} \text{ h}^{-1}$) and k is a constant ($\text{mg N L}^{-1} \text{ h}^{-1}$). This result differs from previously reported pseudo first-order kinetics [2]. However, a linear decrease of ammonia with time has also been observed by Van Hege et al. [18] and Vanlangendonck et al. [4]. Suggested pseudo zero-order kinetics could be explained by the oxidation mechanism of ammonia in the electrochemical process with chlorine. Indirect oxidation by HOCl was a complicated process, simplified as several reaction Eqs. (1)–(5). In this study, the ammonia oxidation rate was not associated with the concentration of ammonia. Therefore, the concentration of HOCl controlled the ammonia oxidation rate according to Eqs. (3) or (4). The free chlorine including Cl_2 , HOCl, and OCl^{-} was maintained at less than $2.1 \text{ mg Cl}_2 \text{ L}^{-1}$ as shown in Fig. 2b. The produced HOCl reacted with ammonia rapidly. The rate at which HOCl was produced was the control factor. Furthermore, since the rate of Cl_2 hydrolysis Eq. (2) was higher than that of anode Cl_2 generation Eq. (1), the ammonia oxidation rate may in fact depend on reaction (1). The rate at which Cl^{-} lost electrons at the anode was also a major factor in the overall ammonia oxidation. Therefore, parameters affecting reaction (1) such as current density and initial concentration of Cl^{-} should exert a significant impact on the oxidation of ammonia.

3.3. Effect of several factors on ammonia removal with Cl^{-}

3.3.1. Current density

Fig. 4a shows the variation of ammonia concentrations as a function of the current density at pH 7.0, the initial Cl^{-} concentration 300 mg L^{-1} and ammonia 32 mg N L^{-1} . Again, a zero-order reac-

tion was observed as reported by others [4] with the rate constant clearly depending on the current density (Fig. 4b). With the increase of the current density, the electrons losing rate for the Cl^{-} increased as shown in Eq. (1) [6], which brought higher ammonia oxidation rate.

3.3.2. Cl^{-} concentration

The dependence of the ammonia removal on the initial Cl^{-} concentration is shown in Fig. 5a. The zero-order ammonia oxidation rate increased linearly with the initial Cl^{-} concentration (Fig. 5b); the rate increased one order of magnitude (from 1 to $12 \text{ mg N L}^{-1} \text{ h}^{-1}$) with Cl^{-} concentration from 30 to 300 mg L^{-1} . Previous studies [3–6] have reported similar trends that ammonia oxidation rate increased with initial Cl^{-} . Vanlangendonck et al. [4] recently reported a power function relation between ammonia oxidation rate and initial Cl^{-} , ranging from 1700 to $12,000 \text{ mg L}^{-1}$. The linear relation was first found with the Cl^{-} , ranging from 30 to 300 mg L^{-1} , in this study. Low Cl^{-} concentration and narrow range were the main reason for the linear relation, as it was significant for the treatment of ammonia in municipal wastewater.

3.3.3. pH

Ammonia concentration was found to decrease linearly with time at pH 3.0, 7.0, and 9.3 as shown in Fig. 6a. After 2.5 h of electrolysis, the ammonia concentration decreased from 32.0 mg N L^{-1} to 10.4, 1.3 and 1.8 mg N L^{-1} , respectively. Corresponding ammonia oxidation rates were 8.3, 12.3, $11.2 \text{ mg N L}^{-1} \text{ h}^{-1}$ as shown in Fig. 6b. Neutral and alkaline pH were beneficial to ammonia oxidation. This result is similar to that of Lin and Wu [13], but different from that of Vlyssides et al. [5]. The formation of HOCl was adversely affected by both low pH as listed in Eq. (2) and strong alkaline pH due to the formation of ClO_3^{-} (Eq. (6)).

3.3.4. Constant of pseudo zero-order kinetics

The kinetics constant of ammonia oxidation in electrochemical oxidation was found to depend primarily on the current density and Cl^{-} concentration at pH 7.0–9.0, regardless the effect of pH. Fig. 7 shows that the ammonia oxidation rate was proportional to the product of current density multiplying Cl^{-} concentration with slope of 0.0024 and correlation coefficient of 0.9779. Therefore, the constant of pseudo zero-order kinetics was expressed by

$$k = 0.0024 \times [\text{Cl}^{-}] \times j \quad (8)$$

where $[\text{Cl}^{-}]$ is Cl^{-} concentration (mg L^{-1}) and j is current density (mA cm^{-2}). The application limits of the model in Eq. (8) are that current density ranged from 3.8 to 15.4 mA cm^{-2} , and Cl^{-} from 30 to 300 mg L^{-1} .

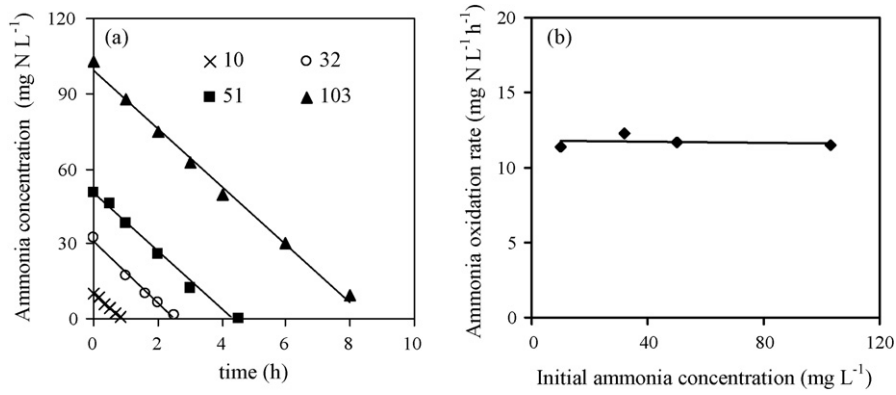


Fig. 3. At different initial ammonia concentrations: (a) ammonia concentration profiles and (b) ammonia oxidation rate.

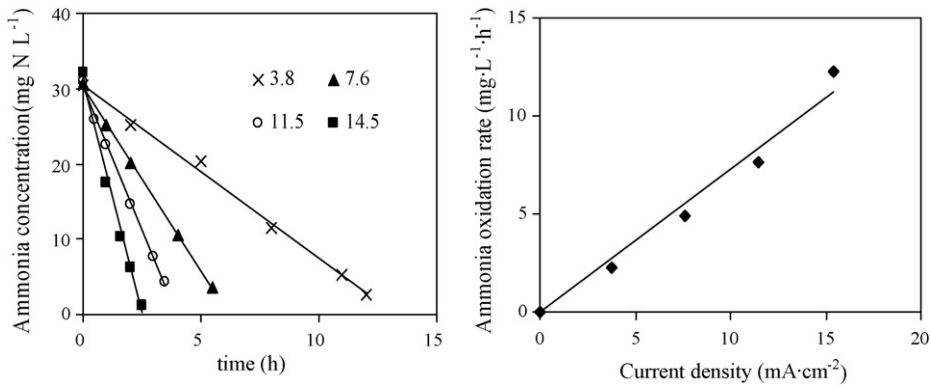


Fig. 4. At different current densities: (a) ammonia concentration profiles and (b) ammonia oxidation rate.

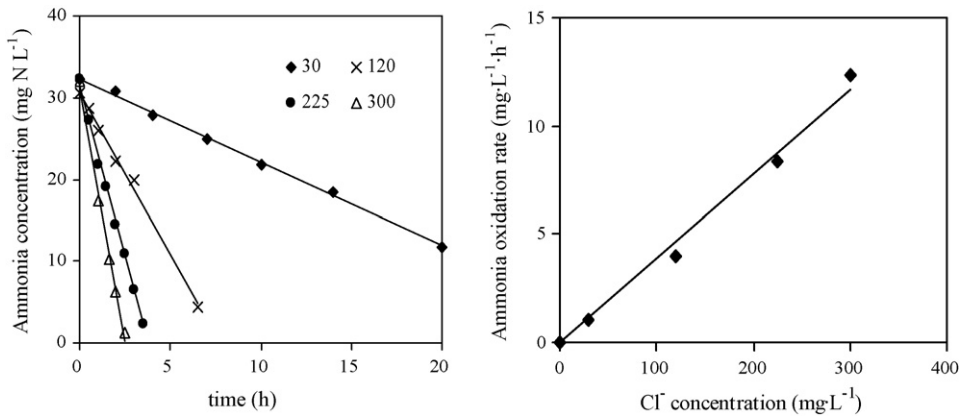


Fig. 5. At different initial Cl⁻ concentrations: (a) ammonia concentration profiles and (b) ammonia oxidation rate.

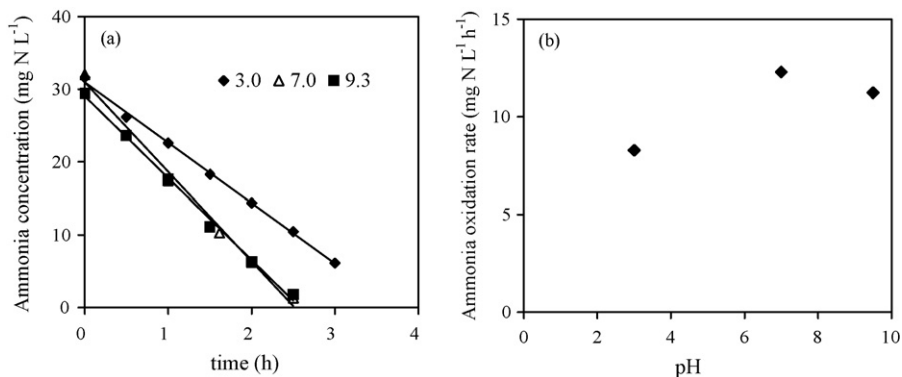


Fig. 6. At different initial pH: (a) ammonia concentration profiles and (b) ammonia oxidation rate.

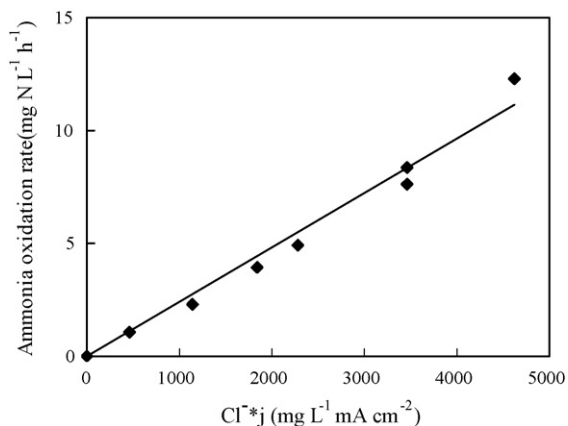


Fig. 7. Variety of ammonia oxidation rate with the product of current density multiplying Cl^- concentration.

3.4. Ammonia oxidation with actual wastewaters

Fig. 8 shows the ammonia concentration profiles with time for two kinds of actual wastewater by electrochemical oxidation at 15.4 mA cm^{-2} of current density and without both the pH control and the addition of external Cl^- . Remarkably, the pseudo zero-order ammonia oxidation rates are almost same, $8.9 \text{ mg N L}^{-1} \text{ h}^{-1}$ for the effluent of the secondary settler of aerobic process and $9.1 \text{ mg N L}^{-1} \text{ h}^{-1}$ for that from an anaerobic reactor, apparently due to the similar characteristics of initial Cl^- ($290\text{--}300 \text{ mg L}^{-1}$) and electro-conductivity ($1315\text{--}1420 \mu\text{S cm}^{-1}$). Also COD shows some reduction, or from $24\text{--}16$ to 11 mg L^{-1} at 2.0 h. A reduction of $26\text{--}28\%$ for ammonia oxidation rates was observed compared to that of ammonia solution without organic matters under similar current density, Cl^- concentration and pH. pH decreased a little from 5.9 to 5.4 for the effluent from aerobic process and 6.8–6.6 for the effluent from an anaerobic reactor, since two kinds of actual wastewaters had alkalinity (235 and $314 \text{ mg CaCO}_3 \text{ L}^{-1}$, respectively) and possessed the buffer ability. The treated wastewater with such low ammonia concentration ($<0.5 \text{ mg N L}^{-1}$) meets strict requirements for ammonia in critical receiving water bodies, such as Dianchi Lake in Yunnan Province, China. The electrochemical oxidation is an effective method for the further removal of ammonia nitrogen for the effluent from aerobic or anaerobic reactors treating municipal wastewater because it could reduce ammonia

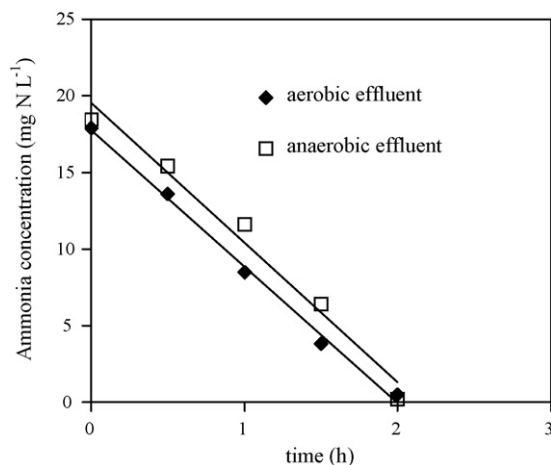


Fig. 8. Concentration profiles of ammonia at current density 15.4 mA cm^{-2} for the effluent from aerobic and anaerobic process.

nitrogen almost to zero. Compared with the conventional methods for ammonia removal from municipal wastewater, this method seems to be more feasible with the following reasons: easy operation, fast ammonia removal rate, reliable treatment efficiency, no bio-solids and low ammonia concentration in the effluent.

4. Conclusions

- (1) The oxidation of ammonia was primarily attributed to the indirect oxidation of HOCl. The ammonia oxidation rates resulted from direct oxidation at electrode–liquid interfaces of the anode by stepwise dehydrogenation, and from indirect oxidation by hydroxyl radicals were so slow that their contribution to ammonia removal was negligible under the condition with Cl^- for electrochemical process using RuO_2/Ti as anode.
- (2) The ammonia oxidation rates ranging from 1.0 to $12.3 \text{ mg N L}^{-1} \text{ h}^{-1}$ were found to be independent of the concentration of ammonia and followed pseudo zero-order kinetics at low Cl^- about 300 mg L^{-1} and below 100 mg N L^{-1} of ammonia.
- (3) Current density and initial Cl^- concentration affected the constant of the pseudo zero-order kinetics, expressed as $k = 0.0024[Cl^-] \times j$, under the condition of 3.8 to 15.4 mA cm^{-2} of current density and 30 to 300 mg L^{-1} of Cl^- .
- (4) Ammonia from the effluent of municipal wastewater treatment plant with aerobic or anaerobic processes was further reduced to 0.5 and 0.2 mg N L^{-1} , respectively. High quality of effluent after electrolysis with low ammonia concentration (less than 0.5 mg N L^{-1}) might meet strict requirement for ammonia in some special receiving water body.
- (5) The electrochemical oxidation is an effective method for the further removal of ammonia nitrogen for the effluent from aerobic or anaerobic reactors treating municipal wastewater.

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References

- [1] M.D. Monica, A. Agostizno, A. Ceglie, An electrochemical sewage treatment process, *J. Appl. Electrochem.* 10 (1980) 527–533.
- [2] L. Szyrkowicz, F. Naumczyk, F. Zilio-Grandi, Electrochemical treatment of tannery wastewater using Ti/Pt and Ti/Pt/Ir electrodes, *Water Res.* 29 (1995) 517–524.
- [3] A.G. Vlyssides, C.J. Israilides, Detoxification of tannery waste liquors with an electrolysis system, *Environ. Pollut.* 97 (1997) 147–152.
- [4] Y. Vanlangendonck, D. Cornisier, A. Van Lierde, Influence of operating conditions on the ammonia electro-oxidation rate in wastewaters from power plants, *Water Res.* 39 (2005) 3028–3034.
- [5] A.G. Vlyssides, P.K. Karlis, N. Rori, A.A. Zorpas, Electrochemical treatment in relation to pH of domestic wastewater using Ti/Pt electrodes, *J. Hazard. Mater.* 95 (2002) 215–226.
- [6] L.C. Chiang, J.E. Chang, T.C. Wen, Indirect oxidation effect in electrochemical oxidation treatment of landfill leachate, *Water Res.* 29 (1995) 671–678.
- [7] P. Wang, I.W.C. Lau, H.H.P. Fang, Electrochemical oxidation of leachate pre-treated in an up flow anaerobic sludge blanket reactor, *Environ. Technol.* 22 (2001) 373–381.
- [8] R.S. Wijesekara, N. Nomura, M. Matsumura, Electrochemical removal of ammonia, chemical oxygen demand and energy consumption from aquaculture waters containing different marine algal species, *J. Chem. Technol. Biotechnol.* 80 (2005) 1408–1415.
- [9] S. Wasmus, E.J. Vasini, M. Krausa, H.T. Mishima, W. Vielstich, DEMS-cyclic voltammetry investigation of the electrochemistry of nitrogen compounds in 0.5 M potassium hydroxide, *Electrochim. Acta* 39 (1994) 23.

- [10] J.F.E. Gootzen, A.H. Wonders, W. Visscher, R.Q. van Santen, J.A.R.A. van Veen, A DEMS and cyclic voltammetry study of NH_3 oxidation on platinized platinum, *Electrochim. Acta* 42 (1998) 1851–1861.
- [11] A.C.A. de Vooy, M.T.M. Koper, R.A. van Santen, J.A.R. van Veen, The role of adsorbates in the electrochemical oxidation of ammonia on noble and transition metal electrodes, *J. Electroanal. Chem.* 506 (2001) 127–137.
- [12] C. Feng, N. Sugiura, S. Shimada, T. Maekawa, Development of high performance electrochemical wastewater treatment system, *J. Hazard. Mater.* 103 (2003) 65–78.
- [13] S.H. Lin, C.L. Wu, Electrochemical removal of nitrite and ammonia for aquaculture, *Water Res.* 30 (1996) 715–721.
- [14] APHA Standard Methods for the Examination of Water and Wastewater, 20th edition, American Public Health Association, Washington, DC, 1998.
- [15] APHA Standard Methods for the Examination of Water and Wastewater, 15th edition, American Public Health Association, Washington, DC, 1980.
- [16] K.W. Kim, Y.J. Kim, I.T. Kim, G.I. Park, E.H. Lee, The electrolytic decomposition mechanism of ammonia to nitrogen at an IrO_2 anode, *Electrochim. Acta* 50 (2005) 4356–4364.
- [17] T.J. Chad, R.L. Valentine, Reaction scheme for the chlorination of ammoniacal water, *Environ. Sci. Technol.* 26 (1992) 577–586.
- [18] K. Van Hege, M. Verhaege, W. Verstraete, Electro-oxidative abatement of low-salinity reverse osmosis membrane concentrates, *Water Res.* 38 (2004) 1550–1558.
- [19] G.C. White, *The Handbook of Chlorination*, 2nd ed., Van Nostrand, New York, USA, 1999.