Ammonia nitrogen removal from acetylene purification wastewater from a PVC plant by struvite precipitation
Lei Zhu, DeMing Dong, XiuYi Hua, ZhiYong Guo and DaPeng Liang

ABSTRACT

Acetylene purification wastewater (APW) usually contains high concentrations of ammonia nitrogen (NH₄-N), which is generated during the production of acetylene in a polyvinylchloride manufacturing plant. In this study, a struvite precipitation method was selected to remove NH₄-N from the APW. Laboratory-scale batch experiments were performed to investigate the effects of the initial APW pH, phosphate (PO₄³⁻) concentration, magnesium (Mg²⁺) concentration, and sources of PO₄³⁻ and Mg²⁺ on NH₄-N removal. The results indicated that the initial APW pH had a significant effect on the removal of NH₄-N, while the other factors had relatively minor effect. The NH₄-N could be effectively removed at an optimum initial APW pH of 9.5, when Na₂HPO₄·12H₂O and MgSO₄·7H₂O were both applied to NH₄-N at a ratio of 1.2. Under these conditions, the efficiency of removal of NH₄-N, total nitrogen and chemical oxygen demand were 85%, 84% and 18%, respectively. The X-ray diffraction analysis indicated that the precipitates were dominated by struvite. The scanning electron microscopy analysis of the precipitates showed a typical morphology of stick-like and prismatic crystals with coarse surface. The energy dispersive spectroscopy analysis indicated that the precipitates contained P, O, Mg and Ca.

Key words | ammonia nitrogen, acetylene purification wastewater, struvite precipitation

INTRODUCTION

Acetylene purification wastewater (APW) is one of the main sources of wastewater generated during the production of acetylene by the calcium carbide method in polyvinylchloride (PVC) manufacturing plant (Zhu et al. 2016). In 2011, there were about 110 PVC factories in China, and the annual production of PVC was about 13 million tons (Bing 2012). To produce 1 ton of PVC, 6 to 7 m³ of APW will be simultaneously generated. Accordingly, about 90 million m³ of APW is produced each year. The APW usually contains high level of ammonia nitrogen (NH₄-N).

Excessive nitrogen discharged from wastewater to natural water is one of the major environmental issues (Liikanen & Martikainen 2003). On the other hand, nitrogen is an important element required by agriculture and industry. Therefore, attention has been paid to the development of methods for nitrogen removal and recovery from wastewater.

Biological treatment methods, such as nitrification and denitrification (Luo et al. 2014) and the CANON (completely autotrophic nitrogen removal over nitrite) process (Zhang et al. 2015), are the conventionally used approaches. Other effective methods for the removal of NH₄-N include ion exchange (Zhou & Boyd 2014), electrochemical transformation (Desloover et al. 2012), chemical precipitation (Huang et al. 2014) and air stripping (Ferraz et al. 2015). APW, however, is not suitable to be treated by biological methods, because the wastewater contains high concentration of NH₄-N and some acetylene, which can inhibit the growth of microorganisms (Aziz et al. 2004; Vazquez et al. 2006). Additionally, the fact that only limited sources of carbon are available in the wastewater is another limitation for the use of a biological method.

Struvite (MgNH₄PO₄·6H₂O, magnesium ammonium phosphate) precipitation is one of the chemical precipitation methods. The basic reaction leading to the formation of struvite is Equation (1) (Doyle & Parsons 2002; Karak & Bhattacharyya 2011):

\[
\text{Mg}^{2+} + \text{NH}_4^+ + \text{H}_n\text{PO}_4^{(3-n)-} + 6 \text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O} + n\text{H}^+ \quad (n = 0, 1, \text{or } 2) \quad (1)
\]
Struvite is a white orthorhombic crystalline precipitate (Arogo et al. 1999). Due to its low solubility (pKs = 12.6, 25 °C), struvite can be easily separated from the liquid phase. NH4-N recovered by struvite could be used for agriculture and horticulture (Abouelien et al. 2010; De la Rubia et al. 2010), and industry (Guo et al. 2010). The method has been investigated to remove NH4-N from different types of wastewater (Li et al. 1999; Ryu et al. 2008; Zhang et al. 2009). Thus, struvite precipitation should be an effective technique for the removal of NH4-N from APW.

The success of the struvite precipitation process depends mainly on the pH value, phosphate (PO4\(^{3-}\)) and magnesium (Mg\(^{2+}\)) concentrations and chemicals applied as Mg\(^{2+}\) and PO4\(^{3-}\) ions source (Li et al. 1999; Zhang et al. 2009). To the best of our knowledge, the feasibility of struvite precipitation in the removal of NH4-N from APW has not yet been reported. Therefore, in this study, the effects of the initial APW pH, PO4\(^{3-}\) and Mg\(^{2+}\) concentrations, and the sources of PO4\(^{3-}\) and Mg\(^{2+}\) were investigated. Additionally, the optimum treatment conditions were obtained, and the structure, morphology and composition of the struvite precipitates were also analyzed to examine the physical properties.

**MATERIALS AND METHODS**

**Acetylene purification wastewater**

The APW used in this study was collected from a PVC manufacturing plant in Jilin Province, China. Some basic information of the wastewater is as follows: pH: 8.5 ± 0.5, NH4-N: 150 ± 2 mg/L (8.33 mmol/L), total nitrogen (TN): 155 ± 5 mg/L, chemical oxygen demand (COD): 232 ± 8 mg/L, phosphate (PO4\(^{3-}\)): 1 ± 1 mg/L, calcium (Ca\(^{2+}\)): 80 ± 2 mg/L. The concentration of NH4-N was high in this wastewater, and about 97% of the TN was from NH4-N.

**Optimization for NH4-N removal**

The laboratory-scale experiments for struvite precipitation were performed at 22–25 °C as follows: APW (200 mL) was added into a 250 mL beaker, and its initial pH was adjusted to the expected values with NaOH and/or H2SO4. Then, powdered phosphate and magnesium salts, as sources of PO4\(^{3-}\) and Mg\(^{2+}\), respectively, were added to the APW and the amounts of the salts were calculated according to initial NH4-N concentration and the expected concentrations of phosphate and magnesium. After the addition of the salts, the beaker was covered with a watch glass, to limit the evaporation of NH3 and the possible effects of atmospheric CO2 on struvite formation. Then the solution was stirred by a magnetic stirrer at 200 rpm for 30 min, and allowed to settle for 10 min. Finally, the solution was filtered with a 0.45 μm membrane filter, and the concentration of NH4-N in the filtrate was measured. The experiment was performed in duplicate.

To accomplish the optimal conditions, the four factors were optimized step by step, in the following order: initial APW pH, phosphate concentration, magnesium concentration and sources of PO4\(^{3-}\) and Mg\(^{2+}\). When a 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 assigned to this factor in the subsequent optimization experiments, and the initial NH4-N concentration in the APW remained the same (8.33 mmol/L) in all the experiments. The initial values assigned to the factors were 8.33 mmol/L for both phosphate and magnesium concentration, and NaH2PO4·2H2O and MgSO4·7H2O were used as sources of PO4\(^{3-}\) and Mg\(^{2+}\), respectively. The ranges of the factors to be optimized were 8.0, 8.5, 9.0, 9.5, 10.0 and 10.5 for initial APW pH; 5.00, 6.66, 8.33, 10.00, 11.66 and 13.33 mmol/L for phosphate concentration (corresponding molar ratio of PO4\(^{3-}\)/NH4-N (P/N) was 0.6, 0.8, 1.0, 1.2, 1.4 and 1.6); 5.00, 6.66, 8.33, 10.00, 11.66 and 13.33 mmol/L for magnesium concentration (corresponding molar ratio of Mg\(^{2+}\)/NH4-N (Mg/N) was 0.6, 0.8, 1.0, 1.2, 1.4 and 1.6); Na3PO4·12H2O, Na2HPO4·12H2O, NaH2PO4·2H2O and H3PO4 (85%) for source of PO4\(^{3-}\); MgSO4·7H2O and MgCl2·6H2O for source of Mg\(^{2+}\). The combinations of the sources of PO4\(^{3-}\) and Mg\(^{2+}\) are shown in Table 1. To simplify the possible practical application of the method, only these initial conditions were controlled and optimized, and no further adjustment of the factors was applied during the course of the experiment. After the treatment of the APW under the

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Source of PO4(^{3-})</th>
<th>Source of Mg(^{2+})</th>
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<tbody>
<tr>
<td>A1</td>
<td>Na2PO4·12H2O + MgSO4·7H2O</td>
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<tr>
<td>A2</td>
<td>Na2HPO4·12H2O + MgSO4·7H2O</td>
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<tr>
<td>A3</td>
<td>NaH2PO4·2H2O + MgSO4·7H2O</td>
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<td>A4</td>
<td>H3PO4 + MgSO4·7H2O</td>
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<td>A5</td>
<td>Na3PO4·12H2O + MgCl2·6H2O</td>
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<td>A6</td>
<td>Na2HPO4·12H2O + MgCl2·6H2O</td>
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<td>A7</td>
<td>NaH2PO4·2H2O + MgCl2·6H2O</td>
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obtained optimum conditions, the concentrations of NH₄-N, TN, COD and pH were measured for the filtrate. The precipitates obtained were dried in an oven at 40 °C for 72 h (Zhang & Chen 2009), and analyzed for their morphology, structure and composition.

Analytical methods

All reagents used in the experiments were of analytical grade. The pH was measured by a pH meter (Model-370, Orion, USA). COD was analyzed by a COD rapid detector (DRB-200, Hach, USA) and a UV-visible spectrophotometer (DR-2800, Hach, USA). TN was measured with a total organic carbon analyzer (TOC-LCPH, Shimadzu, Japan). NH₄-N and PO₄³⁻ were measured according to Standard Methods (APHA 1995). Ca²⁺ was measured using an atomic absorption spectrophotometer (AA-700, Perkin Elmer, USA). The morphology, structure and composition of the precipitates were characterized by scanning electron microscopy (SEM, SU-8020, Hitachi, Japan), X-ray diffraction (XRD, Empyrean II, Panalytical, The Netherlands), and energy dispersive spectrometry (EDS, Quantax-200, Bruker, USA), respectively.

RESULTS AND DISCUSSION

Effect of the initial pH

The removal efficiency of NH₄-N from the APW as a function of the initial pH is shown in Figure 1. According to the results, when the initial pH was less than 9.5, the NH₄-N removal efficiency increased with initial pH to about 59%. In contrast, when the initial pH was greater than 9.5, the removal efficiency decreased with the initial pH. Accordingly, 9.5 was selected as the initial APW pH in this study. This is consistent with some related studies concerning the struvite precipitation method (Booker et al. 1999; Gunay et al. 2008; Zhang et al. 2009). At this initial pH (9.5), the equilibrium pH after the formation of struvite was about 9.0, due to the release of H⁺ from the phosphate.

Variation of the pH affects the formation or solubility of the struvite crystals. pH is generally considered to be the main driving force for the formation and dissolution of struvite (Parsons et al. 2001; Zhang et al. 2009). Therefore, at the initial pH of 8.0 and 8.5, only a limited amount of very small precipitates was produced. When the initial pH was in the range of 9.0–9.5, a large amount of small precipitates was formed. At the initial pH of 10.0 and 10.5, the amount of precipitates was even larger. However, the precipitates were big and loose, and tended to remain suspended. It was found that, at high pH values, some other precipitates such as Mg₃(PO₄)₂ were formed, which were loose in texture (Ryu et al. 2008). This reduced the concentrations of Mg²⁺ and PO₄³⁻ available for the formation of struvite. Therefore, although the amount of the precipitates was increased, the NH₄-N removal efficiency decreased.

Effect of phosphate concentration

The effect of the phosphate concentration on the removal efficiency of NH₄-N is shown in Figure 2. The results...
revealed that the removal efficiency of NH₄-N increased from 44% to 68% as the phosphate concentration increased from 5.00 to 10.00 mmol/L, and then the removal efficiency decreased gradually to 61% with further increase of the phosphate concentration to 13.33 mmol/L. Therefore, we selected 10.00 mmol/L as the optimum phosphate concentration, and the corresponding P/N was 1.2.

The phosphate dosage is a key factor for struvite formation. Ryu et al. (2008) found that in most cases the amount of PO₄³⁻/C₀ affected NH₄-N removal much more prominently than amount of Mg²⁺. Excess NaH₂PO₄·2H₂O did not further increase the removal of NH₄-N, mainly because the release of H⁺ from NaH₂PO₄·2H₂O decreased the pH value of the solution. In this study, the pH value of the solution decreased from an initial value of 9.5 to 7.5 when 13.33 mmol/L phosphate was added. In addition, some extraneous cations contained in the APW can affect the precipitation of struvite (Stratful et al. 2001; Song et al. 2007). Among the extraneous cations, Ca²⁺ is one notable ion that can hinder the formation of struvite, by competing with struvite for PO₄³⁻/C₀, and significantly affect the purity of the struvite precipitation (Song et al. 2007). Therefore, the optimum P/N was 1.2, rather than 1.0, which is the ratio in struvite.

**Effect of magnesium concentration**

The effect of the magnesium concentration on the removal efficiency of NH₄-N is shown in Figure 3. The results indicated that when the magnesium concentration was increased from 5.00 to 10.00 mmol/L, the removal efficiency of NH₄-N increased from 46% to 72%. However, when the concentration was higher than 10.00 mmol/L, the removal efficiency gradually decreased. Therefore, we selected 10.00 mmol/L as the optimum magnesium concentration, and the corresponding Mg/N was also 1.2.

Stratful et al. (2001) found that Mg²⁺ is also a limiting factor to struvite precipitation. Similar to PO₄³⁻, too much Mg²⁺ (Mg/N > 1.2) did not lead to increased NH₄-N removal. Struvite is not the only precipitate that can be formed by Mg²⁺, and too much Mg²⁺ promoted the formation of other precipitates, especially Mg₅(PO₄)₂, which decreased both the available PO₄³⁻ and Mg²⁺ (Song et al. 2007). To further investigate the effect of the Mg²⁺ concentration on struvite formation, we analyzed the formation of precipitates containing Mg, as a function of the Mg²⁺ concentration, in a solution with NH₄⁺ (8.33 mmol/L), PO₄³⁻ (10.0 mmol/L), and Ca²⁺ (2.0 mmol/L), etc. at pH = 9.0, which is the equilibrium pH of the APW solution in the experiments of this section. The calculation was conducted using Visual MINTEQ 3.1 (Jon Petter Gustafsson, KTH, Sweden), and the results are shown in Figure 4. According to the results, the maximum amount of struvite was formed when the concentration of Mg²⁺ was about 9 mmol/L. When the concentration was greater than 9 mmol/L, the amount of struvite slowly decreased with the increase of the Mg²⁺ concentration, due to the formation of Mg₃(PO₄)₂ and magnesite (MgCO₃). Additionally, the results indicate that hydroxyapatite [Ca₅(OH)(PO₄)₃] was also formed, which confirmed the interaction between Ca²⁺ and PO₄³⁻.

![Figure 3](https://iwaponline.com/wst/article-pdf/74/2/508/461082/wst074020508.pdf)

**Figure 3** | Effect of magnesium (MgSO₄·7H₂O) concentration on the removal efficiency of NH₄-N from the APW. Reaction conditions: ammonia nitrogen concentration – 8.33 mmol/L, initial pH – 9.5, phosphate (NaH₂PO₄·2H₂O) concentration – 10.00 mmol/L.

![Figure 4](https://iwaponline.com/wst/article-pdf/74/2/508/461082/wst074020508.pdf)

**Figure 4** | Model-predicted precipitate composition as a function of Mg²⁺ concentration. Some key simulation conditions: [NH₄⁺] = 8.33 mmol/L, [PO₄³⁻] = 10.00 mmol/L, [Ca²⁺] = 2.0 mmol/L, equilibration pH = 9.0, pCO₂ = 0.000076 atm.
Effect of the sources of $\text{PO}_4^{3-}$ and $\text{Mg}^{2+}$

The results of the analysis of the effect of the sources of $\text{PO}_4^{3-}$ and $\text{Mg}^{2+}$ are shown in Figure 5. The results revealed that all the eight combinations achieved a removal efficiency of NH$_4$-N higher than 50%, and both A2 and A6 were similarly the most efficient combinations with 82%–83% of NH$_4$-N removed. In both combinations, Na$_2$HPO$_4$·12H$_2$O was used as the source of $\text{PO}_4^{3-}$. Accordingly, Na$_2$HPO$_4$·12H$_2$O was used as the best source of $\text{PO}_4^{3-}$ under the experimental conditions used. Additionally, the pairs A1 and A5, A3 and A7, and A4 and A8 had similar removal efficiency, and each pair shares the same phosphate. Under these experimental conditions, the effects of the sources of $\text{PO}_4^{3-}$ were significant, whereas the effects of the sources of $\text{Mg}^{2+}$ were negligible, as both Cl$^-$ and SO$_4^{2-}$ completely ionized in water and had no effects on struvite formation. To prevent too much Cl$^-$ entering the treated water, whose Cl$^-$ concentration was already fairly high, MgSO$_4$·7H$_2$O was selected as the source of $\text{Mg}^{2+}$.

The addition of different types of phosphates to the APW would change the equilibrium pH of the solution in different ways. In this study, the initial pH of the APW was first optimized, using NaH$_2$PO$_4$·2H$_2$O as the source of $\text{PO}_4^{3-}$, at a concentration of 8.33 mmol/L. Under these conditions, the optimized initial pH value was 9.5, and the corresponding final/equilibrium pH was about 9.0. Afterward, the concentration of NaH$_2$PO$_4$·2H$_2$O was optimized, to be 10.00 mmol/L. Under these conditions, as more NaH$_2$PO$_4$ (1.67 mmol/L) was added to the solution, the final pH decreased from about 9.0, the optimum value, to about 8.7. When Na$_2$HPO$_4$·12H$_2$O was used as the source of $\text{PO}_4^{3-}$ at a concentration of 10.00 mmol/L, the final pH increased to about 9.0, around the optimum value again. Therefore, the effect of the sources of $\text{PO}_4^{3-}$ was actually due to the effect of the (final) pH.

Removal of NH$_4$-N under the optimal conditions

According to the above results, the optimal conditions were as follows: initial APW pH of 9.5; Na$_2$HPO$_4$·12H$_2$O applied at P/N = 1.2; MgSO$_4$·7H$_2$O applied at Mg/N = 1.2. Under these conditions, the average removal efficiencies of NH$_4$-N, TN and COD were 85%, 84% and 18%, respectively. The yield of the precipitates was about 3.7 g/L. The pH of the APW after treatment dropped from 9.5 to 9.0, due to the H$^+$ released into the solution from Na$_2$HPO$_4$ when struvite formed (Stratful et al. 2013). Apparently, most of the NH$_4$-N and TN were removed. The obtained high removal efficiency of NH$_4$-N and low removal efficiency of COD imply that the struvite precipitation technique is highly selective for NH$_4$-N. This is consistent with other studies using the struvite precipitation technique (Li et al. 2013; Li & Zhao 2013). After precipitation, a subsequent biological treatment process for COD removal may be applied. The optimal conditions obtained in this study are compared with those obtained in other similar studies in Table 2. Generally, those conditions were similar to this study. Some departures could be due to different wastewater sources.
composition, initial NH$_4$-N concentration, phosphate used, and the operation of the experiment.

Usually, struvite is a white powder. In this study, the precipitate generated under the optimal conditions was a light-grey crystalline powder. This was due to the co-precipitation of some other compounds present in the APW. The SEM micrograph of the precipitates is shown in Figure 6. The published morphology types range from needle-like (Song et al. 2007) and stick-like (Wang et al. 2010) to trapezoidal (Münch & Barr 2001). In our study, a typical morphology of stick-like or prismatic crystals is more manifest than other types. Furthermore, the surface of the crystals is not smooth and is covered with other matters. The result of the EDS analysis of the precipitates is listed in Table 3. This analysis revealed that the surface of the precipitates contains a great deal of C, O, P, Mg and some Ca. The XRD pattern of the precipitates is shown in Figure 7. It matches well with the database model for struvite (JCPDS No. 15-0762 1996), specifically the position and intensity of the peaks, indicating that the precipitates were dominated by struvite.

To confirm the optimal conditions obtained, Visual MINTEQ 3.1 was also used to calculate the composition of precipitates at different equilibrium pH values, in a simulated solution under the optimal conditions (Figure 8). To investigate the possible effect of atmospheric CO$_2$ on precipitate formation, both closed system without atmospheric CO$_2$ (Figure 8(a)) and partially open system equilibrium with 20% atmospheric CO$_2$ (Figure 8(b)), which was similar to the APW in the beaker covered by a watch glass in this study, were calculated. The calculated percentages of the precipitated NH$_4$-N (as struvite) and the measured NH$_4$-N removal efficiency (85%) under the optimal conditions (at equilibrium pH of 9.0, the corresponding initial pH is 9.5) in this study are shown in Figure 9. These results indicate that the formation of struvite was severely affected by pH. The optimal equilibrium pH for struvite formation was near 9.0, which is consistent with the results of our experiment. At higher pH (higher than 9.0), the atmospheric CO$_2$ had a major effect on the composition of the precipitates and the formation of struvite. Therefore, limiting the dissolution of atmospheric CO$_2$ into the APW was necessary during the treatment. The result in Figure 9 also confirmed that at equilibrium pH near 9.0, the precipitates were dominated by struvite.

### CONCLUSIONS

Under the treatment by the struvite precipitation technique, the removal efficiency of NH$_4$-N was affected by the initial pH of the APW, phosphate concentration, magnesium concentration and the sources of PO$_4^{3-}$ and Mg$^{2+}$. The initial APW pH had significant effects on the removal of NH$_4$-N. A very satisfactory removal of NH$_4$-N (85%) was obtained with the initial APW pH of 9.5, when Na$_2$HPO$_4$·12H$_2$O and MgSO$_4$·7H$_2$O were applied with ratios to NH$_4$-N both
at 1.2. In comparison, the removal efficiencies of TN and COD were 84% and 18%, respectively. The residual concentrations of PO₄³⁻ and Ca²⁺ were very low. The stick-like crystal was coarse and the surface composition contained a great deal of C, O, P, Mg and some Ca. The precipitates were dominated by struvite.

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