Ammonia nitrogen removal and recovery from acetylene purification wastewater by air stripping
Lei Zhu, DeMing Dong, XiuYi Hua, Yang Xu, ZhiYong Guo and DaPeng Liang

ABSTRACT
Ammonia nitrogen (NH₄-N) contaminated wastewater has posed a great threat to the safety of water resources. In this study, air stripping was employed to remove and recover NH₄-N from acetylene purification wastewater (APW) in a polyvinylchloride manufacturing plant. Investigated parameters were initial APW pH, air flow rate, APW temperature and stripping time. The NH₄-N removal by air stripping has been modeled and the overall volumetric mass transfer coefficient (KLa) of the stripping process has been calculated from the model equation obtained. In addition, the ability of H₂SO₄ solution to absorb the NH₃ stripped was also investigated. The results indicated that under the experimental conditions, the APW temperature and its initial pH had significant effects on the NH₄-N removal efficiency and the KLa, while the effects of other factors were relatively minor. The removal efficiency and residual concentration of NH₄-N were about 91% and 12 mg/L, respectively, at the optimal operating conditions of initial APW pH of 12.0, air flow rate of 0.500 m³/(h·L), APW temperature of 60°C and stripping time of 120 min. One volume of H₂SO₄ solution (0.2 mol/L) could absorb about 93% of the NH₃ stripped from 54 volumes of the APW.

INTRODUCTION
Acetylene purification wastewater (APW), produced during the production of acetylene by the calcium carbide method in polyvinylchloride (PVC) manufacturing plants, is considered to be one of the wastewater types exerting the greatest environmental impact, as it contains a high concentration of ammonia nitrogen (NH₄-N), generally in the range of 100–200 mg/L (Zhu et al. 2016). Excessive NH₄-N discharged into natural waters may cause serious environmental problems (Bodalo et al. 2005). On the other hand, nitrogen is an important element for all living organisms, and it plays an irreplaceable role in agriculture and industry. Therefore, NH₄-N should be removed and recovered from wastewater before entering surface waters.

NH₄-N in wastewater is usually removed by biological technologies, such as the anoxic/oxic process (Bassin et al. 2012). Other effective methods for the removal of NH₄-N include struvite precipitation (Tüney et al. 1997), ion exchange (Karadag et al. 2008) and membrane filtration (Zhang et al. 2015). APW, however, is not suitable to be treated by biological technologies, because the wastewater contains high concentrations of sodium (Na⁺) and NH₄-N, and some organic pollutants, which are harmful to microorganisms (Aziz et al. 2004; Ryu & Lee 2010). Additionally, the NH₄-N in wastewater can not be recovered by biological technology.

Air stripping is an alternative to remove NH₄-N from APW. In this method, when alkali is added to the wastewater, nonvolatile ammonium ions (NH₄⁺) convert to volatile ammonia molecules (NH₃), which can be stripped from the water phase into the gas phase when air is aerated into the water (Guo et al. 2016). Then, by aerating the NH₃ containing air into an acid solution, the NH₃ in the gas phase can be absorbed and recovered. The related chemical equilibriums include:

\[
\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3(aq) + \text{H}_2\text{O} \quad (1)
\]

\[
\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+ \quad (2)
\]
Compared with other methods, air stripping generates no extra sludge and is associated with modest reagent costs and easy operation (Quan et al. 2009; Degermenci et al. 2012). The method has been used for the removal of NH₄-N from different kinds of wastewater successfully (Nurisepehr et al. 2012; Zhang et al. 2012; Ferraz et al. 2013), and the NH₄-N removal efficiency obtained in these studies was in the range of 85–99%. The APW has a high level of pH value and temperature, and limited volatile compounds. Therefore, air stripping is suitable for the APW. To the best of our knowledge, the application of air stripping in the removal and recovery of NH₄-N from APW has not yet been studied. Therefore, the aim of this study was to evaluate the effects of the initial APW pH, air flow rate, and APW temperature on the NH₄-N removal efficiency and kinetics of the stripping process. Furthermore, the ability of H₂SO₄ solution to absorb the stripped NH₃ was investigated.

MATERIALS AND METHODS

Characteristics of APW

The APW used in this experiment was collected from a PVC manufacturing plant located in Jilin Province, China. The APW temperature usually ranges from 52 to 55 °C. Some parameters of the APW are shown in Table 1.

Table 1 | Some parameters of the APW

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>9.3 ± 0.2</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>155 ± 5</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>11 ± 3</td>
</tr>
<tr>
<td>TN (mg/L)</td>
<td>129 ± 1</td>
</tr>
<tr>
<td>NH₄-N (mg/L)</td>
<td>125 ± 2</td>
</tr>
<tr>
<td>Mg²⁺ (mg/L)</td>
<td>13 ± 3</td>
</tr>
<tr>
<td>Ca²⁺ (mg/L)</td>
<td>43 ± 2</td>
</tr>
<tr>
<td>Na⁺ (mg/L)</td>
<td>2,057 ± 7</td>
</tr>
<tr>
<td>PO₄³⁻ (mg/L)</td>
<td>1 ± 1</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>55 ± 5</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>477 ± 4</td>
</tr>
<tr>
<td>Br⁻ (mg/L)</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>BOD₅ (mg/L)</td>
<td>21 ± 1</td>
</tr>
</tbody>
</table>

Mean (n = 3) ± 1 standard deviation.

Experimental methods

Experimental setup

A schematic diagram of the experimental apparatus is comprehensively given in Figure 1. The air stripping column with a working volume of 0.7 L was made of Plexiglas tubes (45 cm height × 5 cm internal diameter). Air was introduced into the wastewater via an aquatic air stone, and the air flow rate was adjusted by a flow meter to obtain the required value. The tail gas, a mixture of air and NH₃, was released through a condenser on the top of the column and then absorbed by an absorption unit, which was filled with 0.2 mol/L H₂SO₄ solution (0.2 L).

Optimization for NH₄-N removal

Before air stripping, the APW was alkalized using sodium hydroxide (NaOH) solution. Therefore, the relationship between NaOH dosage and APW pH was tested in the first instance. APW of 0.1 L in a beaker stirred by a magnetic stirrer was alkalized by a 50 g/L NaOH solution added dropwise by a burette, and both pH value of the APW and quantity of the NaOH solution added were recorded.

Then, experiments for air stripping were performed as follows: APW (0.4 L) was added into the stripping column, after its initial pH and temperature adjusted to the given values. The column was then placed in a water bath to maintain the designated temperature. Air was aerated into the bottom of the column at a certain rate. After the expected stripping time approached, APW in the column was sampled and measured for NH₄-N and pH. All experiments were performed in duplicate.

To accomplish the optimal conditions, three important factors were optimized in the order of initial APW pH, air flow rate and APW temperature. When one factor was
being optimized, other factors were fixed (at initial or optimal values). After the optimal value had been obtained for a specific factor, the value was then assigned to this factor. The initial values assigned to the factors were 0.375 m³/(h·L) for air flow rate and 25 °C for APW temperature. The ranges of the factors to be optimized were chosen in respect of the economically feasible operating conditions in the plant, namely 10.0, 11.0 and 12.0 for initial APW pH; 0.375, 0.500, 0.625 and 0.750 m³/(h·L) for air flow rate; and 30, 40, 50 and 60 °C for APW temperature. The stripping time was selected according to the NH₄-N removal efficiency.

Absorption of NH₃ in tail gas

Experiments for absorption were carried out as follows: APW (0.4 L) was added into the stripping column, and its initial pH and temperature were 12.0 and 60 °C, respectively. The column was then placed in the water bath, and connected with the absorption unit, which was filled with 0.2 mol/L H₂SO₄ solution (0.2 L, initial pH 0.63). Air was aerated into the column at 0.500 m³/(h·L) for 120 min. After air stripping, the values of NH₄-N concentration and pH in the absorption solution were measured. The column was discharged and refilled with 0.4 L of the APW, and the processes above were repeated until the pH value of the absorption solution approached a neutral pH (about 7.0).

Analytical methods

The pH was measured using a pH meter (Model-370, Orion, USA). The concentrations of NH₄-N, PO₄³⁻ and total nitrogen (TN) were determined according to Standard Methods # 4500-N C, # 4500-P E and # 4500-N B, respectively (APHA 1995). Chemical oxygen demand (COD) was analyzed by a COD rapid detector (DRB-200, HACH, USA) and a UV-Vis spectrophotometer (DR-2800, HACH, USA). Biochemical oxygen demand (BOD₅) was measured by the pressure sensor method using an automated measurement apparatus (BOD Trak II, HACH, USA). Total organic carbon (TOC) was determined by a TOC analyzer (TOC-LCPH, Shimadzu, Japan). Anions such as SO₄²⁻, Cl⁻ and Br⁻ were quantified using an ion chromatograph (ICS-2100, Dionex, USA). Metal ions such as Mg²⁺, Ca²⁺ and Na⁺ were quantified using an atomic absorption spectrophotometer (AA-6000, Shimadzu, Japan).

Determination of mass transfer coefficient of NH₃

Various studies (Miller 1985; Quan et al. 2009) have demonstrated that the NH₄-N removal by air stripping followed first-order kinetics, therefore, the decrease of the liquid phase concentration of NH₄-N (C, mg/L) with stripping time (t, min) can be described according to Equation (3):

\[
\frac{dC}{dt} = -K_LaC
\]

where \( K_L \) is the overall mass transfer coefficient of NH₃ from water to air, m/min; \( a \) is the specific gas-liquid interfacial area, m⁻¹.

After integration, Equation (3) can be expressed as Equation (4):

\[
-ln\frac{C_t}{C_0} = K_Lat
\]

where \( C_t \) and \( C_0 \) are the liquid phase concentrations of NH₄-N at any given time \( t \) and at the beginning (mg/L), respectively. \( K_La \) is identified as the overall volumetric mass transfer coefficient (Quan et al. 2009; Degermenci et al. 2012) of NH₃ from water to air, min⁻¹.

RESULTS AND DISCUSSION

Effect of initial APW pH

The relationship between NaOH dosage and APW pH is illustrated in Figure 2. As shown in the figure, the pH increased sharply with the increase in NaOH dosage before it approached 12.0, and then increased slowly with increasing dosage. The dosage of NaOH at APW pH = 11.0, 12.0, 13.0 and 14.0 was about 1.25, 3.62, 10.25 and

![Figure 2](https://iwaponline.com/wst/article-pdf/75/11/2538/452850/wst075112538.pdf)

17.7 %

82.3 %

NaOH dosage (g/L)

9

10

11

12

13

14

15

16

17

18

19

20

21

pH

NaOH concentration – 50 g/L, APW volume – 0.1 L.
20.50 g/L, respectively. If taking the NaOH dosage used to adjust the APW pH from 9.3 (initial pH) to 14.0 as 100%, only 17.7% of the total NaOH dosage was consumed to increase the APW pH to 12.0. This indicates that the NaOH amount and cost will considerably increase when the required pH exceeds 12.0. Therefore, the initial APW pH examined in this study was in the range of 10.0–12.0.

The NH4-N removal efficiency and the –ln (Ct/C0) under different initial APW pH are shown in Figure 3(a) and (b), respectively. It can be observed from the figures that the NH4-N removal efficiency and the –ln (Ct/C0) increased as the time increased, and a higher initial APW pH could achieve a higher NH4-N removal efficiency and a higher –ln (Ct/C0). For example, after 360 min of air stripping, the NH4-N removal efficiency and the –ln (Ct/C0) were 37% and 0.46 at initial APW pH 10.0, while they were 75% and 1.38 at initial APW pH 12.0. Making a linear regression between –ln (Ct/C0) and t, and the KLa can be obtained (the slope of the line). It was observed that the linear relationship had good relative coefficients (R² > 0.9419), and the KLa increased about threefold from 0.0014 to 0.0040 min⁻¹/C0 when the initial APW pH increased from 10.0 to 12.0. Therefore, we selected 12.0 as the optimum initial APW pH. This is consistent with some studies concerning the air stripping method (Ozturk et al. 2003; Quan et al. 2009).

pH is one of the most important factors controlling the air stripping process (Quan et al. 2009). According to Equation (1), abundant OH⁻ could promote the equilibrium to shift towards the direction of NH₃, and increase the vapor pressure of the NH₃. Therefore, the NH₃ can easily enter the bubbles present in the APW, and is then removed by the air (Elsayed 2015). After 360 min of air stripping, the pH of the APW was 8.5, 8.7 and 9.3 for the initial APW pH 10.0, 11.0 and 12.0, respectively, due to the removal of NH₄-N and the effect of carbonation (Bonmati & Flotats 2003).

### Effect of air flow rate

The NH₄-N removal efficiency and the –ln (Ct/C0) under different air flow rates are shown in Figure 4(a) and (b), respectively. The figures indicated that both the NH₄-N removal efficiency and the –ln (Ct/C0) increased with the air flow rate. For example, after 300 min of air stripping, the NH₄-N removal efficiency increased from 68 to 88% when the air flow rate increased from 0.375 to 0.750 m³/(h·L), while the –ln (Ct/C0) increased from 1.13 to 2.11. However, when the air flow rate increased from 0.375 to 0.500 m³/(h·L), both the NH₄-N removal efficiency and the –ln (Ct/C0) increased remarkably, while they increased only slightly with further increase in the air flow rate. Despite the high NH₄-N removal efficiency obtained at an air flow rate above 0.500 m³/(h·L), a high air flow rate is not appropriate for the absorption unit, because it might result in the overflow of the absorption solution and some other problems (Liao et al. 1995). The linear relationship between –ln (Ct/C0) and t had good relative coefficients (R² > 0.9581), and the KLa increased from 0.0043 to 0.0074 min⁻¹/C0 when the air flow rate increased from 0.375 to 0.750 m³/(h·L). Accordingly, taking account of the energy consumption and removal efficiency, 0.500 m³/(h·L) was selected as the optimum air flow rate in this study.

The air flow rate is a decisive factor for NH₄-N removal (Pi et al. 2009; Gustin & Marinsek 2011). Increasing the air flow rate could increase air bubbles into the wastewater, which is beneficial to mix the wastewater and remove NH₃ from the water phase (Wang et al. 2008; Elsayed 2015).
A higher air flow rate can also increase the gas entrainment and gas-liquid interfacial area, thus increasing the NH$_4$-N removal efficiency as well as the $K_La$ (Degermenci et al. 2015). Furthermore, the overall mass transfer resistance for NH$_4$-N removal is mainly present in the gas film side due to the high dissolution of NH$_3$ in liquid. The mass transfer resistance in the gas film can be reduced by increasing the air flow rate, thus promoting stripping of NH$_3$ (Quan et al. 2013).

**Effect of APW temperature**

The NH$_4$-N removal efficiency and the $-\ln (C_t/C_0)$ under different APW temperatures are shown in Figure 5(a) and (b), respectively. It can be observed from the figures that a higher APW temperature could achieve both a higher NH$_4$-N removal efficiency and a higher $-\ln (C_t/C_0)$. For example, after air stripping for 360 min, the NH$_4$-N removal efficiency and the $-\ln (C_t/C_0)$ were increased from 82 to 99% and 1.74 to 4.72 when the APW temperature increased from 30 to 60 °C, respectively. The linear relationship between $-\ln (C_t/C_0)$ and $t$ also had good relative coefficients ($R^2 > 0.9730$), and the $K_La$ increased from 0.0055 to 0.0146 min$^{-1}$ when the APW temperature increased from 30 to 60 °C, and the $K_La$ increased almost 2.6 fold. According to the results and the APW temperature in the plant, we selected 60 °C as the optimum APW temperature. Considering the Discharge Standard for Municipal Wastewater Treatment Plant in China (MEPC 2002) for NH$_4$-N (<15 mg/L, first grade), the air stripping time required could be 120 min. In this case, the residual NH$_4$-N concentration in the APW was about 12 mg/L.
Wastewater temperature is also a limiting factor for air stripping (Gustin & Marinsek 2014). Increasing the temperature could increase the proportion of NH3 and enhance the molecular diffusion of NH3 in both the liquid and gas film (Lincoff & Gossett 1984). In addition, the increasing temperature strongly aids NH3 desorption from liquid because of decreasing the solubility of NH3 (Saracco & Genon 1994). The correlation between temperature and the amount of removed NH4-N was also reported by Liao et al. (Liao et al. 2018), and they concluded that higher temperatures in the batch stripping of swine manure increase the NH4-N removal efficiency.

Removal of NH4-N under the optimal conditions

According to the above results, the optimal conditions were as follows: an initial APW pH of 12.0; air flow rate of 0.500 m³/(h·L); APW temperature of 60 °C and air stripping time of 120 min. Under these conditions, the average residual concentrations of NH4-N and COD were 12 and 140 mg/L, respectively. After air stripping, a subsequent treatment process for COD removal, such as coagulation–flocculation (Abood et al. 2013) and Fenton oxidation (Sun et al. 2015), may be applied. The pH of the APW dropped from 12.0 to 9.9 after the treatment. The optimal conditions obtained in this study are compared with some related studies concerning air stripping in Table 2.

It can be noted from the table that similar NH4-N removal efficiency could be achieved by various treatment conditions. In this study, we could also change the wastewater treatment conditions according to the discharge demand and the operating conditions in the plant. For example, to meet the first grade Discharge Standard, we could select either the conditions of initial APW pH of 12.0, air flow rate of 0.500 m³/(h·L), APW temperature of 60 °C and air stripping time of 120 min or the conditions of initial APW pH of 12.0, air flow rate of 0.500 m³/(h·L), APW temperature of 40 °C and air stripping time of 300 min. Increasing the stripping time could further reduce the concentration of NH4-N remaining in the wastewater to meet a stricter standard. Therefore, the treatment conditions are very flexible in removing NH4-N from APW in a PVC plant.

NH3 absorption experiments

The NH3 absorption experiments were performed under the APW treatment conditions of initial APW pH of 12.0; air flow rate of 0.500 m³/(h·L); APW temperature of 60 °C and air stripping time of 120 min. The absorption solution pH along with absorption times are shown in Figure 6. As indicated in the figure, when the absorption time was less than 25 min, the absorption solution pH increased slightly with absorption time to about 3.6, and then increased sharply to 7.2 as the absorption time reached 27 min. In addition, the NH4-N concentration in the absorption solution increased from 239 to 5,462 mg/L as the absorption time increased from 1 to 27 min. Therefore, the optimum absorption time was 27 min in this study, and 1 volume of H2SO4 solution (0.2 mol/L) could absorb about 93% of the NH3 stripped from 54 volumes of the APW (corresponding to 1 mol of H2SO4 absorbing about 1.8 mol of the stripped NH3). On an industrial scale, the absorption solution could be monitored continuously by a pH probe.

Table 2 | Comparison of the NH4-N removal efficiencies and the KLa in different wastewaters

<table>
<thead>
<tr>
<th>Reference</th>
<th>pH</th>
<th>Air consumption, Qa/V [m³/(h·L)]</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>Removal efficiency (%)</th>
<th>KLa (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>12.0</td>
<td>0.50</td>
<td>60</td>
<td>2</td>
<td>91</td>
<td>0.0146</td>
</tr>
<tr>
<td></td>
<td>12.0</td>
<td>0.50</td>
<td>50</td>
<td>3</td>
<td>91</td>
<td>0.0125</td>
</tr>
<tr>
<td></td>
<td>12.0</td>
<td>0.50</td>
<td>40</td>
<td>5</td>
<td>91</td>
<td>0.0084</td>
</tr>
<tr>
<td>Ozturk et al. (2003)</td>
<td>12.0</td>
<td>0.46</td>
<td>N.A.</td>
<td>2</td>
<td>72</td>
<td>0.0021</td>
</tr>
<tr>
<td>Pi et al. (2009)</td>
<td>11.0</td>
<td>7.00</td>
<td>50</td>
<td>24</td>
<td>89</td>
<td>0.0013</td>
</tr>
<tr>
<td>Ferraz et al. (2015)</td>
<td>11.0</td>
<td>0.38</td>
<td>25</td>
<td>24</td>
<td>99</td>
<td>0.0030</td>
</tr>
<tr>
<td>Degermenci et al. (2012)</td>
<td>11.0</td>
<td>0.13</td>
<td>50</td>
<td>13</td>
<td>100</td>
<td>0.0098</td>
</tr>
<tr>
<td></td>
<td>11.0</td>
<td>0.13</td>
<td>40</td>
<td>21</td>
<td>100</td>
<td>0.0048</td>
</tr>
<tr>
<td>Gotvajn et al. (2009)</td>
<td>11.0</td>
<td>0.15</td>
<td>22</td>
<td>50</td>
<td>80</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

Qa: air flow rate; V: solution volume; N.A.: not available.
time. In the studied range, the APW temperature and its removal efficiency and the $K_L a$ with respect to initial APW pH of 12.0, air flow rate of 0.500 m$^3$/h-L, APW temperature of 60°C, stripping time of 120 min, $H_2SO_4$ concentration of 0.2 mol/L.

Figure 6 | NH$_4$-N concentration and pH in the absorption solution at different absorption times. Reaction conditions: NH$_4$-N concentration = 127 mg/L, initial APW pH = 12.0, air flow rate = 0.500 m$^3$/h-L, APW temperature = 60°C, stripping time = 120 min, $H_2SO_4$ concentration = 0.2 mol/L.

CONCLUSION

Experiments were conducted to investigate the NH$_4$-N removal efficiency and the $K_L a$ with respect to initial APW pH, air flow rate, APW temperature and stripping time. In the studied range, the APW temperature and its initial pH had significant effects on the NH$_4$-N removal efficiency and the $K_L a$, while the other factors had relatively minor effects. The NH$_4$-N could be effectively removed under the conditions of initial APW pH of 12.0, air flow rate of 0.500 m$^3$/h-L, APW temperature of 60°C and stripping time of 120 min. Under these conditions, the NH$_4$-N removal efficiency and residual concentration were about 91% and 12 mg/L, respectively. One volume of $H_2SO_4$ solution (0.2 mol/L) could absorb about 93% of the NH$_3$ stripped from 54 volumes of the APW.

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