Kinetics for ammonium ion removal using a three-dimensional electrode system
Qicheng Qiao, Yuemin Zhao and Lizhang Wang

ABSTRACT

Electrochemical oxidation of ammonium ions (NH$_4^+$) by using a three-dimensional electrode (TDE) composed of IrO$_2$–Ta$_2$O$_5$/Ti anode and bamboo carbon was carried out in this paper. Experimental results reveal that the NH$_4^+$ oxidation follows first-order kinetics at lower NH$_4^+$ concentration and the rate constant is highly dependent on the applied current density, dosage of chlorine ions and initial NH$_4^+$ concentration. In addition, increasing current density, more Cl$^-$ dosage and higher initial NH$_4^+$ concentration are beneficial for NH$_4^+$ removal. By inspecting the relation between rate constant and those operating factors, an overall empirical equation for estimation of the rate constant of NH$_4^+$ oxidation is presented. The estimated model is in good agreement with the experimental results and it could also be used for accurate design of the TDE system.

Key words | ammonium ion (NH$_4^+$), electrochemical oxidation, kinetics, three-dimension electrode (TDE)

INTRODUCTION

Ammonia (NH$_3$) and the ammonium ion (NH$_4^+$), both with the ability of promoting eutrophication, are fatal to aquatic organisms. They can also hinder the disinfection of water supplies, leading to offensive odors and carcinogenic effects. Recently, many methods, e.g. biological processes, ion exchange, air stripping and breakpoint chlorination, have been introduced to deal with these kinds of material (Huang et al. 2001), and high removal efficiency was achieved using these methods. Electrochemical oxidation is another attractive alternative for NH$_3$/NH$_4^+$ removal due to its advantages of the minimal generation of secondary waste, easy operation and remote control (Kim et al. 2006). Further, the possibility of completely converting NH$_3$/NH$_4^+$ to nitrogen makes the technology superior to other processes.

Many wastewaters such as power plant effluents, municipal discharges, landfill leachate and sludge digester effluent can be effectively treated by pure anodic oxidation (PAO), and greater NH$_3$/NH$_4^+$ removal could be obtained, while lower current efficiency and larger power consumption were observed from these experiments (Wang et al. 2001; Vlyssides et al. 2002; Vanlangendonck et al. 2005; Xie et al. 2006). Hence, many effective measures should be taken in order to make this process cost effective. Packing materials with an adsorption ability, e.g. activated carbon, into electrode gaps can meet the requirements and increase space–time yields for the expansion of the anode area as a function of the carbon bipolarity (Ma & Wang 2006). This kind of reactor, the so-called three-dimensional electrode (TDE), is characterized by all-direction oxidation and reduction of power demand due to the employment of carbon particles as microelectrodes and a significant reduction of mass transfer distance (Kong et al. 2006; Zhao et al. 2010). Therefore, many organic compounds have been successfully oxidized by using the TDE (Fochedey & Lierde 2002; Xiong et al. 2005). However, the employment of this method for NH$_3$/NH$_4^+$ removal has not been reported yet.

To obtain the probability of NH$_4^+$ oxidation with high efficiency, a TDE system composed of an IrO$_2$–Ta$_2$O$_5$/Ti anode, Ti cathode and bamboo carbon (BC) was designed in this paper. Further, a kinetics analysis of many influencing factors, such as applied current density, dosage of chlorine ions and initial NH$_4^+$ concentration, was provided to estimate the oxidation rate, which is associated with the accurate design of the TDE system. The kinetics was also checked by adequate experiments. Compared with other research using PAO, the application of TDE for NH$_4^+$ removal, at least, has two typical advantages. One is the large NH$_4^+$ removal efficiency because of the increase of...
the space–time yields. The other is the conventional acquirement of the most important influencing factor, thus easily making the reaction effective and cost saving.

EXPERIMENTAL

Chemicals

All reagents used for the analysis were obtained in extra pure condition, and distilled water and ammonium sulfate (99.5% pure) were used for the preparation of synthetic wastewater. The reagents of 1 M H2SO4 and 1 M NaOH were used to adjust the initial solution pH to a value of 6.5. NaCl in analytical pure condition was employed to enhance the NH4\textsuperscript{+} oxidation.

Set-up

A continuous electrochemical reactor with working volume, length, breadth and height of 0.6 L, 12 cm, 5 cm and 10 cm, respectively, was constructed by polymethyl methacrylate plastics in our laboratory. IrO2–Ta2O5/Ti and a Ti plate, having areas of 120 cm\textsuperscript{2} (12 × 10 cm), were used as anode and cathode, respectively. BC with an average particle size of approximately 3 mm and specific surface area of 520 m\textsuperscript{2}/g according to the BET method was packed into the electrode gaps to a height of about 10 cm. Prior to the experiments, BC was washed using distilled water several times and dried in an oven at 105 °C for 2 days to a constant weight. A direct current power supply having a maximum output of voltage/current of 30 V/5 A was used in these experiments. Approximately 2 L of synthetic wastewater was prepared and the solution was pumped at a constant flowrate of 135 mL/h by a metering pump from a reservoir to the TDE system. All the experiments were performed at a constant temperature (25 ± 1 °C) controlled by a water-bath. The detailed information of the process was provided in our previous paper (Wang et al. 2007).

Experimental procedure

During these experiments, four sets of tests were designed with different purposes under constant pH and temperature, respectively, as shown in Table 1. Aiming to compare the removal efficiency of NH4\textsuperscript{+} by adsorption, PAO and TDE, the first set of tests was conducted. The second set of tests was performed at different applied current densities \( j \) of 5, 10, 15, 20 and 25 mA/cm\textsuperscript{2} to identify the effect on oxidation rates of NH4\textsuperscript{+}. In order to determine the influence of chloride ion concentration \( C_{C1} \) and initial NH4\textsuperscript{+} concentration \( C_0 \) on the oxidation kinetics, the third and fourth sets of tests were carried out, respectively.

Analytical methods

The NH4\textsuperscript{+} concentration was determined by Standard Methods (APHA 1998) and a pH meter (model HACA pHs-3C) was used to obtain the initial solution pH values.

RESULTS AND DISCUSSION

Comparison of the three processes for NH4\textsuperscript{+} removal

Figure 1 shows the three processes, i.e. adsorption, PAO and TDE, could effectively remove NH4\textsuperscript{+} from solutions, but to different degrees. During adsorption, the removal efficiency continuously decreased, down to an ignorable level of 2.3% at an elapsed time of 12 h (curve (a)), whereas when the current is applied across the carbon bed, the BC could keep its adsorption ability even under a larger operational time (curve (c)), and an average removal efficiency of 62.2% is obtained, which is much higher than that for PAO (44.6%, curve (b)). These results reveal that BC adsorption is unsuitable for NH4\textsuperscript{+} removal and could cause a sharp increase in operating cost. In addition, TDE is superior to PAO, and the

<table>
<thead>
<tr>
<th>Test\textsuperscript{a}</th>
<th>Description</th>
<th>( j ) (mA/cm\textsuperscript{2})</th>
<th>( C_{C1} ) (mg/L)</th>
<th>( C_0 ) (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure adsorption</td>
<td>0</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>PAO</td>
<td>20</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>TDE</td>
<td>20</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>( j ) = 5</td>
<td>5</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>( j ) = 10</td>
<td>10</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>( j ) = 15</td>
<td>15</td>
<td>300</td>
<td>50</td>
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<tr>
<td></td>
<td>( j ) = 20</td>
<td>20</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>( j ) = 25</td>
<td>25</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>( C_{C1} ) = 100</td>
<td>20</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>( C_{C1} ) = 200</td>
<td>20</td>
<td>200</td>
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</tr>
<tr>
<td></td>
<td>( C_{C1} ) = 300</td>
<td>20</td>
<td>300</td>
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</tr>
<tr>
<td></td>
<td>( C_{C1} ) = 400</td>
<td>20</td>
<td>400</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>( C_0 ) = 10</td>
<td>20</td>
<td>300</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>( C_0 ) = 30</td>
<td>20</td>
<td>300</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>( C_0 ) = 50</td>
<td>20</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>( C_0 ) = 70</td>
<td>20</td>
<td>300</td>
<td>70</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The overall reaction time = 120 min.
former would be the preferred method for rapid degradation of NH₄⁺.

In the TDE system, NH₄⁺ removal is performed by two pathways: one is that the process would be conducted at the electrode surface and it could also be performed for direct/indirect oxidation by electro-generated oxidants, such as hydroxyl radicals (–OH), hydrogen peroxide (H₂O₂) and chlorine (Lee et al. 2003; Bensalah et al. 2009); the other is that the electrode area is greatly expanded due to the carbon bipolarity, which allows additional oxidation of absorbed NH₄⁺ on the bipolar electrode and leads to the consecutive reactions of adsorption, oxidation and electro-generation within the system (Berenguer et al. 2010). Moreover, the mass transfer property could also be enhanced by shortening the transport distance. From curve (d), we observed the NH₄⁺ oxidation could be described by the relationship 

\[ C_t = C_0 e^{-0.0278t} \quad (R^2 = 0.9539) \]

at 20 mA/cm², which indicates the NH₄⁺ oxidation obeys first-order kinetics at lower concentration (50 mg/L); here C₀ and Cₜ are the NH₄⁺ concentrations of raw water and at reaction time t (mg/L), 0.0278 is the first-order reaction rate constant (min⁻¹) and t is the reaction time (min).

**Kinetics**

Based on our previous experiment and other publications (Wen 1999; Kim et al. 2006), NH₄⁺ oxidation can be described by first-order kinetics at proper current density and NH₄⁺ concentration, i.e.

\[ \frac{C_t}{C_0} = e^{-kt} \quad (1) \]

Many researchers reported that the reaction rate constant (k) was highly affected by the current density (j), dosage of chloride ions (C_{Cl}) and C₀ (Li & Liu 2009; Liang et al. 2011). Hence, an empirical model was presented to describe their relations:

\[ k = f(j, C_{Cl}, C_0) = mj^a C_{Cl}^b C_0^c \quad (2) \]

where m, a, b and c are constants.

These parameters can be obtained by the relation between j, C_{Cl} and C₀ and the rate constant using the experiments designed in Table 1, respectively.

**Effect of the current density**

Figure 2 depicts the NH₄⁺ oxidation at current densities ranging from 5 to 25 mA/cm² and the rate constants were determined by Equation (1). As can be seen from this figure, the oxidation rate is highly affected by the applied current density. For example, the rate constant is only...
0.0064 min\(^{-1}\) at 5 mA/cm\(^2\), while it is 0.0278 min\(^{-1}\) at 20 mA/cm\(^2\). The latter is about four times higher than the former. Such enhancement is because the applied voltage is increased at a higher applied current density, leading to the rapid transfer of NH\(_4^+\) to the electrode surface under a strengthened electric field. The results also indicate that increasing the current density is a preferred alternative, to obtain higher electrochemical performance.

It is assumed that the dependence of the rate constant on the current density can be expressed as:

\[
k = k_1 j^a
\]

(3)

where \(k_1\) is the observed rate constant determined by applied current density.

According to the experiments, \(k_1 = 0.0011\) and \(a = 1.0679\) (\(R^2 = 0.9815\)) are achieved; Equation (3) can be represented in the form:

\[
k = 0.0011 j^{1.0679}
\]

(4)

**Effect of the dosage of chloride ion**

In the presence of chloride ions, active chlorine can be electro-generated on the IrO\(_2\)-Ta\(_2\)O\(_5\)/Ti anode, which can participate in the NH\(_4^+\) oxidation and be employed as catalyst (Li & Liu 2009). The reaction mechanisms are shown as follows (Szpyrkowicz et al. 2000):

On the anode:

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e
\]

(5)

In solution:

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{H}^+ + \text{Cl}^-
\]

(6)

Then HClO can be reacted with ammonium ions, and the chloride ions would be released into the solution by the complete conversion of NH\(_4^+\) to nitrogen:

\[
\begin{align*}
\text{HClO} + \text{NH}_4^+ &\rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} + \text{H}^+ \\
\text{HClO} + \text{NH}_2\text{Cl} &\rightarrow \text{NHCl}_2 + \text{H}_2\text{O} \\
\text{NHCl}_2 + \text{H}_2\text{O} &\rightarrow \text{NOH} + 2\text{H}^+ + 2\text{Cl}^- \\
\text{NHCl}_2 + \text{NOH} &\rightarrow \text{N}_2 + \text{HClO} + \text{H}^+ + \text{Cl}^-
\end{align*}
\]

(7a-d)

The overall reaction can be expressed as:

\[
3\text{HClO} + 2\text{NH}_4^+ \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 5\text{H}^+ + 3\text{Cl}^-
\]

(8)

The influence of the dosage of chloride ions on the oxidation rate of NH\(_4^+\) is shown in Figure 3. The results reveal that, the higher the dosage of NaCl, the faster the NH\(_4^+\) oxidation; however, the removal efficiency is only slightly enhanced when the dosage is up to 400 mg/L. This may be because of the transfer limitation of chloride ions at a constant applied current density. Similar trends were also shown in previous work (Vlyssides et al. 2002; Vanlangendonck et al. 2005). The experiments indicate the employment of Cl\(^-\) is an effective measure to improve the electrochemical performance, while excessive dosage could not provide a considerable NH\(_4^+\) removal. Hence, a relation between Cl\(^-\) concentration and \(k\) is presented as:

\[
k = k_2 C_{\text{Cl}}^b
\]

(9)

where \(k_2\) is the observed rate constant associated with the dosage of chloride ions. From Figure 3, the parameters \(k_2\) and \(b\) with values of 0.0001 min\(^{-1}\) and 0.9227 (\(R^2 = 0.9874\)) respectively, were achieved, and Equation (9) is rearranged as:

\[
k = 0.0001 C_{\text{Cl}}^{0.9227}
\]

(10)
Effect of initial NH$_4^+$ concentration

The oxidation rate could be determined by the initial NH$_4^+$ concentration and the effect is displayed in Figure 4. These results obviously show, the higher the initial NH$_4^+$ concentration, the higher the oxidation rates. The reaction would be in mass transfer control when the oxidation obeys the first-order kinetics, and larger quantities of substrate could effectively reduce the side reactions (e.g. water decomposition) and thus enhance the NH$_4^+$ oxidation due to the increase of mass transfer limitation (Wang & Balasubraman-nian 2009). Here, it is assumed that the relation between the rate constant and the initial NH$_4^+$ concentration can be expressed as:

\[ k = k_3 C_0^c \]  

(11)

where \( k_3 \) is a constant related to initial NH$_4^+$ concentration. When the obtained \( k \) values were substituted into Equation (11), we can get:

\[ k = 0.0016 C_0^{0.7406} \]  

(12)

Development of rate constant equation

A series of experiments were conducted in this study to assess the effects of key factors such as \( j \), \( C_{Cl} \) and \( C_0 \) on NH$_4^+$ oxidation. Parameters \( a \), \( b \) and \( c \) achieved values of 1.0679, 0.9227 and 0.7406, respectively. By substituting these values into Equation (2), an overall form of \( k \) can be displayed by:

\[ k = mj^{-1.0679} C_{Cl}^{-0.9227} C_0^{-0.7406} \]  

(13)

By substituting data determined by the experiments designed in Table 1 into Equation (13), we obtain the parameter \( m \) with a value of $3.06 \times 10^{-7}$. Hence, Equation (14) was used for the estimation of the rate constant covering a wide range of applied current density, dosage of chlorine ion and initial NH$_4^+$ concentration:

\[ \frac{C_t}{C_0} = e^{-5.06 \times 10^{-7} j^{1.0679} C_{Cl}^{-0.9227} C_0^{-0.7406}} \]  

(14)

Figure 5 illustrates the theoretical rate constant calculated by Equation (14) is in accordance with the experimental one with greater agreement ($R^2 = 0.9566$) under the conditions of $j = 30$ mA/cm$^2$, $C_{Cl} = 300$ mg/L and $C_0 = 40$ mg/L. However, due to the uncertainty and instantaneity of real-time mass transport properties, less error is still observed in this figure, i.e. the estimated values are slightly higher than those from the experiments when the reaction time is between 10 and 70 min, and lower than those of the experimental values when the reaction time is more than 90 min.

CONCLUSIONS

The experimental investigation validated that NH$_4^+$ could be eliminated continuously by using electrochemical oxidation
and the TDE system is an efficient method for NH₄⁺ oxidation, whereas adsorption and PAO are both unsuitable for dealing with NH₄⁺ removal due to the rapid saturation and low space–time yields. By checking the influence of applied current density, dosage of chlorine ions and initial NH₄⁺ concentration, an empirical model described as:

\[ C_t = C_0 e^{-3.06 \times 10^{-7} C_0^{1.9879} t^{0.7406}} \]

could be used to predict the variation of NH₄⁺ concentration during electrochemical oxidation. The results obtained by the proposed equation are in good agreement with experimental data. Therefore, the proposed kinetics can accurately estimate the electrochemical performances and provide a proper design of the TDE system.

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