Electro-thermal treatment optimization of high concentration ammonia nitrogen by gaseous oxidation in liquid phase (GOLP)
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ABSTRACT
This study is focused on optimizing the treatment parameters for high concentration ammonia using gaseous oxidation in liquid phase (GOLP). The conversion of ammonia was achieved electro-thermally over mono-crystalline silicon supported CoOx catalyst. The experimental results demonstrated that factors including the co-anions, pH of the solutions, air flowrate and the current showed apparent influences on the ammonia removal. The higher the Cl\(^-\) concentration and/or current, the better the efficiency of ammonia degradation. The increase of the air flowrate would increase the ammonia removal accordingly. And it was also observed that the pH declined during the ammonia conversion, and the neutral and alkaline pH were beneficial to the ammonia removal. The preliminary cost analysis based on lab data was also provided for future reference.

Key words | ammonia, catalysis, electro-thermal, oxidation, wastewater

INTRODUCTION
Ammonia is a useful chemical in the synthesis of important products such as urea and ammonia phosphate. And it’s universal in the industrial wastewaters which are commonly detrimental to the environment from several aspects: ammonia could affect the acidification and eutrophication of the natural water bodies, which is fatal to fish and aquatic life; the use of such water is also detrimental to human health, especially that of infants (Fang et al. 1995; van der Weerden & Jarvis 1997; Vukcevic 1997; Feng et al. 2005; Sutton et al. 2008).

Attention has been drawn to the ammonia removal in the past due to the need for the control of nitrogen nutrient to prevent eutrophication. There are various ways to eliminate ammonia from wastewaters, including biological nitrification and denitrification, air-stripping, activated carbon fibre adsorption, ozonation, electrochemical methods, break-point chlorination, and ion exchange etc. However, each of these methods has constraints such as generating sludge and/or adsorbent which need further treatment (Hao et al. 1994). Biological treatment is widely used, but this process requires the ammonia concentration to be low and no toxicants present; for the air-stripping process, subsequent catalytic oxidation is required to selectively convert ammonia to N\(_2\) as much as possible instead of forming hazardous nitrates as final products. Hence, there is considerable interest in developing alternative treatment approaches for the ammonia removal.

One novel chemical process developed recently is catalytic conversion of ammonia (Luck 1999), which holds great potential due to its advantages such as simple reactor, flexibility and so on. As reviewed by Oliviero et al. (2003), it is clear that the supported catalysts of precious metals or base metals are required in this reaction to increase the conversion of ammonia as well as to alleviate the severity of the oxidation reaction condition. However, most of these studies are focused on the gas phase NH\(_3\) and few works have covered catalytic oxidation of ammonia in liquid phase.

In our previous study (Cao et al. 2010), silicon supported CoO\(_x\) catalysts for high concentration ammonia removal by GOLP (gaseous oxidation in liquid phase) were investigated. The preliminary results have shown that the GOLP method is efficient at NH\(_4^+\) cleanup. Therefore, it is important to investigate the influence of factors including current, pH, the co-anions, air flowrate etc. on the ammonia catalytic oxidation over the CoO\(_x\) catalysts. It is in this context that the current study was undertaken with a primary view to optimize the treatment parameters through systematic experiments.
METHODS

Materials

The simulated wastewaters with varying ammonia concentrations were prepared using NH4Cl and (NH4)2SO4 in distilled water. All chemicals were analytical reagent grade and were used without any further purification. Catalysts composed of Co on mono-crystalline silicon chip were prepared by incipient wetness impregnation method (Cao et al. 2010). The pH of the simulated wastewater was adjusted using 10 M NaOH or 1 M HCl. The detailed experimental procedures could be referred to our previous publication (Cao et al. 2010).

Setup

The experimental setup consisted of the electrochemical apparatus; the recycle-cooling system for the wastewater; and the gas washes and collecting system as shown in Figure 1.

The apparatus

The apparatus employed in our experiments consists of a reaction chamber (R2 × H = 952 × 100 mm) with two graphite electrodes (Shanghai Carbon Company of China) inside (Cao et al. 2010). Between the two electrodes there is the Si substrate (Shanghai Yiyang Electron Material Company of China) covered by catalyst. The DC electric power supply (Shanghai Liyou Electrification Company of China) was used to apply a controlled current to the substrate. After the simulated wastewater was filled into the reaction chamber, O2 gas was pumped into the chamber by an air-pump (Guangdong Chuangxing Electrical Appliance Company of China).

The recycle-cooling system

The main effect of the recycle-cooling system is to control the temperature of the wastewater in the reaction chamber so that it is lower than its boiling point. The recycle-cooling system includes two sections: one section is the cooling-regurgitated pipe; the other one is water-cooling. High-temperature water in the reaction chamber was pumped into the pipe by the centrifugal pump (Baoding Longer Precision Pump Company of China), then through the cooling water. Cooling water was then circulated. Gaseous ammonia escaping from the reactor was absorbed into 100 mL 20 g L−1 boric acid solution through the gas washer.

Analytical methods

Samples were taken from the reactor periodically and filtered through a 0.45 µm membrane. The concentration of ammonia was evaluated by the absorbance of the solutions at 420 nm using a UV/Vis Spectrophotometer (UNICO Instruments Company) using standard method (American Public Health Association/American Water Works Association/Water Environment Federation 1998). The pH value was measured with a PHS-3C pH meter (Model, Shanghai, China). DO was determined by a dissolved oxygen meter (Shanghai Precision & Scientific Instrument Company-Shanghai REX Instrument Factory, China). The ion species were determined by the Ion Chromatogram (DX-320, Dionex, America).

RESULTS AND DISCUSSION

Factors affecting the ammonia removal

Recent research in catalytic oxidation of ammonia has proved that the efficiency and rate of the ammonia removal are strongly influenced by several factors such as the co-anions, current and the pH value of solution, etc. (Chiang et al. 1995; Lin & Wu 1996; Vlyssides & Israilides 1997; Wang et al. 2001; Vlyssides et al. 2002; Vanlangendonck et al. 2005).

Applied current

It has been demonstrated that higher temperatures favour the ammonia removal and the selectivity for N2. In our experiments, the catalyst was heated through the direct current and the effect was explored by manipulating the current flowing throughout the mono-crystalline silicon.
Similar results could be drawn from Figure 2(a) that, with the increase of current, the efficiency of ammonia removal increases accordingly and the trend is apparent. As current directly relates to the surface temperature of catalyst, the higher the temperature of the catalyst, the higher the reaction efficiency (Tanaka et al. 1982; Ito et al. 1989; Vanlangendonck et al. 2005; Li & Liu 2008).

**Initial pH**

pH is a critical factor affecting the ammonia species distribution in solutions. The following equilibrium exists in a closed system (Cao et al. 2003; Enick et al. 1998):

\[
\text{NH}_4^+ + \text{OH}^- \leftrightarrow \text{NH}_4\text{OH} \leftrightarrow \text{NH}_3(l) + \text{H}_2\text{O} \leftrightarrow \text{NH}_3(g) + \text{H}_2\text{O} \tag{1}
\]

The mechanism of ammonia oxidation has been studied by some researchers (Cao et al. 2010). It is generally believed that the conversion is initiated by the hydrogen abstraction reaction (Ploeger et al. 2008) as follows:

\[
\text{NH}_3(l) \rightarrow \text{NH}_3(g) \tag{2}
\]

\[
4\text{NH}_3(g) + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O} \tag{3}
\]

However, if the N in the solution exits as \(\text{NH}_4^+\), which is always true in alkaline environment, the de-nitrification process would then be longer and it would be more difficult for it to happen, as shown in Equation (1).

Figure 2(b) shows the above assumption. It can be seen that neutral and alkaline pH are beneficial to ammonia oxidation, as shown in Figure 3, which is similar to the results of Lin & Wu’s (1996) studies.

Also from Equation (1), it could be inferred that when more ammonia is removed from the water, the pH should decrease accordingly and the de-nitrification would be more
difficult to occur. The results in Figure 3 verify this idea. It has been shown in Figure 2(a) that high current removes more ammonia in the solution and therefore the pH drop should be bigger, which can be seen in Figure 3. The trend is also obvious: the higher the current, the lower the final pH.

In the experiments, it is interesting to observe that solutions with initial pH at 10 have final pH between 8–9.5 at the end of the reaction, and solutions with initial pH at 7 have final pH between 2–3.4. Although the removal is better in the alkaline range, the pH drop in Figure 3(b) is bigger than that in Figure 3(a). This discrepancy could be explained by the solution having the biggest buffer capacity around pH 9.27 because of the pK_a of ammonia.

Another possible reason for the pH declination during the treatment might be attributed to the formation of acidic products such as NO_3^-, NO_2^- etc.

**The co-anions in water**

Cl^- and SO_4^{2-} are common co-existing ions with NH_4^+ in water. The effect of the two ions in water on the catalytic oxidation of ammonia removal was studied in Figure 4(a).

Figure 4(a) shows the comparison of removal efficiency under the same conditions in NH_4Cl and (NH_4)_2SO_4 solutions. It could be seen that, in the presence of chloride ion, the removal was increased around 1–2% consistently. According to Krstajic & Nakic (1987), the chloride ion in the aqueous solution will be converted to chlorine, which is further converted to hypochloric acid for ammonia oxidation. The reaction sequence can be represented by

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \quad (4)
\]

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad (5)
\]

\[
\text{HOCl} \rightarrow \text{OCl}^- + \text{H}^+ \quad (6)
\]

\[
\text{HOCl} + (2/3)\text{NH}_4^+ \rightarrow (1/3)\text{N}_2 + \text{H}_2\text{O} + (5/3)\text{H}^+ + \text{Cl}^- \quad (7)
\]

\[
\text{HOCl} + (1/4)\text{NH}_4^+ \rightarrow (1/4)\text{NO}_3^- + (1/4)\text{H}_2\text{O} + (3/2)\text{H}^+ + \text{Cl}^- \quad (8)
\]

The ion analysis verified Krstajic and Nakic’s results as shown in Table 1. It could be seen that, as the reaction proceeded, Cl^- concentration decreased, while the concentration of NO_3^- increased evidently because of Equation (6). Previous studies (Vanlangendonck et al. 2005; Wang et al. 2007; Li & Liu 2008) have reported similar trends that the ammonia oxidation rate increased with initial Cl^- concentration. Meanwhile, Vanlangendonck et al. (2005) reported that sulfate had a negative effect on the oxidation of ammonia.

However, the decrease of Cl^- concentration is not linearly related to the increase of NO_3^- at different pH, as shown in Table 1. At lower pH, ammonia is selectively converted to...
N₂, while at higher pH NO₃⁻ is the major product. Since Cl⁻ could be regenerated in the loop formed in Equations (4)–(8), this could explain why the increase of NO₃⁻ is higher than the decrease of Cl⁻ at pH 12.

**Air flowrate**

Oxygen is crucial for the GOLP process since it could shift the equilibrium of the oxidation as shown in Equation (3). Oxygen is crucial for the GOLP process since it could shift the equilibrium of the oxidation as shown in Equation (3). Therefore, the overall process could be described as follows:

\[
\text{NH}_3^+ + \text{H}_2\text{O} \leftrightarrow \text{NH}_3^{(aq)} + \text{H}_3\text{O}^+ \quad (9)
\]

\[
\text{NH}_3^{(aq)} \leftrightarrow \text{NH}_3^{(gas)} \quad (10)
\]

\[
2\text{NH}_3^{(gas)} + 1.5\text{O}_2^{(gas)} \rightarrow \text{N}_2^{(gas)} + 3\text{H}_2\text{O} \quad (11)
\]

Meanwhile, it has been speculated that the following reactions could occur in the gas-liquid inter-phase (Lee 2003).

\[
\text{O}_2^{(gas)} \leftrightarrow \text{O}_2^{(aq)} \quad (12)
\]

\[
\text{O}_2^{(aq)} \leftrightarrow 2\text{O}^- \quad (13)
\]

\[
\text{NH}_3^{(aq)} + \text{O}^- \rightarrow \text{NH}_2^- + \text{H}_2\text{O} \quad (14)
\]

Catalytic oxidation of ammonia is initiated by the reaction of NH₃(aq) with O*, as shown in Equation (13). This could also contribute to the fact that, with the increase of dissolved oxygen in water, the efficiency of ammonia removal increases accordingly and the increase trend is apparent.

**Economic analysis**

The cost of ammonia removal by GOLP has been done considering the energy cost and the cost of electrode. The energy cost has been considered in our previous studies (Cao et al. 2010). Taking the electricity consumption of 1.45 kWh kg⁻¹ ammonia removals and the cost of electricity as 8 cents (US $0.082) per kWh, the relevant energy cost for removing ammonia by the process is found to be US$0.119 per kg ammonia removal. In the year 2009 the average cost of graphite piece was US $2.635 per kg, and the cost of the electrode materials for the GOLP could be estimated from the electrode corrosion rate. Therefore, the cost of using the GOLP process to remove high concentration ammonia is attractive.

**CONCLUSIONS**

In this paper, the effect of parameters affecting the GOLP process was investigated systematically. The experimental results demonstrated that the co-ions, the pH of the solutions, air flowrate and the current showed apparent influences on the ammonia removal. The higher the Cl⁻ concentration and/or current, the higher the rate and efficiency for the ammonia degradation. The increase of the air flowrate would increase the ammonia removal accordingly. And it is also shown that the pH declines during the treatment, and the neutral and alkaline pH were beneficial for the ammonia removal.

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