

EFFICIENT ELECTROCHEMICAL AMMONIA REMOVAL SYSTEM

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Abstract. Efficient electrochemical ammonia oxidation system was studied with an objective to enhance the selectivity of ammonia to nitrogen gas and to remove the by-products in an undivided electrochemical cell, in which various cathodes (Ti, Cu/Zn, Fe) and Ti/IrO₂-Pt anode were assembled. In the present study, anodic oxidation of ammonia and cathodic reduction of by-products were achieved, especially with Cu/Zn cathode. The ammonia-N decreased from 100.0 mg/L to 0.0 mg/L in the presence of 1.0 g/L NaCl after 120 min electrolysis at the current density of 30.0 mA/cm² with Cu/Zn cathode and Ti/IrO₂ anode. No nitrite was detected in the treated solutions. The concentration of chloramine was 0.24 mg/l. About 97.34% of initial TN was transformed into nitrogen gas in Cu/Zn system, indicating that Cu/Zn cathode has better performance than Ti and Fe cathode. The results indicated that Cu/Zn cathode exhibited a little higher reduction ability, possibly attributed by the higher electrocatalytic activity of brass containing Zn (35-41 wt%) which significantly influenced the kinetics of current density. As ammonia could be completely removed by the simultaneous oxidation and reduction in this study, it is suitable for deep treatment of ammonia polluted water.

Keywords: *water pollution, electrocatalysis, ammonia nitrogen, dimensionally stable anode, electrocatalytic activity*

Introduction

Ammonia contamination in water bodies is a widespread environmental problem. Usually, two main categories of treatment processes, physicochemical and biological treatment methods, were employed for ammonia removal from domestic and industrial wastewaters, including ion exchange, air stripping, breakpoint chlorination, and biological process and so on (Rahmani et al., 2004; Du and Liu, 2005; Wang and Liu, 2006). As electrochemical oxidation of ammonia has high treatment efficiency, minimized sludge production, small area occupied and relatively low investment cost, many researchers have focused on it in decades.

The electrochemical method is widely used to remove ammonia from ammonia-containing underground water or industrial wastewater, which contains low concentrations of organic matter and cannot be effectively treated by biological method. In the last decades, researchers have tried to improve electrochemical denitrification by different ways, such as using different electrodes, designing different electrochemical

cells, addition of different supporting electrolytes and employing different power supply, etc.

In the past years, various electrodes such as Pt, Ru, Ir, Ti, graphite, Ni, Lead dioxide, dimension stable anode (DSA), boron-doped diamond (BDD) and bimetallic or multi-metallic electrodes have been used in electrochemical oxidation (Feng, 2003; Vitse et al., 2005; Chen et al., 2007; De et al., 2009). It was shown that ammonia is effectively removed from solution while active chlorine was electrogenerated on the Ti/PtO_x-IrO₂ electrode with nitrogen gaseous being postulated to be the main by-product of ammonia electrolysis (Kapalka et al., 2010a). In general, during the electrochemical process of ammonia, nitrogen gas was the most favorable reduction product. One of the problems is the generation of nitrate, which needs to be further treated.

Although electrochemical method has been investigated and used to deal with ammonia issue, most researchers mainly focused on the anode effect on ammonia removal. However, few of them paid attention to the effect of cathode which may play an important role in the by-products (NO₃⁻-N, NO₂⁻-N and chloramines) generated during the process of electrochemical ammonia oxidation. On the other hand, some researchers found that the cathodes such as Cu/Zn and Fe had high efficiency on nitrate and nitrite removal. Therefore, it is possible to decrease the production of side products by employing cathode with high nitrate and nitrite reduction ability.

From previous study, ammonia could be efficient removed by Ti/RuO₂-Pt anode via electrochemical oxidation process (Wang et al., 2012). To compare with previous studies in order to design a better treatment system and study the effects of different anodes on experimental results simultaneously.

In present study, an efficient electrochemical ammonia oxidation system was designed with various cathodes (Ti, Cu/Zn, Fe) and Ti/IrO₂-Pt anode. The effect of different cathodes on the reduction efficiency of ammonia to nitrogen gas and the formation of by-products during the electrochemical process are studied in 2017, at Zhejiang Ocean University labs. The optimum operating conditions are also discussed, to enhance the selectivity of ammonia to nitrogen gas and to remove the by-products simultaneously.

Materials and methods

Electrochemical apparatus

The experiments are carried out in undivided cells using Ti, Fe and Cu/Zn plates as cathodes and Ti/IrO₂-Pt anode, respectively for the treatment of synthetic ammonia solution with anodic ammonia oxidation and cathodic reduction rates being compared. During the experiments, the influence of initial chloride ion concentration, current density, temperature and initial pH are investigated and assessed. The concentrations of ammonia, nitrite, nitrate, chloramine, and dissolved metals are determined with standard methods. The current efficiency (include the average current efficiency (ACE) and the instantaneous current efficiency (ICE), reaction kinetics, oxidation rate and one-way analysis of variance are used to analyze and assess this ammonia removal process.

The average current efficiency (ACE) and the instantaneous current efficiency (ICE) are calculated using *Equations 1* and *2*, respectively (Comminellis and Pulgarin, 1991; Van et al., 2004):

$$ACE = 3FV \left[\left(NH_4^+ - N \right)_0 - \left(NH_4^+ - N \right)_t \right] / 14I_t \quad (\text{Eq.1})$$

$$ICE = 3FV \left[\left(NH_4^+ - N \right)_0 - \left(NH_4^+ - N \right)_{t+\Delta t} \right] / 14I_{\Delta t} \quad (\text{Eq.2})$$

where $(NH_4^+ - N)_0$, $(NH_4^+ - N)_t$ and $(NH_4^+ - N)_{t+\Delta t}$ are the concentration of $NH_4^+ - N$ (mg/L) at times zero, t and $t + \Delta t$ (min), respectively, I is the current density (A), F is the Faraday number (96,485 C/mol), t is the time (min), V is the volume of the electrolyte (L), 3 is the number of exchanged electrons for the electrochemical oxidation of ammonia, and 14 is the molecular mass of ammonia (g/mol).

Batch experiments were conducted in an apparatus at room temperature (about 23.0–26.0 °C). An undivided and unbuffered electrochemical cell was designed in our lab with a networking volume of 400.0 mL. The 400.0 mL electrolysis cell was made of acrylic plates with four outer spots for the electrodes assembled. Three metal plates include Cu/Zn (Cu: 62.2 wt.%; Zn: 37.8 wt.%), Ti and Fe plates of 75.0 cm² (15.0 cm × 5.0 cm) were used as the cathode respectively with Ti/IrO₂-Pt (TohoTech company, Japan) as the anode at the same area. A distance of 8.0 mm was set between the two electrodes. The immersed areas of the anode and cathode in the treated solution were the same and calculated as 50.0 cm². A DC power with a voltage range of 0–50.0 V and current range of 0–5.0 A was employed as a power supply. Test synthetic ammonia solutions were prepared using (NH₄)₂SO₄ and distilled water to give a final concentration of 100.0 mg/L with no Cl⁻ ion. In the solution, free ammonia concentration is only 0.0198 mg/L. The NaCl dosage of 0 g/L, 0.5 g/L, 1.0 g/L, 2.0 g/L (w/v) were added into the synthetic ammonia solutions to investigate the effect of influencing factors (sodium chloride dosage, current density, temperature and initial pH value). The current density was varied from 5.0 mA/cm² to 50.0 mA/cm², and the initial pH value was adjusted from 3.0 to 11.0 by NaOH (0.1 M) or H₂SO₄ (0.1 M). 0.5 g/L Na₂SO₄ was added in all solution as supporting electrolyte. At different intervals, 1.5 mL of sample was drawn from the electrochemical cell for analysis. The electrolysis was ceased when either 90.0% of initial ammonia was converted or 2 h elapsed.

Analysis

The concentrations of ammonia and nitrate were determined by spectrophotometer (DR/4000U Spectrophotometer, USA) by standard methods (Clesceri and Eaton, 1998). Nitrite was analyzed by ion chromatography (Yokogawa IC7000, AS9-HC column). Total nitrogen (T-N) was determined with a T-N, T-P autoanalyzer (Autoanalyzer 3, Bran+Luebbe). Dissolved copper and zinc contents in the filtered samples were detected using plasma emission spectrophotometer equipment (ICAP-575, Jareruasshu). Surface morphology of electrodes was characterized *ex-situ* by atomic force microscopy (AFM) (Digital Instruments, DimensionTM3000, USA). Mono-, di- and tri-chloramines were determined by the colorimetric DPD method (Clesceri and Eaton, 1998). All the other analyses were done according to standard methods (Clesceri and Eaton, 1998).

Results and discussion

Influence of NaCl dosages

In the present experiment, as NaCl plays an important role on not only the ammonia oxidation rate but also the formation of the by-product nitrate, the performance of electrochemical ammonia oxidation with different NaCl dosage was investigated.

Figures 1 and 2 were the concentrations of ammonia-N and nitrate-N concerning time. Figure 3 was oxidation rate of ammonia with varied chloride concentration.

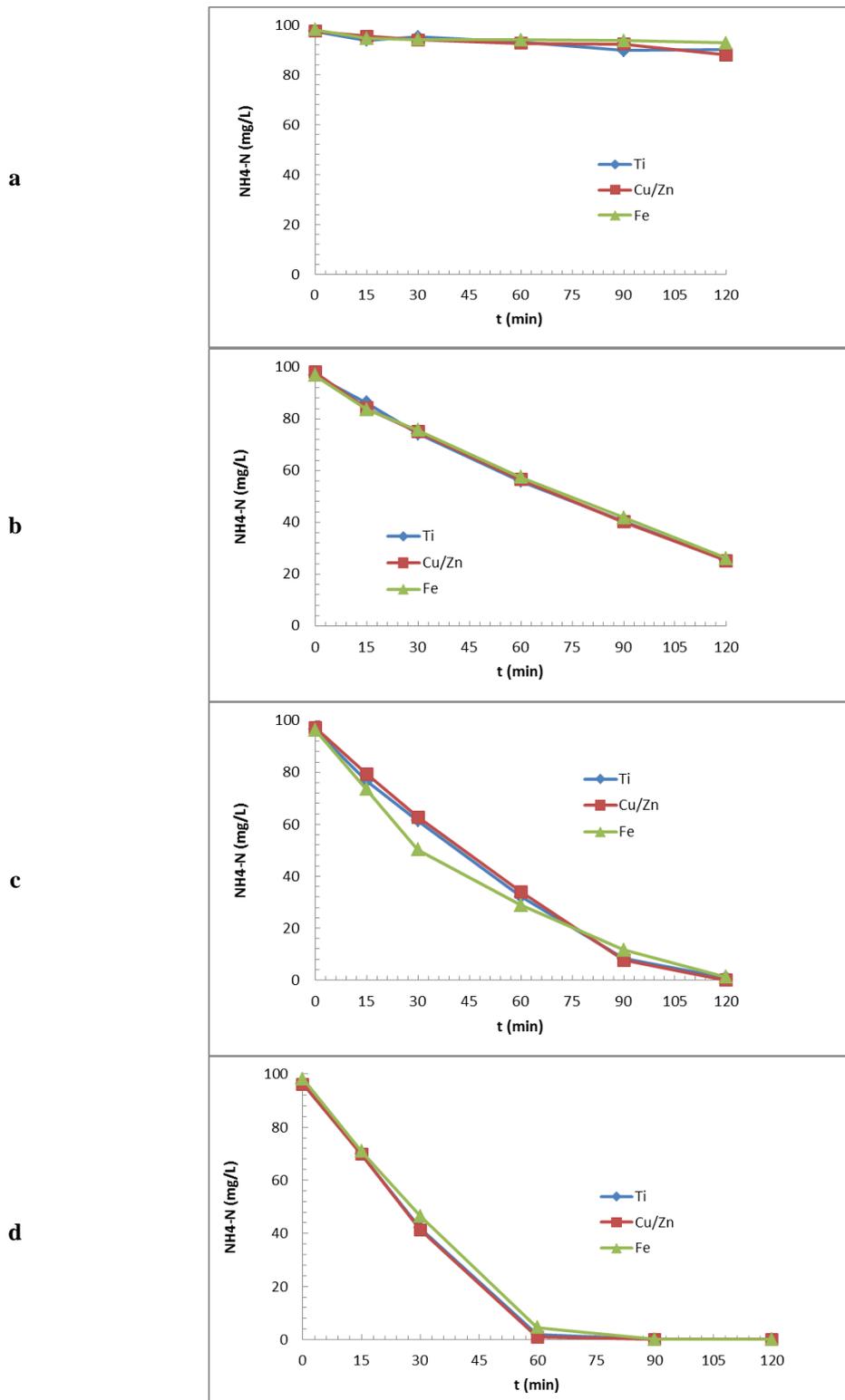


Figure 1. Concentration of ammonia with respect to reaction time. Anode: Ti/IrO₂-Pt, cathode: Ti, Fe, Cu/Zn, 30.0 mA/cm² at 0 (a), 0.5 (b), 1.0 (c), 2.0 (d) g/L of NaCl, respectively

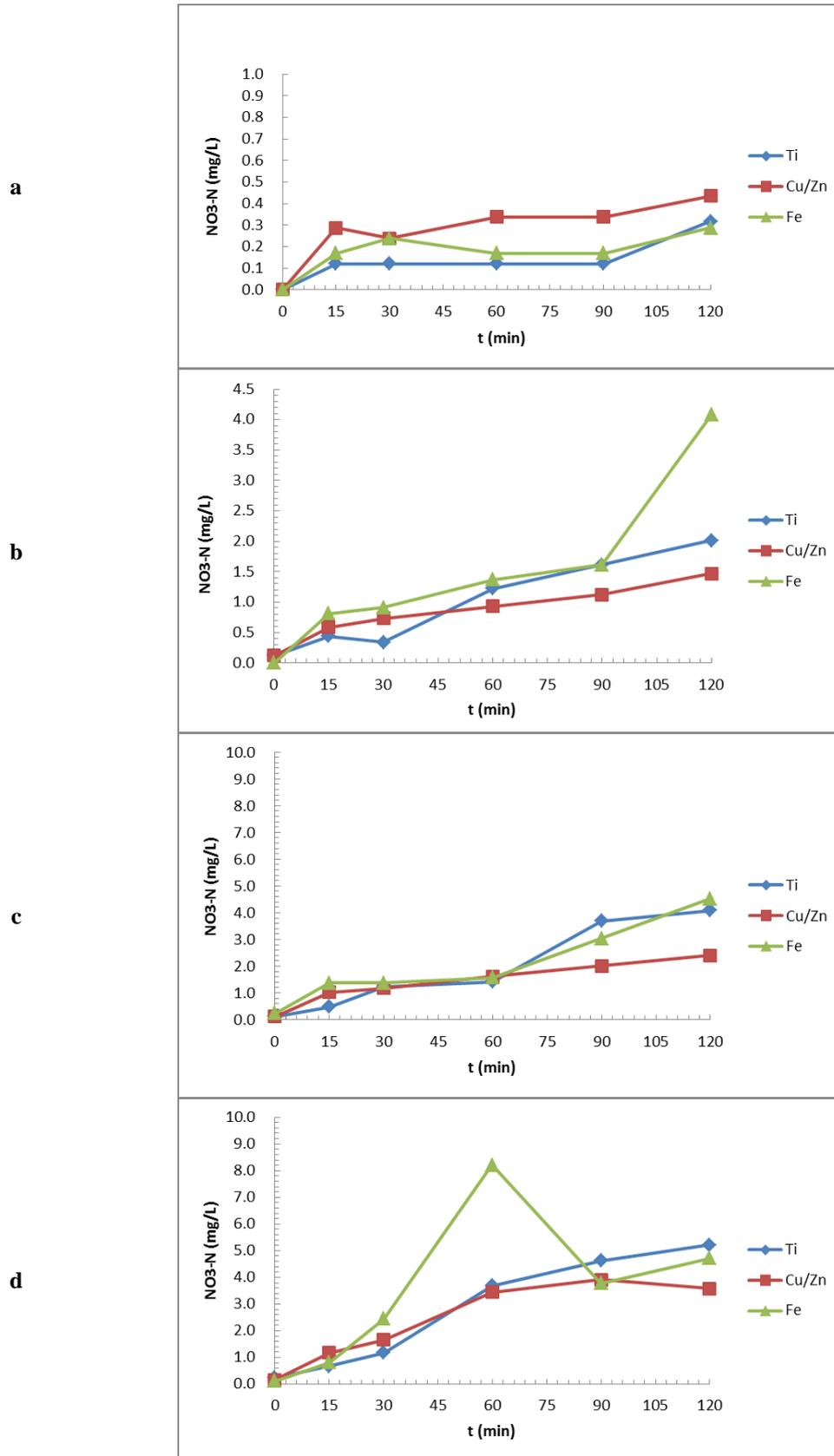


Figure 2. Concentration of nitrate with respect to reaction time. Anode: Ti/IrO₂-Pt, cathode: Ti, Fe, Cu/Zn, 30.0 mA/cm² at 0 (a), 0.5 (b), 1.0 (c), 2.0 (d) g/L of NaCl, respectively

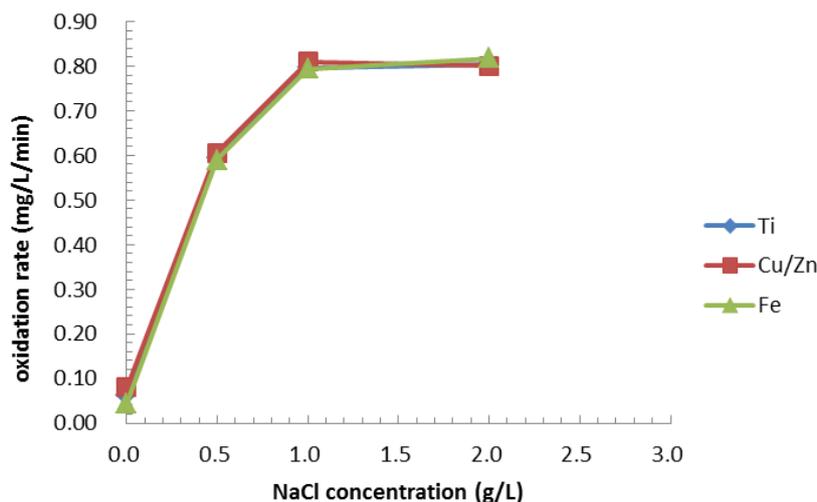
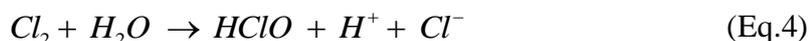


Figure 3. Influence of NaCl concentrations on the ammonia oxidation rate. Anode: Ti/IrO₂-Pt, cathode: Ti, Fe, Cu/Zn, 30.0 mA/cm², respectively

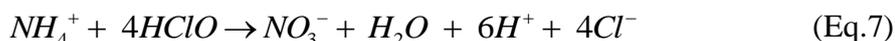
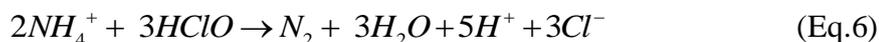
The results showed that without chloride ion, the ammonia removal efficiencies were 0.08, 0.1 and 0.05 with Ti, Cu/Zn and Fe as cathode employed, respectively. Meanwhile, the different amounts of nitrate formation during the electrochemical oxidation of ammonia can be attributed to the difference of the cathodes in the absence of NaCl, in which Cu/Zn cathode showed the lowest by-product formation. Cupro-zinc materials were well-known for their good corrosion resistance. Moreover, zinc has a good electroactivity while copper displays a good activity of electroreduction. As a result, a synergistic effect of alloying Zn with Cu could be expected. From the observed results, it can be concluded that Cu/Zn cathode is more suitable for ammonia removal than Ti and Fe cathodes in the absence of NaCl because of its high selectivity for ammonia oxidation to nitrogen gas. The effect of varying Cl⁻ concentration on ammonia-N and nitrate-N removal was also shown. The results indicated that these three cathodes exhibited almost the same performance of ammonia removal after 60 min electrolysis under NaCl addition. In the presence of 0.5 g/L NaCl after 120 min electrolysis, ammonia-N decreased from 100 mg/L to 25.4 mg/L, 25.3 mg/L and 26.1 mg/L respectively with Ti, Cu/Zn and Fe as a cathode. It is clear that the ammonia-N was significantly decreased compared with that in the absence of NaCl, which proved the key role of indirect oxidation during electrochemical oxidation of ammonia (Deng and Englehardt, 2007). Meanwhile, nitrate-N increased from 0 to 2.0 mg/L, 1.5 mg/L and 4.0 mg/L respectively, and no nitrite was detected through the experiments. In the presence of 1.0 g/L and 2.0 g/L NaCl, the ammonia decreased sharply, implying that in the presence of chloride ions, hypochlorite ions may be formed and then oxidize the ammonia and by-product presumably to nitrogen gas (Li et al., 2009) as listed in Equations 3–7.

For the indirect oxidation, in the presence of chloride ion, oxidizing hypochlorite ion will be formed during the electrolysis





The hypochlorite acid formed during the electrolysis would efficiently oxidize the ammonia, which is assumed to be oxidized into nitrogen gas and nitrate.



Stated, above 90% of removed ammonia was assumed to transform into N₂ gas with NaCl addition, which was similar to another report (Kim et al., 2005). The production of N₂ could be calculated as equal to the loss of N element according to the N conservation law (Xiao et al., 2009). Simultaneously, intermediate nitrate ions were formed in the water. On the contrary, the by-product formation had different results. The nitrate formation could come from not only the indirect oxidation of ammonia by HClO but also by hydroxyl radicals. The by-product formation generated by Ti and Fe increased during electrolysis while it increased for the first period and then decreased finally under Cu/Zn cathode condition. As Cu/Zn cathode exhibited high reduction ability, the NO₃⁻ concentration was the lowest. Mácová and Bouzek (2005) found that brass is containing Zn higher than 35 wt. % and lower than 41 wt. % will significantly influence the kinetics of current density, and higher electrocatalytic activity of Cu/Zn than both Cu and Zn was observed.

It can be concluded that ammonia oxidation rate was increased with the increased dosage of NaCl, while nitrate formation was different with various cathodes, which suggested that the cathode and chloride ion concentration can be optimized in the ammonia solution during electrolysis process with effective ammonia removal and relatively low amount of by-products left in the solution. Therefore, the electrochemical process in the presence of chlorides showed a higher capacity and selectivity in ammonia transformation into nitrogen gas (Xiao et al., 2009) In this study, the optimum NaCl concentration was 1.0 g/L and the best cathode was Cu/Zn cathode. As the combination of Ti/IrO₂-Pt anode and Cu/Zn cathode showed a good performance for ammonia oxidation, the influence of several other factors, such as current density initial pH and temperatures were also studied.

Influence of current density

Figure 4 shows that current density had some effect on the removal of ammonia and the nitrate-N production. In this work, current densities ranged from 5.0 mA/cm² which is the minimum required to achieve effective oxidation of ammonia (Cossu et al., 1998).

The ammonia concentration decreased from 100.0 mg/L to 80.9 mg/L, 59.3 mg/L, 23.2 mg/L, 0.0 mg/L in 120 min respectively (*Fig. 4a*). This observation is in agreement with the previous report that an increase in current density improves ammonia-N treatment efficiencies under the same charge loading. The possible reason is that the increased current density during electrochemical oxidation could enhance chlorine generation, which was responsible for subsequent removal of pollutions (Deng et al., 2007).

Figure 4b shows the variation of nitrate-N during electrolysis at different current densities. The final concentration of nitrate-N decreased with the increase of current

density. The nitrate-N increased from 0 to 2.6 mg/L, 2.4 mg/L, 1.3 mg/L, 2.4 mg/L, 3.3 mg/L and 2.8 mg/L in 120 min, respectively. Ammonia oxidation rate has been reported to be linearly by current density (Vanlangendonck et al., 2005), which is in agreement with the present experiments. A similar tendency was obtained in the present experiments. At lower current density, less amount of hypochlorite acid was produced, which was not enough to oxidize all the ammonia present in the solution.

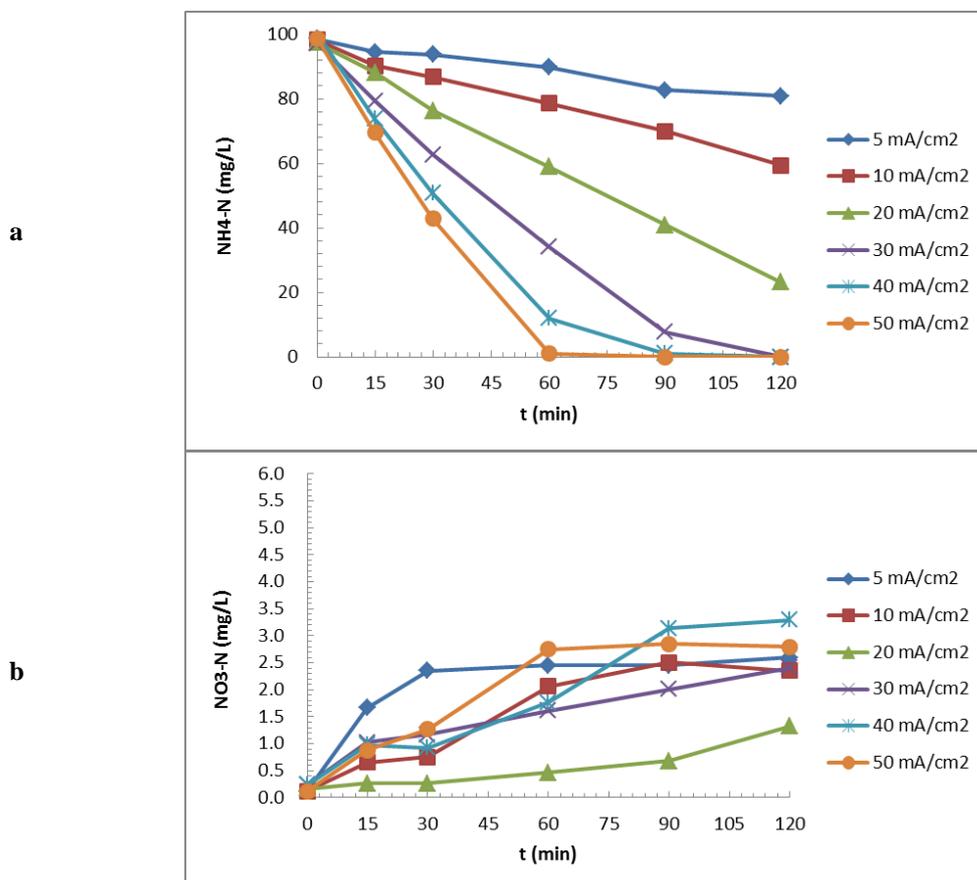


Figure 4. The concentration of ammonia (a) and nitrate (b) concerning reaction time at different current densities. Anode: Ti/IrO₂-Pt, cathode: Cu/Zn, 1.0 g/L NaCl

And from *Figure 5*, the ammonia oxidation rate almost increased with current density increased from 5.0 to 50.0 mA/cm². This enhancement could be attributed to more chlorine generated responsibly for subsequent removal of pollutions (Deng et al., 2007).

The impact of current density on both ICE and ACE during electrolysis are also investigated (data not shown). At a higher current density, the ICE and ACE decreased rapidly as the duration of electrolysis increased. Initially, the ammonia concentration and chloride ion concentration were high, and the electrical energy was mainly consumed by the ammonia oxidation. With the electrolysis progressed the electrical energy was mainly consumed by oxygen evolution and chlorate formation, thus resulting in a decrease in current efficiency.

Therefore, in the present experiments, to remove all of the ammonia with the consideration of ACE and ICE, the optimum current density was determined at 30.0 mA/cm².

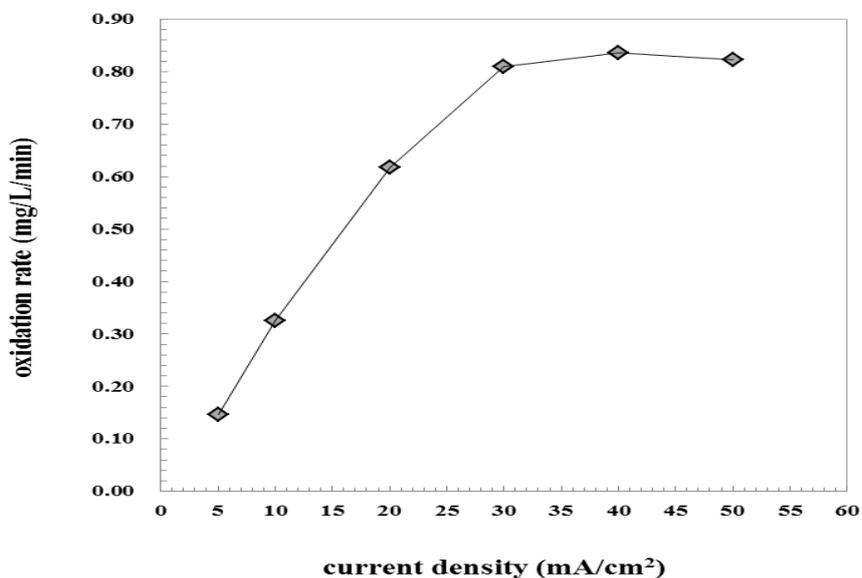


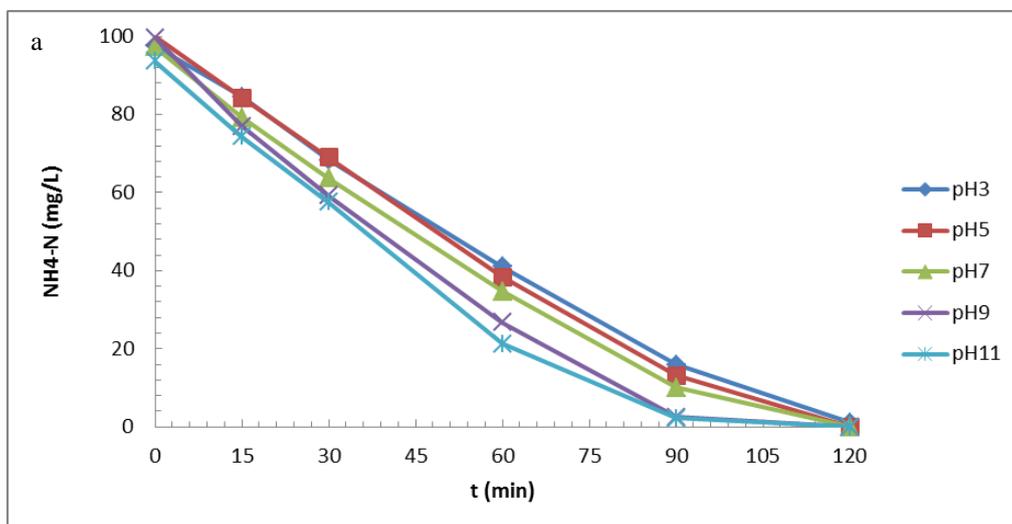
Figure 5. Effect of current density on ammonia oxidation rate under 1.0 g/L of NaCl condition

Influence of initial pH

Figures 6 and 7 present the ammonia oxidation rate under different initial pH conditions. Initial pH of 3, 5, 7, 9 and 11 were tested.

The ammonia decreased from 100.0 mg/L to 1.0 mg/L and 0 mg/L in 120 min, respectively under initial pH 3.0, 5.0, 7.0, 9.0 and 11.0 conditions. The oxidation rates were almost 0.8 mg/L/min.

The results of one-way analysis of variance ($p = 0.991$ for NH₄-N and 0.541 for NO₃-N, > 0.05 , data not shown) confirmed that electrochemical treatment is independent of initial pH. This result agrees with Lin and Wu (Lin and Wu, 1996), but different from Kapałka et al. (2010b, 2011).



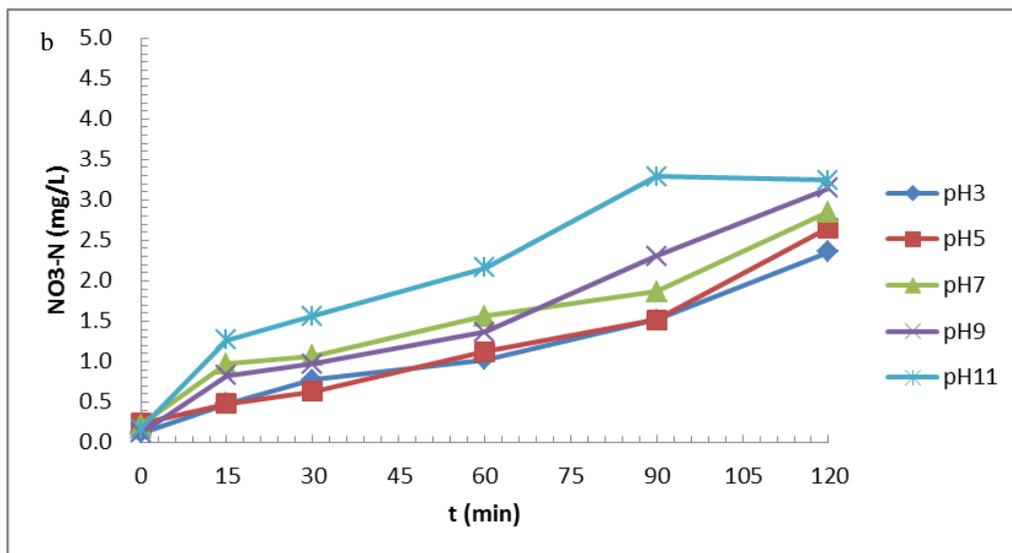


Figure 6. The concentration of ammonia (a) and nitrate (b) VS time at different initial pH. Anode: Ti/IrO₂-Pt, cathode: Cu/Zn, 1.0 g/L NaCl, 30.0 mA/cm²

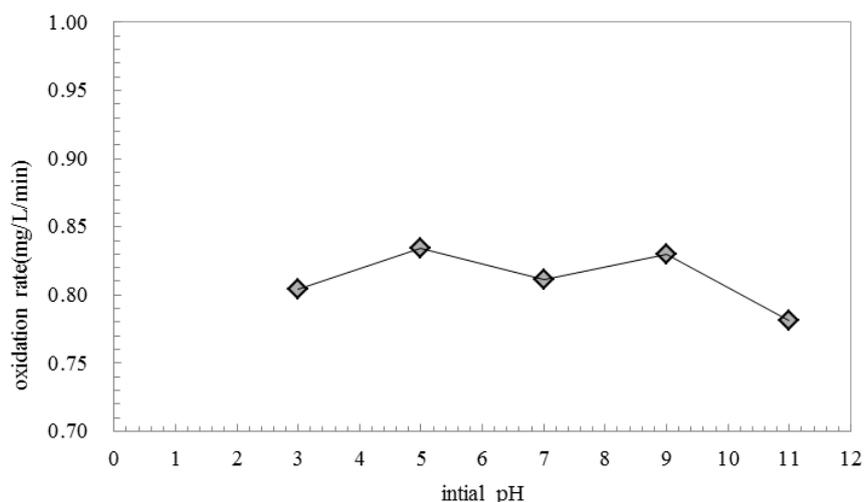


Figure 7. Electrochemical NH₄⁺-N removal as a function of pH under a current density of 30.0 mA/cm² and 1.0 g/L of NaCl

Which can be explained by previously report, in a weak alkaline environment, the circulation of $\text{Cl}^- \rightarrow \text{Cl}_2 \rightarrow \text{ClO}^- \rightarrow \text{Cl}^-$ could be formed, making efficient use of chlorine. In a strong alkaline environment, ClO_3^- was present and competes with Cl^- for electrons, decreasing the removal rate (Wang, 2000). The mechanism for the ammonia removal at anode was like the “breaking point reactions” and a stepwise process, and the reaction at cathode was hydrogen evolution reaction.

Influence of temperature

Figure 8 shows the variation of ammonia-N and nitrate-N during electrolysis at different temperature control conditions. As it was difficult to maintain high temperature throughout experiments, the temperature was only set to be at uncontrolled

and 25.0 °C. Under the uncontrolled temperature condition, the temperature of the treated solution increased from 25.0 to 41.2 °C after 120 min electrolysis with all of the ammonia being destroyed. Under the controlled temperature (25.0 °C) condition, ammonia oxidation was a little slower. This was mainly due to different pH changes in the electrolyte at different temperatures during the electrolysis (data not shown). The pH varied because of the various reactions occurred during ammonia oxidation process. Moreover, increasing temperature could increase the rate of diffusion and the capability of adsorption. Consequently, the ammonia oxidation rate increased when the temperature was increased from 25.0 to 41.2 °C.

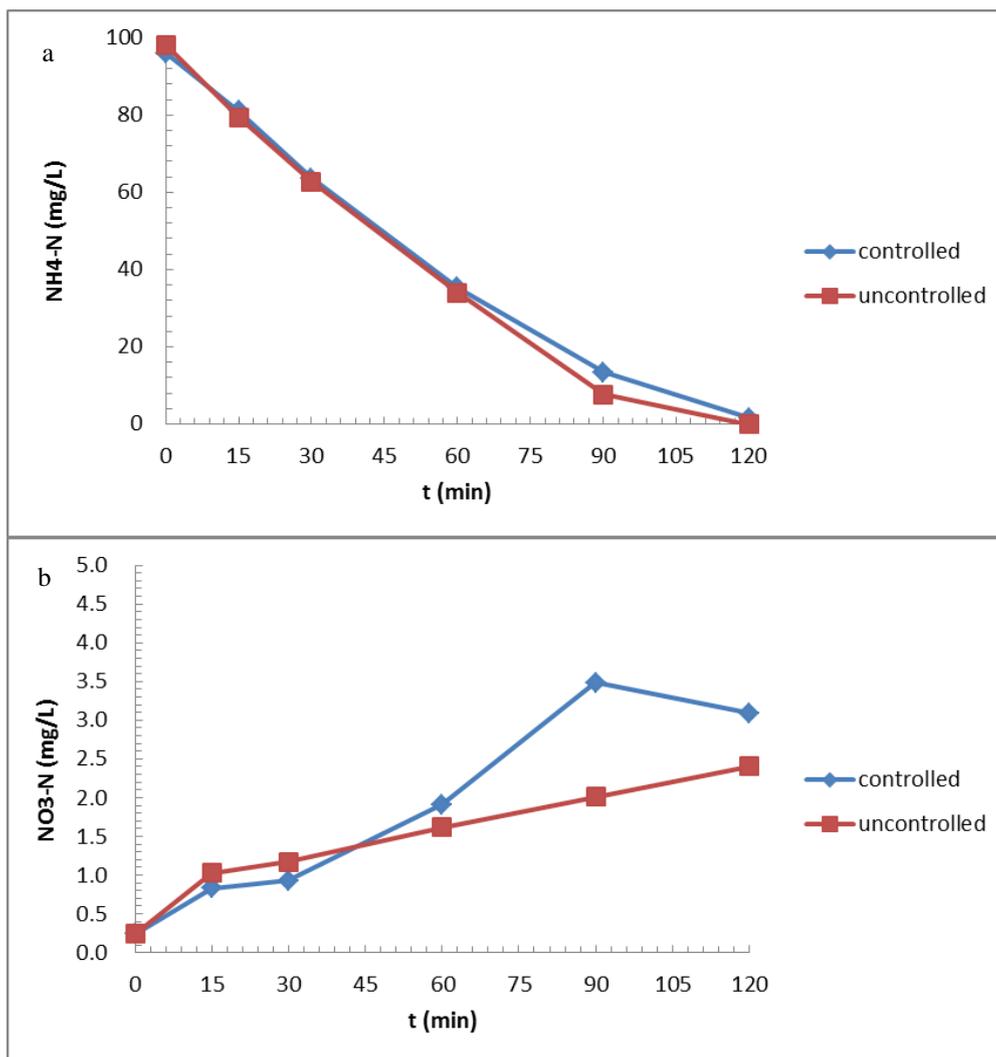


Figure 8. The concentration of ammonia (a) and nitrate (b) concerning time at temperature control methods. Anode: Ti/IrO₂-Pt, cathode: Cu/Zn, 1.0 g/L NaCl, 30.0 mA/cm². The final temperature of the uncontrolled condition is about 41.2 °C

In addition, ammonia in aqueous solution can exist in two forms: un-ionized form (NH₃) and/or ionized form (NH₄⁺) (Körner et al., 2001). Compared these two forms of ammonia, the unionized one is much easier to be oxidized. These two forms of ammonia established an equilibrium following Equation 8 (Lin and Wu, 1996).



Under the uncontrolled condition, with increasing temperature, larger amount of NH_3 formed then subsequently oxidized on the electrode, which also increased ammonia oxidation rate.

The enhancement of ammonia oxidation could also be attributed to either the accelerated diffusion of ammonia from the bulk solution through the diffusive layer to the electrode surface (mass-transfer effect) or the rapid electro-oxidation reactions (activation effect).

In general, increasing temperature could enhance ammonia oxidation rate in several ways; the uncontrolled condition was a little favorable for electrochemical oxidation of ammonia.

Mass balance of nitrogen

Under the optimal condition, the mass balance of nitrogen in each treatment system is shown in *Figures 9 and 10*. The initial mass of ammonia nitrogen in the solution was 100 mg/L. The concentrations of ammonia, nitrite, nitrate and chloramines were determined during the electrolysis as listed in *Table 1*. It can be seen that the ratio of ammonia transferred into nitrogen gas was the highest in Cu/Zn cathode system, 97.34% and the others were 94.91% 94.38% in Ti and Fe cathode systems, respectively. This result indicated that the activity of the Cu/Zn electrode is relatively higher concerning the oxidation of ammonia ions and reduction of nitrate and nitrite.

Table 1. Final concentrations of N species under different cathode conditions with 30.0 mA/cm² and 1.0 g/L NaCl in 120 min

Cathode	Nitrate-N (mg/L)	Nitrite-N (mg/L)	Chloramine-N (mg/L)	Ammonia-N (mg/L)
Cu/Zn	2.40	0.00	0.24	0.00
Ti	4.08	0	0.24	0.92
Fe	4.52	0	0.00	1.16

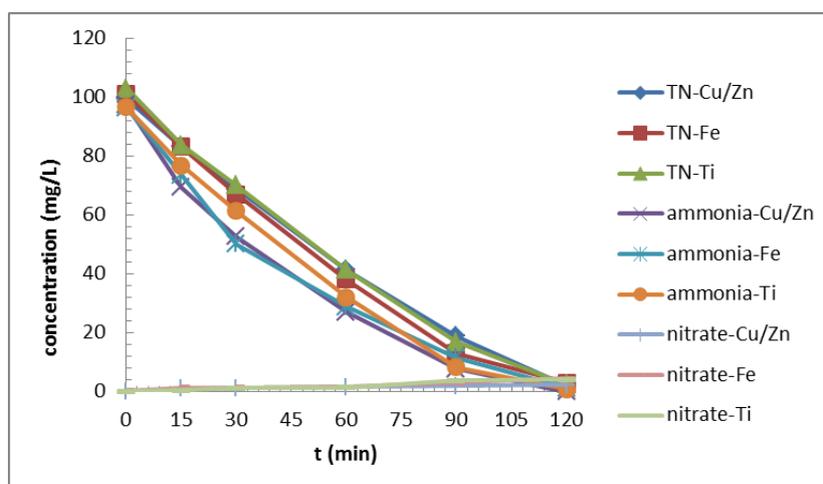


Figure 9. The concentration of TN, ammonia-N and nitrate-N concerning time. Anode: Ti/IrO_2 -Pt, cathode: Cu/Zn, Ti and Fe, 1.0 g/L NaCl, 30.0 mA/cm²

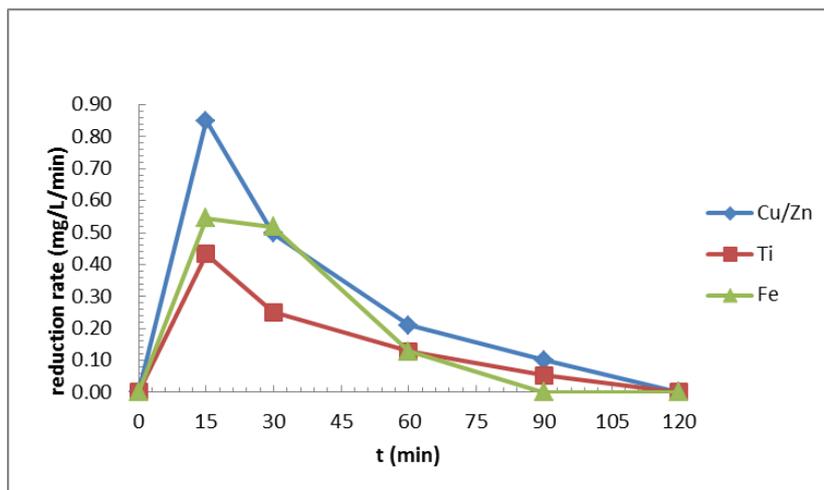


Figure 10. Reduction rate concerning time. Anode: Ti/IrO₂-Pt, cathode: Cu/Zn, Ti and Fe, 1.0 g/L NaCl, 30.0 mA/cm²

Kinetic studies

$$\ln \left(\frac{[NH_4^+ - N]_0}{[NH_4^+ - N]_t} \right) = K_t \quad (\text{Eq.9})$$

where $[NH_4^+ - N]_0$ and $[NH_4^+ - N]_t$ respectively correspond to the initial ammonia concentration and the concentration after a period of reaction, and K is the reaction rate constant.

Application of Equation 9 to the experimental data produces straight line plots as shown in Figure 11. These data can be represented by pseudo first-order kinetics. However, when the NaCl concentration is at low levels (0.0 g/L, 0.5 g/L), the fitness was not good, possibly caused by diffusion and consumption of Cl⁻ ions during the electrochemical process.

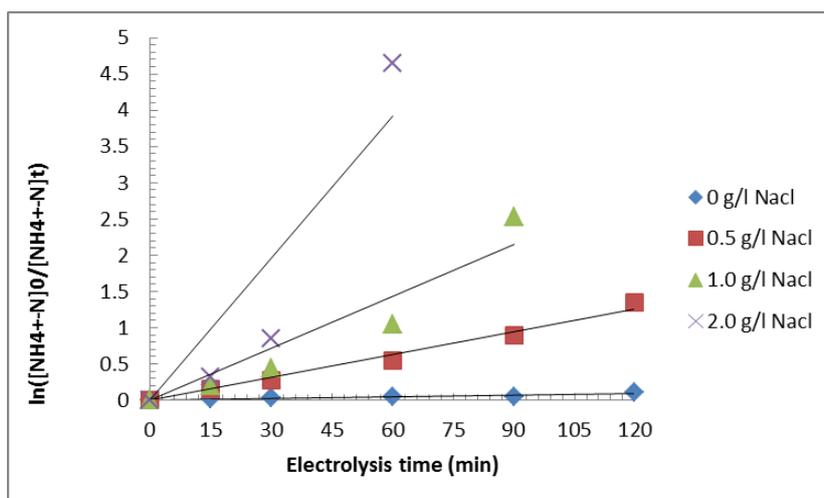


Figure 11. Pseudo-first-order kinetic model of the electrochemical treatment data, with a current density of 30.0 mA/cm²

The kinetic rate coefficients were determined from the slopes of the straight lines under each set of operating condition (data not shown). The values of the kinetic rate coefficients obtained at different NaCl concentrations ranged between 0.01-0.07 min⁻¹. Higher values of correlation coefficients ($R^2 = 0.84-0.98$) confirmed the hypothesis of the pseudo first-order reaction of ammonia oxidation. The result also indicated that ammonia could be completely removed if appropriate conditions provided.

Analysis of electrode surfaces and the electrochemical solution

Analysis of the electrolyte after electrolysis for 2 h at the current density of 30.0 mA/cm² revealed that the concentrations of copper and zinc in the electrolyte were less than 0.2 and 1.5 mg/L, respectively, which are allowable limits for National Secondary Drinking Water Regulations (EPA 816-F-09-0004, May 2009). The low concentrations of Cu and Zn observed in the solutions may be attributed to limited corrosion of the electrodes under constant potential conditions.

As Ti/IrO₂-Pt anode and Cu/Zn cathode system had the best performance for ammonia oxidation in the presence of NaCl; the AFM investigation was carried out. The surface roughness of the anode had no change after electrolysis, implying that the Ti/IrO₂-Pt anode was stable for ammonia oxidation.

Conclusions

In this work, we have investigated the electrochemical ammonia removal system. To complete electrochemical oxidize of ammonia and reduce the formation of by-products, cathodic reduction of by-products, and anodic oxidation of ammonia was investigated in an undivided cell using Ti/IrO₂-Pt plate as an anode and three plates as a cathode for treatment of the synthetic ammonia solution respectively. It can be concluded:

(1) The ammonia-N decreased from 100.0 mg/L to 0.0 mg/L in the presence of 1.0 g/L NaCl after 120 min electrolysis at the current density of 30.0 mA/cm² with Cu/Zn cathode and Ti/IrO₂-Pt anode. No nitrite was detected in the treated solutions. Dissolved copper and zinc were 0.2 mg/l and 1.5 mg/l, respectively. The concentration of chloramine was 0.24 mg/l. About 97.34% of initial TN was transformed into nitrogen gas in Cu/Zn system, indicating that Cu/Zn cathode has good performance on by-production reduction.

(2) Initial pH had no obvious effect on electrochemical ammonia removal.

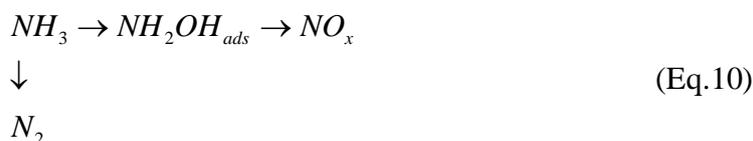
(3) Cu/Zn cathode possessed the highest ammonia oxidation rate (0.81 mg/L/min) and reduction rate of by-product (0.849 mg/L/min). The ammonia oxidation rates with Cu/Zn cathode was higher than that with Ti and Fe cathode. The nitrate formed during electrolysis with Cu/Zn was the lowest than that with other cathodes. The reason why the nitrate-N concentration was the lowest with Cu/Zn cathode was that because of its high reduction ability

(4) It was a little favorable for electrochemical oxidation of ammonia under uncontrolled temperature condition.

(5) The data obtained from the experiments could be represented by pseudo first-order kinetics.

From above, the mechanism of ammonia electro-oxidation on Cu/Zn cathode and Ti/IrO₂-Pt anode and formation of N₂ as a final product was indicated, that ammonia is

oxidized through several steps to various nitrogen compounds, which was in accordance with previous reports, as *Equation 10*.



In the present study, the ammonia was completely removed with less amount of by-products using Cu/Zn cathode and Ti/IrO₂-Pt anode electrochemical system.

Present experiments confirmed that the order of oxidation ability of those two anodes was Ti/IrO₂-Pt > Ti/RuO₂-Pt. The possible reasons are listed as follows:

(1) High oxidation ability of the Ti/IrO₂-Pt lead to more amounts of hydroxyl radicals and hypochlorite ion formed than at Ti/RuO₂-Pt anode, and they could lead to the passivation of the cathode, which resulted in the slightly lower ammonia oxidation rate.

(2) As it is likely that, the presence of Cl⁻ ions affected the performance of each electrode. Experimental data showed that the higher oxidant generation of FAC (Free available chlorine) under Ti/IrO₂-Pt anode condition than the other anode was particularly observed.

(3) On the other hand, previous studies indicated that EAN (anode potential) of Ti/IrO₂-Pt electrode was lower and electrocatalytic activity toward chlorine evolution was higher which was confirmed by Szyrkowicz et al. (2005).

In general, Ti/IrO₂-Pt anode had highest oxidation ability by various pathways, which combined with Cu/Zn cathode exhibited good performance on ammonia oxidation that could be employed for practical use in the future.

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