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ORIGINAL PAPER

Electrochemical treatment of ammonia in wastewater by RuO_2–IrO_2–TiO_2/Ti electrodes

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Abstract This study investigated the removal of ammonia in wastewater by an electrochemical method using titanium electrodes coated with ruthenium and iridium (RuO_2–IrO_2–TiO_2/Ti) with low chlorine evolution overvoltage. The effects of operating parameters, including chloride ion concentration, current density and initial pH, were also investigated. The results were evaluated primarily by considering the efficiency of the elimination of NH_4^+-N. The removal of ammonia by electrochemical oxidation mainly resulted from the indirect oxidation effect of chlorine/hypochlorite produced during electrolysis. The direct anodic oxidation efficiency of ammonia was less than 5%, and the current efficiency was less than 10%. The ammonia removal followed pseudo-first-order kinetics. The electrochemical process can be applied successfully as a final polishing step, or as an alternative method to biological nitrification. The process seems to be most beneficial for small coastal cities

Keywords Ammonia removal · Current efficiency · Electrochemical treatment · Kinetics · Indirect anodic oxidation · RuO_2–IrO_2–TiO_2/Ti electrode

1 Introduction

Due to the worldwide emphasis on the eutrophication problem, especially in lakes and recreational areas, the discharge of ammonia-containing wastewater into aquifers is of major concern. Well-developed methods such as biological processes, air stripping, and breakpoint chlorination have been applied to remove ammonia from some domestic and industrial wastewaters [1]. Unfortunately, nitrification is not only easily inhibited by the toxicity of industrial wastewater [2–4], but it is also very sensitive to temperature variation [5]. The synergic effect of low temperature and the presence of inhibitory substances prevent the nitrification of industrial wastewaters even at 15–16 °C, a temperature at which nitrification of domestic wastewater still proceeds well. With air stripping or the breakpoint chlorination method [6], however, the large increase in total dissolved solid (TDS) in the resultant treated water reduces the possibility of water reuse. Water reuse has become an important issue in the field of pollution control.

Due to the shortage of fresh water, seawater has been used for cooling and sanitation in many coastal cities. This approach increases the chloride content, as well as the salinity and conductivity in wastewater. This presents favourable conditions for using electrochemical oxidation for wastewater treatment, a method that has proved promising in recent years. Many pollutants, including ammonia and organic impurities, can be effectively removed by direct or indirect anodic oxidation. The electrochemical oxidation process is very efficient for the destruction of refractory pollutants such as cyanide [7], EDTA [8], aniline [9], 2-naphthol [10], phenol [11], and nitrogen compounds such as nitrate or nitrite ions [12]. However, there are few studies on electrolytic decomposition characteristics for ammonia removal.

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In general, pollutants can be decomposed electrochemically by direct or indirect oxidation processes [13, 14]. In an investigation of the direct oxidation of ammonia on platinum and titanium platinized anodes, Marinerc and Lectz [15] found that this reaction proceeded well on a platinum anode. Direct oxidation can be expressed by the following equation:

$$2NH_3 + 6^{\bullet}OH \rightarrow N_2 + 6H_2O + 6e^- \tag{1}$$

Indirect anodic oxidation can be applied to wastewater containing a high concentration of chloride ions. In this case, free chlorine, a strong oxidizing agent produced on the anode, reacts with many compounds present in the wastewater. As is well known, free chlorine reacts with ammonia to produce nitrogen as a final product (breakpoint chlorination) [16]. The overall reaction can be expressed as follows:

$$2NH_4^+ + 3HClO \rightarrow N_2 + 3H_2O + 5H^+ + 3Cl^- \tag{2}$$

COD and ammonia can be removed simultaneously by indirect oxidation during electrolysis and the removal of ammonia is the dominant reaction in this method [17–18].

Since the anodic oxidation of chloride occurs readily, indirect oxidation may take place during the electrochemical oxidation process for wastewater treatment. However, the chloride effect is often ignored and so little research has been performed on this aspect [17]. As a result, it is not clear whether the ammonia in wastewater is removed mainly by indirect oxidation or by direct anodic oxidation at a chlorine evolving anode in an electrochemical process. This paper presents the results of a study on the electrochemical treatment of ammonia in wastewater.

The effects of operating parameters, including chloride ion concentration, current density and initial pH, during the treatment of ammonia-containing wastewater (about 40 mg L^{-1}) were studied. A titanium electrode coated with ruthenium and iridium (RuO_2–IrO_2–TiO_2/Ti) with low chlorine evolution over-voltage was used. The results were evaluated primarily by considering the efficiency of the elimination of NH_4^+-N. A tentative description of the kinetics of NH_4^+-N elimination is presented.

2 Materials and methods

2.1 Materials

The raw wastewater used in the experiment was a synthetic mixture of ammonium sulfate and saline water and was prepared by dissolving an appropriate amount of ammonium sulfate in tap water. The salinity of the sample wastewater was adjusted by adding a suitable amount of table salt. The ammonia in the water was kept constant at about 40 mg L^{-1}, which is approximately the concentration of ammonia in municipal wastewater. The chloride ion concentration varied from 0 to 400 mg L^{-1}.

2.2 Apparatus

The experiments were conducted in a 2-L Plexiglass batch electrolytic cell, rectangular in shape (15×14.5 cm^2) and 15 cm in height. The cell was equipped with a magnetic stirrer in order to keep the electrolyte well mixed. Power was provided by a DC power supply (WYK—3010, EAST GROUP, China) with current-voltage monitoring and a maximum output of 10 A-30 V. The anode was prepared by coating a titanium screen with ruthenium and iridium (RuO_2–IrO_2–TiO_2/Ti). A titanium screen was used as the cathode. The total effective surface area of the anodes was 480 cm^2, which was calculated according to the equation of Alexeyev [19]. The current density was based on this area. Both the anodes and cathodes were placed vertically and were parallel to each other. The electrodes were fixed at 2 cm above the cell bottom. The inter-electrode gap was kept constant at 5 mm.

2.3 Methodology

The batch experiments were carried out under various operating conditions, including initial chloride ion concentration, current density and initial pH. Each experiment was a batch operation and lasted 3 h. Samples were taken from the reactor at intervals.

The ammonia was determined by the Nessler method [20].

The NH_4^+-N method was used to determine the current efficiency. In this method, the concentration of NH_4^+-N was measured during the electrolysis. The average current efficiency (ACE) and the instantaneous current efficiency (ICE) were calculated using the following equations, respectively [21–22]:

$$\mathrm{ACE} = \frac{3\left[\left(NH_4^+ \text{ - } N\right)_0 - \left(NH_4^+ \text{ - } N\right)_t\right]FV}{14It} \tag{3}$$

$$\mathrm{ICE} = \frac{3FV}{14I}\frac{\left[\left(NH_4^+ \text{ - } N\right)_t - \left(NH_4^+ \text{ - } N\right)_{t+\Delta t}\right]}{\Delta t} \tag{4}$$

where $(NH_4^+\text{-}N)_0$, $(NH_4^+\text{-}N)_t$ and $(NH_4^+\text{-}N)_{t+\Delta t}$ are the concentration of NH_4^+-N (g L^{-1}) at times zero, t and $t + \Delta t$ (s), respectively, I is the current density (A), F is the Faraday number (96,485 C mol^{-1}), t is the time (s), 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^{-1}).

3 Results and discussion

3.1 Effects of various operating conditions

The oxidation time depends on the stability and concentration of compounds, concentration of NaCl, temperature, solution pH, anode size, current and voltage [23]. The electrochemical reactions during electrolysis are complicated and are not entirely known.

3.1.1 Chloride ion concentration

The ammonia removal efficiency as a function of the chloride ion concentration and electrolysis time is demonstrated in Fig. 1. The current density was kept constant at 5 mA cm^{-2}, the initial pH was neutral and the water conductivity varied from 858 to 1,913 μS cm^{-1}. The efficiency of electrochemical oxidation of ammonia increased with chloride ion concentration and electrolysis time. Without chloride ion, the ammonia removal efficiency was less than 5% (from 37.9 to 36.6 mg L^{-1}) and the ammonia oxidation rate was nearly zero during the 3-h electrolysis. This indicates a very slow rate of direct electrochemical oxidation of ammonia using the Ru_2O–Ir_2O–Ti_2O/Ti anodes. However, a large decrease in ammonia concentration, from 38.6 to 3.1 mg L^{-1} (during 3 h of electrolysis), was observed with 400 mg L^{-1} chloride ion in the solution. This result indicates that the ammonia removal was primarily caused by indirect oxidation of the chlorine/hypochlorite formed during electrolysis [17, 24]. Since higher chlorine/hypochlorite production efficiency can be obtained at a higher chloride ion concentration, an increase in the chloride ion concentration enhances the effect of indirect oxidation. The mechanism for the removal of ammonia is similar to the “breakpoint reactions” (chlorine/hypochlorite reacts with ammonia to produce nitrogen as a final product). This indicates that the chloride ion plays a vital role in the electrochemical oxidation of ammonia when Ru_2O–Ir_2O–Ti_2O/Ti anodes are used. Figure 2 confirms the positive impact of the chloride ion concentration on the ammonia oxidation rate. The oxidation rate increased linearly within the tested range.

The direct electrochemical oxidation rate of pollutants is dependent on the catalytic activity of the anode, and the Ru_2O–Ir_2O–Ti_2O/Ti anodes used in this experiment are not suitable for direct electrochemical oxidation.

3.1.2 Current density

The effect of current density on ammonia removal was tested with the chloride ion concentration constant at 400 mg L^{-1}; the initial pH was neutral and the water conductivity was 1,990 μS cm^{-1}. As shown in Fig. 3, the ammonia concentration decreased with the increase in current density and electrolysis time. A current density less than 6 mA cm^{-2} was too low to produce an effective result. When the current density was higher than 6 mA cm^{-2}, the treatment was satisfactory, resulting in near-complete removal of ammonia in all experiment runs. When the current density was at 6 mA cm^{-2} 48.6% of ammonia removal efficiency was achieved in 60 min, and complete elimination of ammonia was achieved at 10 mA cm^{-2}. Figure 4 confirms the positive impact of the current density on the ammonia oxidation rate. The oxidation rate increased linearly within the tested range.

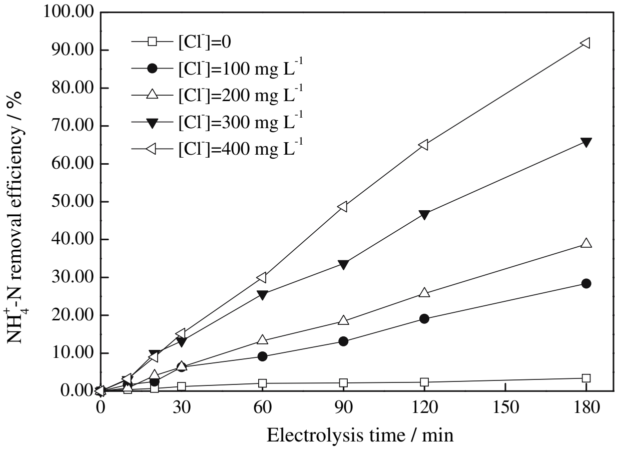

Fig. 1 Electrochemical NH_4^+-N removal as a function of chloride ion concentration, with a current density of 5 mA cm^{-2} and an initial pH of 7

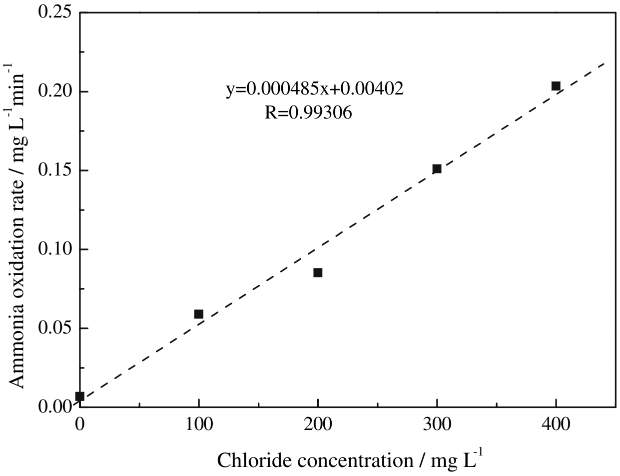

Fig. 2 Influence of chloride concentration on the ammonia oxidation rate, with a current density of 5 mA cm^{-2} and an initial pH of 7

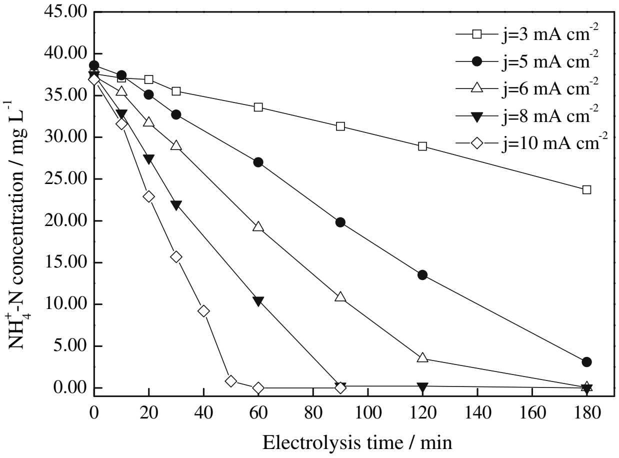

Fig. 3 Electrochemical NH_4^+-N removal as a function of the current density, with 400 mg L^{-1} chloride ion concentration, an initial pH of 7 and a conductivity of 1,990 μS cm^{-1}

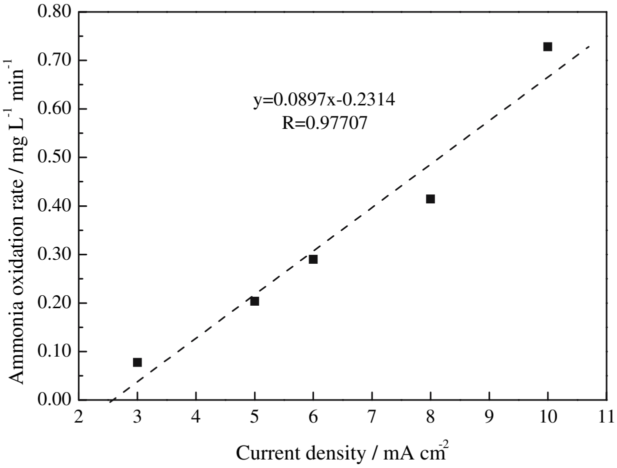

Fig. 4 Effect of current density on ammonia oxidation rate, with 400 mg L^{-1} chloride ion concentration, an initial pH of 7, and a conductivity of 1,990 μS cm^{-1}

3.1.3 *Initial pH*

Figure 5 presents the ammonia removal efficiency under different initial pH conditions during the electrochemical oxidation treatment of wastewater. Initial pH of 2.82, 5.22, 7, 9.03 and 10.51 were applied and the water conductivity values under these pH conditions were 3,010, 2,130, 2,000, 2,040 and 2,140 μS cm^{-1}, respectively. The initial pH, especially in neutral or moderate alkaline conditions, had an insignificant influence on the efficiency of ammonia removal. Under these conditions electrolysis was more efficient. This can be explained by the fact that in neutral to moderate solutions, a cycle of chloride–chlorine–hypochlorite–chloride occurred, causing the initial concentration of chlorides to remain stable. In strong alkaline solutions, the cycle of chloride–chlorine–chloride was blocked due to the production of ClO_3^-, which is a stable chlorate anion. At low pH, chlorides are reduced with the production of free chlorine; while at high pH, the chlorides are oxidized and chlorates are produced, consequently causing the loss of chloride ion. Therefore, only under neutral to moderate alkaline conditions does the initial concentration of chloride ion remain stable during the continuous production of free hydroxyl radicals [23], ensuring a high electrochemical oxidation rate (Fig. 6), and this results in good electrolysis.

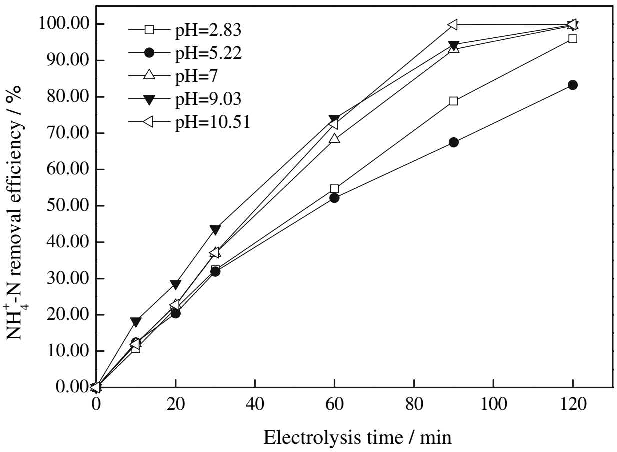

Fig. 5 Electrochemical NH_4^+-N removal as a function of pH with a current density of 8 mA cm^{-2} and 400 mg L^{-1} chloride ion concentration

The pH consistently dropped to about 2–3 after 2 h of electrolysis. The pH is influenced by both cathodic and anodic processes and also by the reactions of chlorine in water. However, the electrochemical oxidation process produces a mass of CO_2 when the wastewater contains a high COD, which keeps the electrolyte at a relatively steady pH.

3.2 Kinetic studies

It is assumed that the elimination of ammonia can be described by pseudo first-order kinetics. Its removal rate can be expressed as

$$d[\mathrm{NH}_4^+ \text{ - N}]/dt = -k[\mathrm{NH}_4^+ \text{ - N}] \tag{5}$$

In this equation, the gross effect of direct and indirect processes is considered without quantifying their relative contribution.

After integration the above equation gives

$$\ln\left([\mathrm{NH}_4^+ \text{ - N}]_0/[\mathrm{NH}_4^+ \text{ - N}]_t\right) = kt \tag{6}$$

where $[NH_4^+\text{-N}]_0$ and $[NH_4^+\text{-N}]_t$ correspond, respectively, to the initial ammonia concentration and the concentration after a period of time.

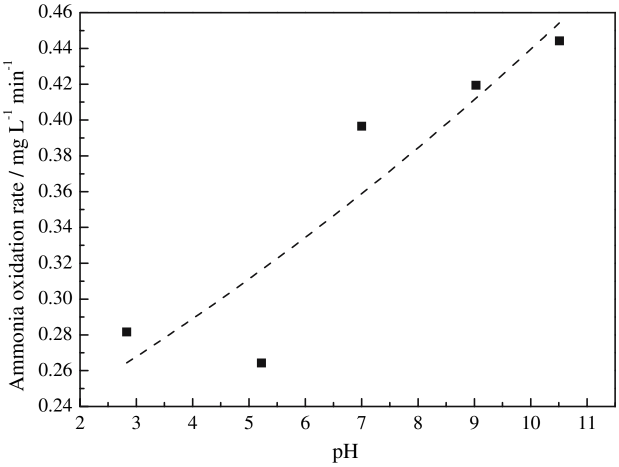

Fig. 6 Influence of the initial pH values with a current density of 8 mA cm^{-2} and 400 mg L^{-1} chloride ion concentration

Application of Eq. 6 to the ammonia elimination data produces straight line plots as shown in Fig. 7. These data can be represented by pseudo first-order kinetics. However, when the ammonia concentration is low, the fit is not good. One possible explanation may be that diffusion is the dominant process at low ammonia concentrations.

The kinetic rate coefficients were determined from the slopes of the straight lines under each set of operating condition. In Table 1, the values of the kinetic rate coefficients obtained at different chloride ion concentrations and current densities are presented with the calculated half lives (ln2/*k*). High values of correlation coefficients (above 0.9) confirmed the hypothesis of the pseudo first-order reaction of ammonia oxidation.

The ammonia removal efficiency increased as the chloride ion concentration and current density increased. Table 1 clearly shows that the ammonia could be completely removed when the chloride ion concentration and current density were appropriate. In the experiment with an initial concentration of ammonia of about 40 mg L^{-1}, a chloride ion concentration of 400 mg L^{-1}, a current density of 10 mA cm^{-2} and a neutral pH, the elimination of ammonia was completed in less than 60 min.

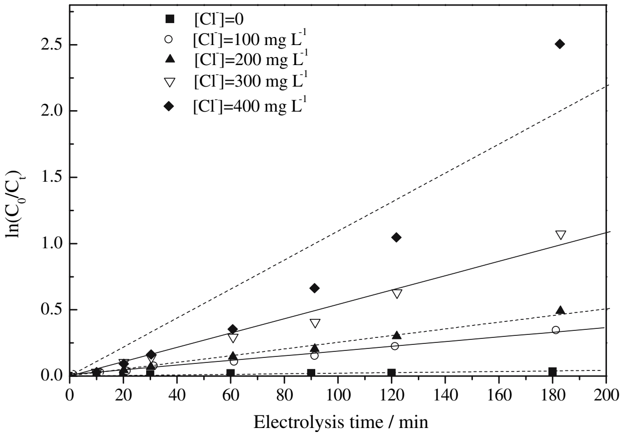

Fig. 7 Pseudo first-order kinetic model of the electrochemical treatment data, with a current density of 5 mA cm^{-2} and an initial pH of 7

3.3 Current efficiency (ICE and ACE)

The chloride concentration is critical for the formation of hypochlorite, as a higher concentration boosts chlorine production and indirectly affects the ammonia oxidation. Figures 8 and 9 show the impact of the chloride ion concentration on the instantaneous current efficiency (ICE) and the average current efficiency (ACE).

At a current density of 5 mA cm^{-2}, the ICE and ACE of the electrochemical oxidation of ammonia were very low (less than 10%). The ICE and ACE increased with increasing chloride ion concentration. The ACE fit linearly with the chloride concentration. The ICE and ACE were kept at low constant values during the duration of the electrolysis.

Increasing the current density is always an easy approach to speed up an oxidation reaction (Fig. 4), but it typically results in a decrease in both current efficiency and selectivity. Czarnetzki and Janssen [25] previously reported that a higher current density resulted in an increase in oxygen evolution and chlorate formation.

The impacts of current density on both the ICE and ACE during electrolysis are shown in Figs. 10 and 11. At low current density (less than 6 mA cm^{-2}), the ICE and ACE remained almost constant during electrolysis, which confirmed the results shown in Figs. 8 and 9. At a higher current density (more than 6 mA cm^{-2}), the ICE and ACE decreased rapidly as the duration of electrolysis increased (Fig. 12). Initially, the ammonia concentration and chloride ion concentration were high and the electrical energy was mainly consumed by the ammonia oxidation. As the duration of electrolysis increased the electrical energy was mainly consumed by oxygen evolution and chlorate formation, thus resulting in a decrease in current efficiency.

3.4 Anodic efficiency

The anode efficiency of the electrode measured in g NH_4^+-N removed per hour per square meter of the anode surface and per ampere applied (g NH_4^+-N_r h^{-1} m^{-2} A^{-1}) is shown in Figs. 13 and 14. At a low chloride ion concentration (less than 300 mg L^{-1}) and current density (less than 8 mA cm^{-2}), a constant low anode efficiency of less than 0.3 g NH_4^+-N_r h^{-1} m^{-2} A^{-1} was achieved. Peak efficiency was achieved at approximately 30 min. The efficiency gradually decreased when various chloride ion concentrations and current densities were applied.

Table 1 Kinetic rate constants and half lives for different chloride ion concentrations and current densities

Run No.	Chloride ion concentration (mg L^{-1})	Current density (mA cm^{-2})	k (min^{-1})	Correlation coefficient	Half life (min)
1	0	5	0.0002	0.928	3465.74
2	100	5	0.0018	0.995	385.08
3	200	5	0.0026	0.995	266.60
4	300	5	0.0055	0.990	126.03
5	400	5	0.0111	0.939	62.44
6	400	3	0.0023	0.988	301.37
7	400	6	0.0281	0.895	24.67
8	400	8	0.0302	0.956	22.95
9	400	10	0.0515	0.842	13.46

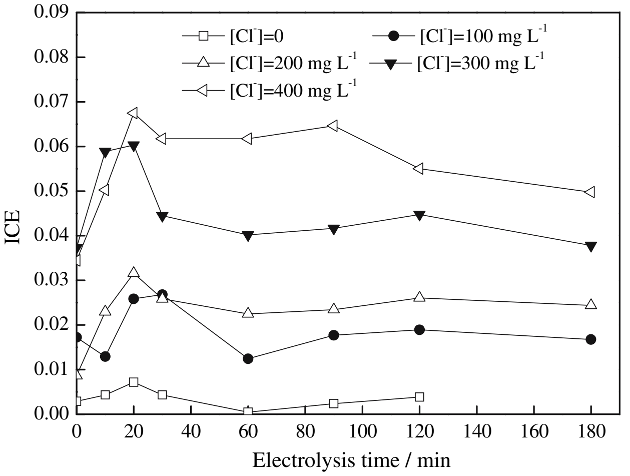

Fig. 8 Influence of chloride concentration on ICE, with a current density of 5 mA cm^{-2}, and an initial pH of 7

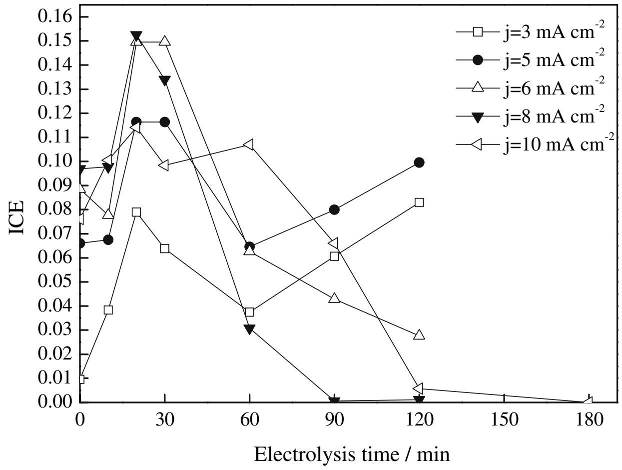

Fig. 10 Influence of current density on ICE, with 400 mg L^{-1} chloride ion concentration, and an initial pH of 7

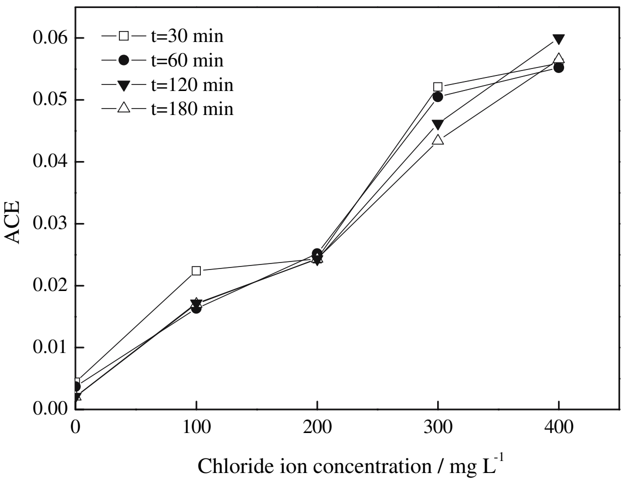

Fig. 9 Influence of chloride concentration on ACE, with a current density of 5 mA cm^{-2}, and an initial pH of 7

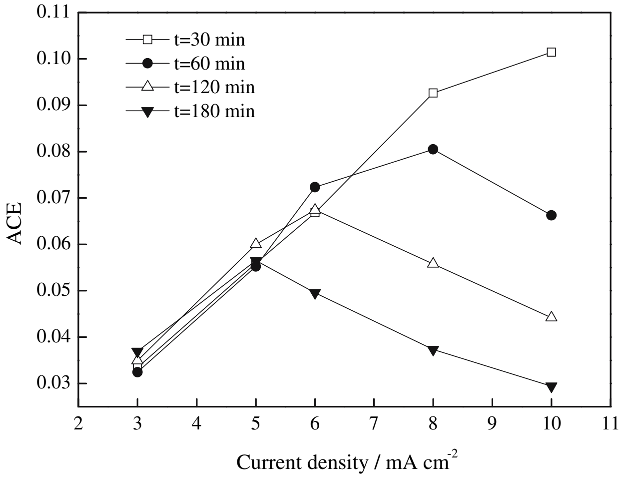

Fig. 11 Influence of current density on ACE, with 400 mg L^{-1} chloride ion concentration, and an initial pH of 7

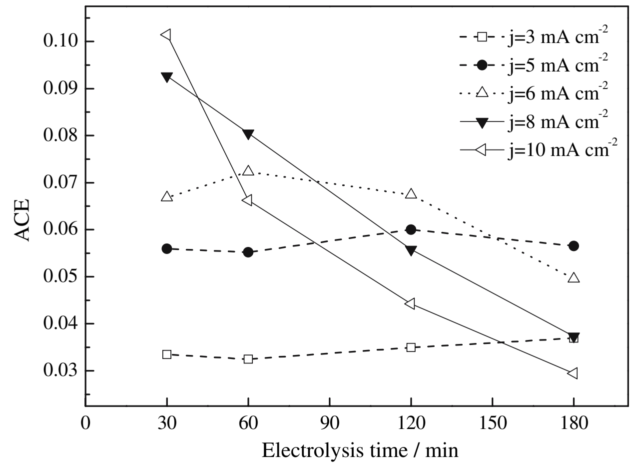

Fig. 12 Effect of electrolysis duration on ACE for various current densities, with 400 mg L^{-1} chloride ion concentration, and an initial pH of 7

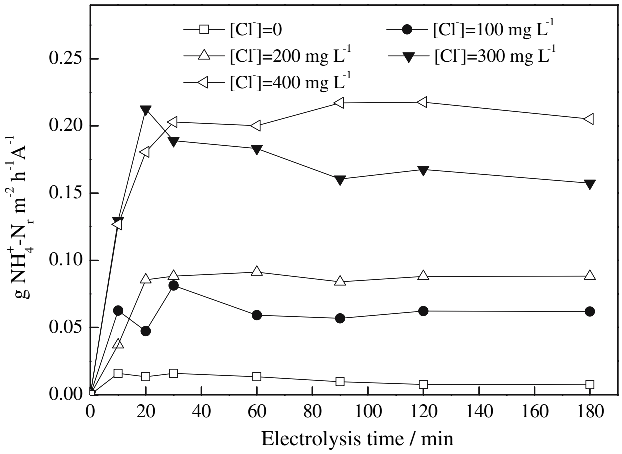

Fig. 13 Relation of anode efficiency to chloride ion concentration and duration of electrolysis

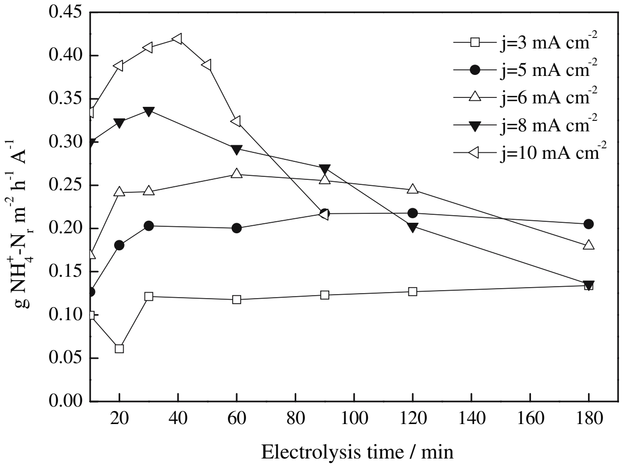

Fig. 14 Relation of anode efficiency to current density and electrolysis duration

4 Conclusions

An electrochemical method has been applied to the treatment of ammonia-containing wastewater. Several operating parameters, such as chloride ion concentration, current density and initial pH were studied. The following principal conclusions can be drawn.

(1) The ammonia removal efficiency increased with increasing chloride ion concentration and operating current density.
(2) The direct anodic oxidation efficiency of ammonia was less than 5%. The removal of ammonia by electrochemical oxidation is mainly attributable to the indirect oxidation effect of chlorine/hypo-chlorite produced during electrolysis.
(3) It was found that electrolysis was more efficient in neutral to moderate alkaline conditions.
(4) Kinetic investigations using pseudo first-order kinetics provide a reasonable fit to the experimental data.
(5) The current efficiency (ICE and ACE) of electrochemical oxidation of ammonia with RuO_2–IrO_2–TiO_2/Ti electrodes was very low (less than 10%). Additional studies need to be conducted to find a more suitable electrode material for ammonia oxidation with low chloride ion concentration.

Although the energy demand is higher when compared to an aerobic biological reactor for the same treatment results, the electrochemical process occupies less area, and is easier to operate, control and maintain. The results are more reliable. Furthermore, no waste biomass is produced. In summary, the electrochemical process offers a feasible approach for treating ammonia-containing wastewater. It can be applied successfully as a final polishing step, or as an alternative to biological nitrification, and seems to be favourable for small coastal cities.

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