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Treating ammonium-rich wastewater with sludge from water treatment plant to produce ammonium alum

Wen-Po Cheng^{a, *}, Ping-Hung Chen^b, Ruey-Fang Yu^a, Wei-Ni Ho^a^a Department of Safety, Health and Environmental Engineering, National United University, Miaoli 360, Taiwan^b Institute of Natural Resource Management, National Taipei University, New Taipei City 237, Taiwan

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ABSTRACT

This study applies a process to treat ammonium-rich wastewater using alum-generated sludge from water purification plant, and gain economic benefit by producing ammonium alum ($\text{Al}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$). The factors affecting production of ammonium alum include molar ratio of ammonium to aluminum concentration, sulfuric acid concentration, mixing speed, mixing time, standing time, and temperature. According to the equation for the ammonium removal reaction, the theoretical quantity of ammonium alum was calculated based on initial and final concentrations of ammonium. Then, the weight of ammonium alum crystal was divided by the theoretical weight to derive the recovery ratio. The optimum sludge and sulfuric acid dosage to treat about 17 g L^{-1} ammonium wastewater are 300 g L^{-1} and 100 mL L^{-1} , respectively. The optimal dosage for wastewater is molar ratio of ammonium to aluminum of about 1 due to the aluminum dissolving in acidified wastewater. The ammonium removal efficiency is roughly 70% and the maximum recovery ratio for ammonium alum is 93% when the wastewater is mixed for 10 min at the mixing velocity gradient of 100 s^{-1} . Ammonium alum production or ammonium removal can be enhanced by controlling the reaction at low temperatures.

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1. Introduction

Ammonium pollution from industrial wastewater adversely affects the water quality of water bodies and causes several environmental problems such as surface-water eutrophication, reduced disinfection efficiency, increased dissolved oxygen consumption and has toxic effects on fish. Hence, Taiwan Environmental Protection Agency (TEPA) regulates industrial wastewater and defines ammonium as a pollutant. In 2012, TEPA set a new effluent standard for the high-tech and chemical industries (10 mg L^{-1} , in tap water quality protection area). These standards are predicted to remove approximately 16,000 kg of ammonium from water bodies daily. To remove ammonium ions from industrial wastewater, three methods are commonly used. The first is physical chemistry method, including air stripping, membrane filtration, absorption, and ion exchange techniques [1]. The second method comprises chemical methods, including break-point chlorination, chemical

precipitation, catalysis enhanced wet oxidation, and sulfuric acid adsorption [2–5]. The last group of biological methods includes trickling filtration, biofilm reaction techniques, and aerobic nitrification [6,7]. Traditionally, the main methods for treating ammonium-rich wastewater are air stripping, chemical precipitation, and membrane filtration [8]. However, the safety of air stripping is always debatable, such that this method is carefully used in industry. Conversely, chemical precipitation requires adding a tremendous amount of a chemical, which makes it cost prohibitive in most cases [9]. Although membrane filtration is relatively safe, filtration capacity, operation, and facility maintenance are major problems.

In chemical precipitation, aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) can easily react with other ions, such as Na^+ , K^+ , and NH_4^+ , to form a crystal compound. In the previous researches, crystallization of ammonium aluminum sulfate dodecahydrate ($\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, ammonium alum) is an important step in production of high purity aluminum compounds [10–12] or recovery of aluminum and sulfate from waste solutions [13–15]. Thus, when a large amount of $\text{Al}_2(\text{SO}_4)_3$ is added to ammonium-rich wastewater, the dissolved $\text{Al}_2(\text{SO}_4)_3$ reacts with ammonium to form ammonium alum crystal. Therefore, ammonium alum precipitation process can reduce the

* Corresponding author.

E-mail address: cwp@nuu.edu.tw (W.-P. Cheng).

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amount of ammonium in wastewater. Although this method is operationally safe, the amount of alum added is considerable, such that operational cost is high. Some researchers have attempted to improve this method [16,17]. They soaked aluminum minerals in sulfuric acid solution to convert the aluminum oxide in the mineral into soluble aluminum sulfate, which was then added to ammonium-rich wastewater to precipitate the ammonium alum. However, because this acid soaking method lacks a thermal heating process, aluminum is not easily dissolved during the reaction. Therefore, a large amount of acid is wasted.

In drinking water and wastewater treatment processes, a coagulant, such as aluminum sulfate or poly aluminum chloride may react with colloids/particles in raw water forming settled flocs. After settling the flocs, the resultant chemical sludge is dewatering to produce a sludge cake. This sludge cake contains a considerable amount of aluminum hydroxide ($\text{Al}(\text{OH})_3$), which dissolves easily to form aluminum ions (Al^{3+}) under room temperature and acidic conditions [18–23]. When chemical sludge needs to be reused, sulfuric acid is commonly used to acidify the sludge and leaches out the Al^{3+} ions, which are then reused as a coagulant [24]. In other words, by adding sulfuric acid to chemical sludge, aluminum ions can be leaching out. The chemical sludge may become the source of aluminum for generating crystallized ammonium alum, such that operational cost is decreased. Furthermore, ammonium alum is an important chemical widely used as an additive compound for water purification in chemical, food, and dye manufacturing industry, as well as for synthesizing jewels [25–27]. Thus, crystallized ammonium alum, recovered as an industrial raw material, potentially becomes an economically valuable product. In this study, sludge from water purification plant was used as the aluminum source to develop a method to generate ammonium alum, by removing high concentration ammonium in wastewater and recovering aluminum from waster sludge.

Ammonium alum crystallization is a nucleation process, which produces primary or secondary nucleuses [28,29]. Typically, when a saturated factor α ($\alpha = c/c_s$, where c is the substance concentration in the solution, and c_s is the saturation concentration of the substance) is in the range of 1.0–1.3, it is in the metastable region. During a reaction in this region, an existing nucleus may increase its diameter and a secondary nucleus is formed gradually. Therefore, the secondary nucleus with a relatively large critical radius may easily form a large crystal. Additionally, a dehydrated substance may grow near the crystal surface resulting in increasing crystal size. These crystal particles can be precipitated or recovered easily.

In this study, dewatered sludge from water purification plant was added to ammonium-rich wastewater. Sulfuric acid was then added to leach out the aluminum from the sludge. After mixing, crystallized ammonium alum formed. Then, a 16-mesh-size sieve (1.19 mm) was used to separate the crystallized ammonium alum from the sludge suspension. The coarse crystallized ammonium alum on the sieve was harvested for further refining. In crystallization process, the factors affecting α , crystal size, and number of ammonium alum particles, such as sludge amount, mixing time, mixing strength, and mixing temperature, are discussed and optimum operational conditions are identified for recovering the ammonium alum.

2. Materials and methods

2.1. Water purification sludge

The sludge samples were collected from the sludge drying bed of Ming-Der Water Treatment Plant (Miaoli, Taiwan), dried at 105 °C, and then homogenized for laboratory use. The acidified

ammonium-rich wastewater was collected from the effluent after recovering precious metals from waste catalysis and the average concentration of ammonium is about 17,000 mg L⁻¹. The ammonium concentration was determined by an ammonium ion-selective electrode (RZ-27502-03; Cole-Parmer, Canada). Each experiment was repeated twice and average values are reported. The relative bias of each replicate tests is less than or equal to 15%.

2.2. Sludge quantity effect on aluminum dissolution from sludge

Suspensions with 60, 120, 180, 240 and 300 g L⁻¹ sludge were prepared by mixing dry sludge in 1000 mL pure water. Then, 100 mL concentrated sulfuric acid solutions were individually added into each set sludge suspension in each aluminum experiment. Suspensions were mixed for 5 min and then allowed to settle for 60 min. While standing, solution pH was measured at 10 min interval and the supernatant was collected at same time. The suspension was filtered after each interval and the filtrate was analyzed for its aluminum concentration by an atomic absorption analysis (Z-5000 Hitachi, Japan). The analytical result may help elucidate the effect of sulfuric acid on the aluminum dissolution rate.

2.3. Sludge quantity effect on crystallization of ammonium alum

Various weight of water purification sludge (60, 120, 180, 240, 300, 400, 500, 600, and 700 g) were added separately in different sets of 1000 mL wastewater containing approximately 17,000 mg L⁻¹ ammonium ions. The suspensions were mixed at the velocity gradient value of 100 s⁻¹ for 10 min. They were then allowed to stand for the ammonium alum crystallization procedure. A series of water samples were taken from the supernatant of the suspensions for analyses of their aluminum, ammonium and heavy metal concentrations. In Table 1, it shows not only the aluminum salt, but also the crustal elements (Fe, Mn) and the heavy metals dissolving in sulfuric acid. Therefore, the data of Table 1 indicate that the Mn concentration in the supernatant of the suspensions is 60 times higher than the maximum allowed concentration of coagulant used in the water treatment, so the acidification solution is not suitable to be reused as coagulant. After the standing period ended, the suspensions was filtrated with a 16-mesh sieve, and the coarse ammonium alum crystal was obtained. The crystal was dried at 30 °C for 3 d. The structure of the crystal was observed using an X-ray diffraction (XRD, D/Max 2550PC, Rigaku, Japan). The results in Fig. 1 indicate there is ammonium alum in the crystal product. The concentrations of

Table 1

The concentrations of heavy metals in the acidified sludge solution (suspension concentration is 300 g L⁻¹), and in ammonium alum crystal.

Heavy metals	Acidification sludge	Ammonium alum crystal	Limitation ^a
Al	25,830	5810	
As	6.5	ND	10
Cd	2.2	ND	2
Cr	1.8	ND	10
Cu	6.7	ND	–
Fe	3190	9.24	200
Ga	0.7	ND	–
Mn	1519	4.51	25
Ni	2.1	ND	–
Zn	7.2	ND	10
Pb	0.8	ND	10
Hg	ND	ND	0.2

Unit: mg L⁻¹; ND: not detectable.

^a The limitation of heavy metals in aluminum sulfate used in drinking water treatment of Taiwan, R.O.C.

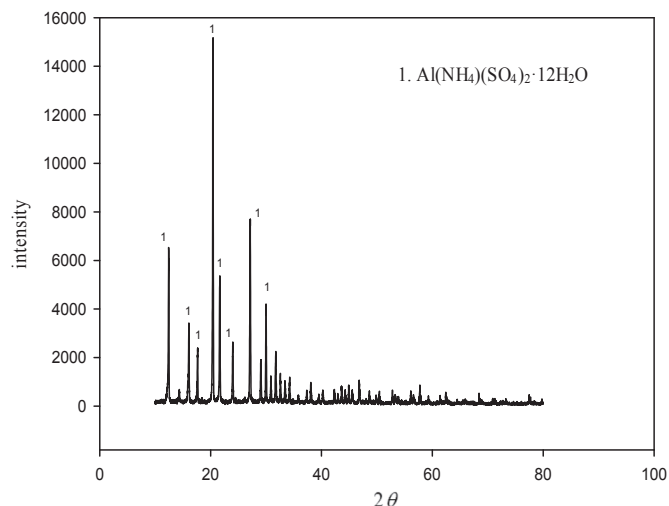


Fig. 1. Results of XRD analyses of crystal sample.

aluminum and heavy metals in the crystal were measured through dissolving 100 g ammonium alum crystal in 1000 mL water (solubility for ammonium alum was 150 g L^{-1}). Based on the molecular weight of ammonium alum, the theoretical weight of aluminum in 100 g L^{-1} ammonium alum solution is calculated to be 5970 mg L^{-1} . In Table 1, concentration of aluminum (5810 mg L^{-1}) is very close to the theoretical value. This experimental result confirms that the ammonium alum is the major component of the crystal product. In addition, only little crustal elements (Fe, Mn) may be attached to the crystal surface so that “impurities” exist in the crystal solution (Table 1). Thus, the crystallization method described in this study can reduce the impurity in the acidified sludge solution (Table 1) and can be used to recycle and reuse the aluminum salt in water treatment or other applications.

The dried ammonium alum was weighed. The dried crystal was dissolved in hot water and the solution was filtered through a $0.45 \mu\text{m}$ filter. After filtration, the filter was dried and weighed for calculation of amount of the impurity (i.e., sludge) in the dried crystal. The recovery ratio for ammonium alum can be expressed in the following equation:

$$\frac{S_0 - S_1}{([\text{NH}_4]_0 - [\text{NH}_4]_1) \times V \times 452 \text{ g/mol}} \times 100\% \quad (1)$$

where $[\text{NH}_4]_0$ is the initial ammonium concentration (M), $[\text{NH}_4]_1$ is the residual ammonium concentration (M), S_0 is dry weight of ammonium alum (g), S_1 is weight of the impurity in the crystallized ammonium alum (g), and V is solution volume.

2.4. Determination of ammonium alum recovery ratio for various mixing times

In total, 300 g sludge was added to 1000 mL wastewater with an ammonium concentration of roughly $17,000 \text{ mg L}^{-1}$. Then, 100 mL concentrated sulfuric acid solutions (98%) were added individually to the sludge suspension. Seven sets of these suspensions were mixed rapidly for 0.5, 2.5, 5, 30, 60, 90, and 120 min with velocity gradients at 100 s^{-1} . After mixing for different durations, the sludge suspension was allowed to stand for 6 d to form any crystal. The relationship between the ammonium alum recovery ratio and mixing duration was discussed according to experimental results.

2.5. Determination of ammonium alum recovery ratio for various mixing speeds

To assess the effect of mixing speed on the ammonium alum recovery ratio, 300 g sludge was added to 1000 mL wastewater with an ammonium concentration of roughly $17,000 \text{ mg L}^{-1}$. In total, 100 mL concentrated sulfuric acid solutions (98%) were added individually into the sludge suspension. Six sets of these suspensions were mixed at various speeds with velocity gradients of 50, 100, 200, 300, 400, and 500 s^{-1} for 10 min. After mixing, suspensions were allowed to stand for 5 d, such that the relationship between mixing speed and ammonium alum recovery ratio was identified.

2.6. Determination of ammonium alum crystallization at various temperatures

In total, 300 g sludge was added to 1000 mL wastewater with an ammonium concentration of about $17,000 \text{ mg L}^{-1}$. To the sludge suspension, 100 mL concentrated sulfuric acid solutions (98%) were added individually. The temperature of these four sets of suspensions was adjusted to 10, 30, 50, and $70 \text{ }^\circ\text{C}$ and mixed at 100 s^{-1} for 10 min. After mixing, while the suspension temperature was stable, the suspension was let stand for 1 d, such that the effect of temperature on the ammonium alum recovery ratio was assessed.

3. Results and discussion

3.1. Sludge quantity effect on aluminum dissolution from sludge

The ammonium of $17,000 \text{ mg L}^{-1}$ in wastewater equals approximately 0.94 M. Based on the molecular weight of ammonium alum ($\text{Al}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), the molar ratio of $\text{Al}:\text{NH}_4:\text{SO}_4$ is 1:1:2 [30]. Therefore, in theory, approximately 184 g sulfuric acid must be added to 1 L ammonium-rich wastewater. Because the density of sulfuric acid is 1.84 g cm^{-3} , 100 mL sulfuric acid added into 1 L wastewater theoretically provides 1.88 mol sulfate ions (SO_4^{2-}). In theory, the weight of aluminum ion should be 25 g (0.94 mol) according to the ratio of $\text{Al}:\text{NH}_4:\text{SO}_4$ is 1:1:2.

To identify the optimal additional amount of the sludge at theoretical 1.88 mol sulfuric acid, various concentrations of sludge suspensions were prepared by adding dry sludge to pure water. After adding 100 mL sulfuric acid, the aluminum ion concentration was determined every 10 min. As shown in Fig. 2, the dissolved aluminum concentration is proportional to the weight of added sludge. When the sludge concentration is 300 g L^{-1} , the dissolved aluminum concentration is roughly $25,000 \text{ mg L}^{-1}$. Therefore, when the sludge concentration is 300 g L^{-1} , the requirement for ammonium alum crystallization is satisfied. Furthermore, the equilibrium condition can be achieved rapidly in the aluminum dissolving reaction at each sludge concentration (Fig. 2). During a sludge acidification process, the aluminum dissolve rate is proportional to the quantity of sludge added. Therefore, as the amount of sludge added increases, the amount of sulfuric acid consumed increases and the amount of aluminum ions that are dissolved also increases. Hence, the acid consumption rate varies with the sludge quantity added. The aluminum concentrations (Fig. 2) at a reaction time of 60 min were used to compare sludge concentrations and the respective pH values (Fig. 3a). Experimental results show that pH is proportional to the sludge concentration (Fig. 3a). Because $\text{Al}(\text{OH})_3$ in the sludge consumes H^+ to dissolve aluminum ions, the acid consumption rate is proportional to the sludge concentration after adding the same amount of sulfuric acid. At the same time,

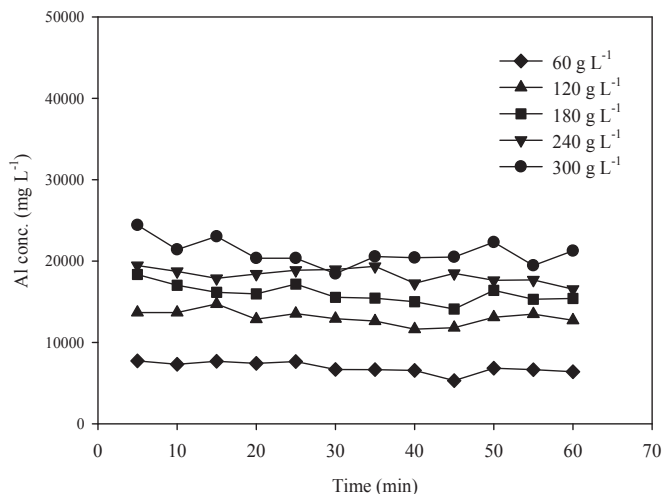


Fig. 2. The dissolved aluminum concentration as a function of reaction time under various sludge concentrations.

because the sulfuric acid concentration was added more than 1 M, the pH value in Fig. 3a is decreased to negative when only a little amount of the sludge was added. Analytical results confirm that the theoretical sulfuric acid (100 mL sulfuric acid added to 1 L pure water) can dissolve enough aluminum to treat an ammonium-rich wastewater with concentration of $17,000 \text{ mg L}^{-1}$.

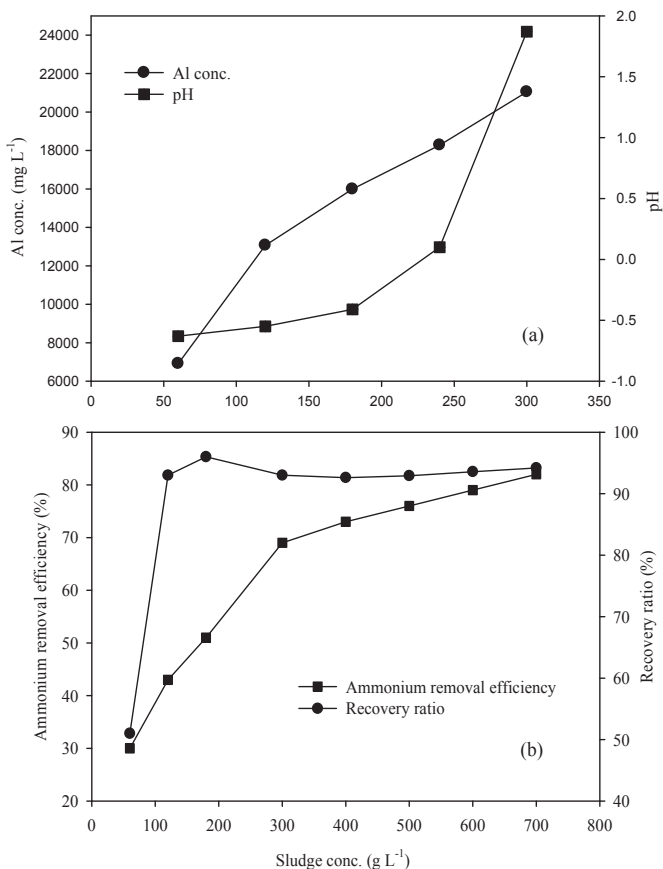


Fig. 3. The relationship among sludge concentration and (a) aluminum concentration, pH (b) ammonium removal efficiency, ammonium alum recovery ratio.

3.2. The effect of sludge quantity on ammonium alum crystallization

To determine the optimal amount of sludge for ammonium alum crystallization, various sludge suspensions were prepared by dissolving dry sludge in 1000 mL ammonium-rich wastewater and 100 mL concentrated sulfuric acid, which was then mixed at a speed of 100 s^{-1} for 10 min. After mixing, the suspensions were let stand for 1 d. Based on the measured ammonium concentration; the ammonium alum recovery ratio was obtained using Eq. (1). The derivational result in Fig. 3b indicates that the ammonium removal efficiency is proportional to the sludge concentration. When the sludge concentration is 120 g L^{-1} , the ammonium alum recovery ratio exceeds 80%, meaning that the water purification sludge can be used to treat ammonium-rich wastewater. However, when the added sludge concentration exceeds 300 g L^{-1} , the ammonium removal efficiency does not increase significantly, meaning that when a certain amount of sludge is added, the amount of theoretical sulfuric acid is insufficient, such that the aluminum dissolve rate does not increase significantly. At this point, the ammonium removal efficiency is more than 70%, which is not easy to increase further. If the sludge concentration added is too high, the mixing and crystallization processes suffer. Therefore, the optimum concentration of sludge is set at 300 g L^{-1} for the following experiments.

3.3. Standing time effect on ammonium alum crystallization

To determine the effect of standing time or crystallization time on ammonium alum recovery ratio, the aluminum and ammonium concentrations were analyzed for different standing durations. Fig. 4 shows the experimental results. Since the aluminum concentration is proportional to the sludge concentration, the maximum ammonium removal efficiency occurred when a large amount of sludge was added to ammonium-rich wastewater. After standing for 6 d, residual ammonium is inversely proportional to the sludge concentration (Fig. 4a). The residual aluminum ion concentration is proportional to the sludge concentration (Table 2), meaning that when the molar ratio of ammonium to aluminum is too high, the number of aluminum ions is insufficient and $(\text{NH}_4)_2\text{SO}_4$ cannot effectively remove ammonium to form ammonium alum. Conversely, when the aluminum concentration increases, the ammonium removal efficiency increases and ammonium alum production is enhanced. Generally, when the sludge concentration is 300 g L^{-1} , an ammonium removal efficiency of 69% can be achieved. Based on this removal efficiency, the theoretical weight of ammonium alum is derived as 254 g. The dry weight of crystallized ammonium alum obtained from filtration is 290 g. After subtracting the impurity weight, the amount of ammonium alum recovered is 236 g. The recovery ratio can be calculated to be 93%, meaning that the ammonium alum can be recovered effectively through filtration with a 16-mesh sieve. When the sludge concentration is 60 g L^{-1} , the ammonium alum recovery ratio falls to 51% (Table 2). An Extremely low sludge concentration may cause insufficient dissolution of aluminum ions. The NH_4^+ and SO_4^{2-} cannot effectively react with the Al^{3+} ion to form a large crystal. The small ammonium alum crystals cannot remain on the 16-mesh sieve and more Al^{3+} ion will present in the solution. Hence, not only the recovery ratio of 60 g L^{-1} is significantly low but also the residual aluminum concentration of 60 g L^{-1} is similar to the concentration of 120 g L^{-1} (Fig. 4b). On the other hand, ammonium and aluminum ion concentrations are eventually stabilized after standing for 1 d (Fig. 4a and b). Similarly, almost all ammonium alum is produced within the first day (Table 3). These experimental results demonstrate that formation of ammonium

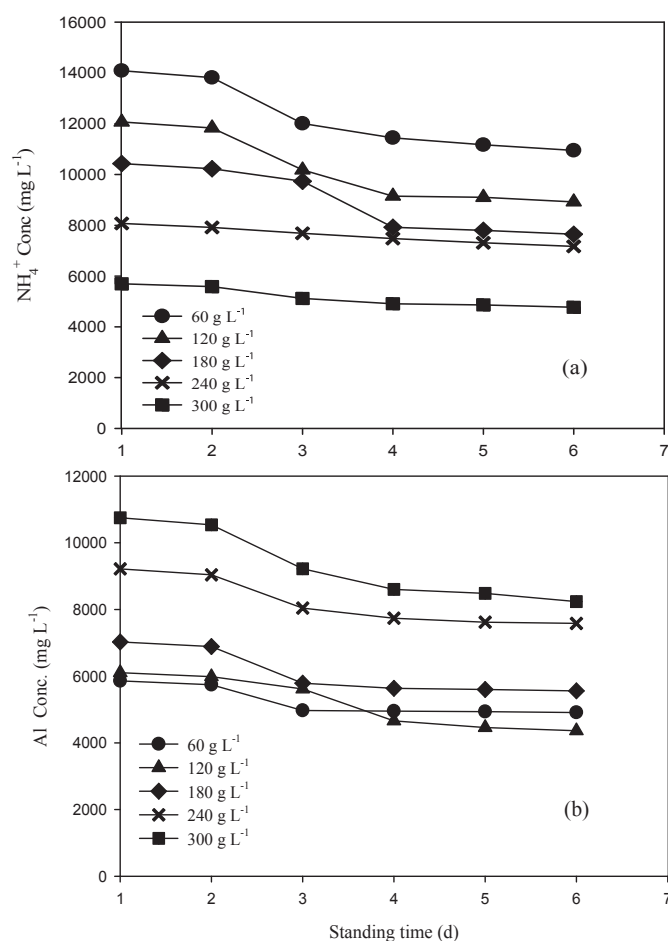


Fig. 4. The (a) ammonium concentration and (b) dissolved aluminum concentration as a function of standing time under various sludge concentrations.

alum does not require considerable time and standing time can be controlled to one day.

3.4. Determination of ammonium alum recovery ratio for various mixing times

In a mixing process, the aluminum ion concentration range may change gradually from the unsaturated region to the metastable

region, such that the secondary nucleus forms and then crystal grows continuously in diameter. However, a long mixing duration may break the secondary nucleus into many nuclei, reducing mean ammonium alum crystal size. To assess the optimum conditions for ammonium alum recovery, a mixing time experiment was conducted with the mixing speed of 100 s⁻¹. Table 4 shows experimental results, identifying the relationship between the ammonium alum recovery ratio and mixing time. In Table 4, mixing time cannot significantly alter ammonium removal efficiencies. Hence, differences among the theoretical weights of ammonium alum calculated from the ammonium removal efficiency are very small, meaning that mixing duration should not affect the ammonium alum recovery ratio. However, the experimental result (Table 4) shows that a long mixing duration may decrease the recovery ratio. As the aluminum ion concentration may increase becoming saturated due to mixing, and when the solute concentration exceeds its equilibrium solubility, a new phase is generated and a small cluster forms, which is a small crystal nucleus and can be precipitated out in the solution. This process of forming a crystal nucleus is called the nucleation process. However, after nucleation, a long mixing duration may break the nucleus into many smaller secondary nuclei [31]. Because the theoretical weight of ammonium alum is similar for all mixing durations (Table 4), the total crystal weight should be similar for all mixing durations. However, when too many secondary nuclei are produced in crystal growth process, the crystal size becomes relatively small and cannot be captured by a 16-mesh sieve to recover the crystallized ammonium alum. Hence, the ammonium alum recovery weight decreases as mixing duration increases. On the other hand, when mixing duration is too short (≤ 2.5 min), the aluminum ions are not immediately saturated and few secondary nuclei are produced. Hence, the crystal recovery rate is low for a short mixing duration. The results of Table 4 indicate the optimum ammonium alum recovery ratio exists when the mixing process is 5–30 min.

To determine the effect of mixing duration on crystallization period, the residual NH₄⁺ concentration was analyzed as shown in Fig. 5. The ammonium concentration gradually decreases under all mixing durations. But when mixing duration increases, the residual ammonium concentration decreases faster, meaning that a long mixing process may form many secondary nuclei, such that the initial surface areas of all nuclei become excessively large. Hence, in situations that have the same super saturation condition (crystal weight), some nuclei will be too small to be captured in a crystal recovery process. Therefore, in long mixing duration, experimental results indicate that the ammonium alum recovery

Table 2
The recovery ratio of ammonium alum.

Sludge amount (g L ⁻¹)	Dry weight ammonium alum (g)	Residual concentration NH ₄ ⁺ (mg L ⁻¹)	Theory weight (g)	Actual weight ammonium alum (g)	Residual concentration Al (mg L ⁻¹)	Recovery ratio (%)
60	53.87	10,948	100.66	51.64	4908	51
120	174.97	8922	148.48	138.26	4361	93
180	271.71	7647	181.20	175.41	5560	96
240	225.38	7169	193.78	184.61	7851	95
300	290.26	4771	254.18	235.89	8234	93

The initial concentration of NH₄⁺ in wastewater is 15,700 mg L⁻¹

Table 3
Ammonium alum recovery weight under different crystallization time.

Crystallization time (d)	Dry weight ammonium alum (g)	Actual weight ammonium alum (g)
1	209.88	198.12
2	216.68	204.92
3	225.76	215.28
4	234.28	230.48
5	248.12	235.92
6	258.76	242.12

Table 4
The amount of crystallized ammonium alum at different mixing time.

Mixing time (min)	Dry weight ammonium alum (g)	Residual concentration NH_4^+ (mg L^{-1})	Theory weight (g)	Actual weight ammonium alum (g)	Residual concentration Al (mg L^{-1})	Recovery ratio (%)
0.5	262.55	9390	224.53	146.99	11,290	65
2.5	318.63	9290	227.36	180.05	11,210	79
5.0	236.40	9370	255.25	184.99	11,170	82
30	261.51	8460	249.33	201.63	11,090	81
60	60.51	9280	227.54	50.55	11,060	22
90	40.12	8880	238.26	33.60	11,010	14
120	33.65	8840	239.38	27.96	10,940	12

The initial concentration of NH_4^+ in wastewater is $17,810 \text{ mg L}^{-1}$.

ratio is inversely proportional to mixing duration (Table 4). Additionally, when mixing duration is short (5 and 40 min), the ammonium concentrations slowly decrease when the suspension stands for less than 200 min (Fig. 5). With the same standing duration, the ammonium concentrations for long mixing times (60 and 120 min) decrease rapidly. However, after standing for over 400 min, the ammonium concentrations are the same for both short and long mixing durations, meaning that mixing duration does not significantly affect the ammonium ion removal efficiency; however, it obviously affects the size of the ammonium alum crystal. Experimental results may be an important reference for preparing crystallized ammonium alum from ammonium-rich wastewater treated by adding water purification sludge.

3.5. Determination of ammonium alum recovery ratio for various mixing speeds

To study the effect of mixing speed on ammonium alum recovery ratio, mixing speeds are varied. When mixing speed exceeds 100 s^{-1} , the ammonium alum recovery ratio decreases (Table 5). This experimental result indicates that when the mixing speed is too fast, the aluminum ions dissolve rapidly and the α increases instantly. Thus, the critical radius of the crystal becomes relatively small and a large number of primary nucleuses are produced. When high speed mixing is continuous, the α is further increased and more primary nucleuses are produced. Therefore, parts of these nucleuses are too small to form a large crystal particle through particle collision and the accumulation process. These small radius

particles cannot be captured by a 16-mesh sieve and therefore the ammonium alum recovery ratio decreases as mixing speed increases. This finding means that high speed mixing may negatively affect crystal radius formation. Furthermore, analytical results (Table 5) indicate that when mixing speed is too low (50 s^{-1}), the highest theoretical weight and lowest residual concentration of NH_4^+ exist. However, the data (Table 5) show that the ammonium alum recovery ratio at mixing speeds of 50 s^{-1} is less than that at 100 s^{-1} , meaning that the secondary nucleus produced at a low speed may be unevenly distributed. This uneven distribution causes some crystal particles to become large and others small. Hence, the ammonium alum recovery ratio is reduced and the ammonium ion removal efficiency reaches its maximum. Therefore, the suitable mixing speed is 100 s^{-1} , which allows for effective crystal production.

3.6. Aluminum alum crystallization at various temperatures

Because ammonium alum crystallization is an exothermic reaction, saturate solubility may increase as temperature increases. According to Table 6, the amount of crystallized ammonium alum decreases as temperature increases. When reaction temperature is 10°C , the crystal weight is 290 g. When temperature is increased to 70°C , crystal weight decreases to 60 g. According to the theory for critical crystal radius [29], the radius is inversely proportional to reaction temperature, meaning that increasing temperature may produce more secondary nucleuses, such that the particle diameter of crystallized ammonium alum becomes small, which is not appropriate for recovering ammonium alum. Therefore, the recovery ratio decreases at high temperatures.

4. Conclusions

In this work, water purification sludge and sulfuric acid were added to acidified ammonium-rich wastewater to produce ammonium alum. Experimental results yield the following conclusions.

- (1) The molar ratio of ammonium to aluminum ions significantly affects the ammonium alum recovery ratio.
- (2) The ammonium alum recovery ratio is also strongly affected by mixing duration and mixing speed. The optimum mixing duration and mixing speed are 5–30 min and 100 s^{-1} , respectively.
- (3) The lower temperature can be used to produce more crystallized ammonium alum. In this work, the ammonium alum crystallization method can recover aluminum from water purification sludge and effectively reduce the concentration of ammonium in ammonium-rich wastewater.

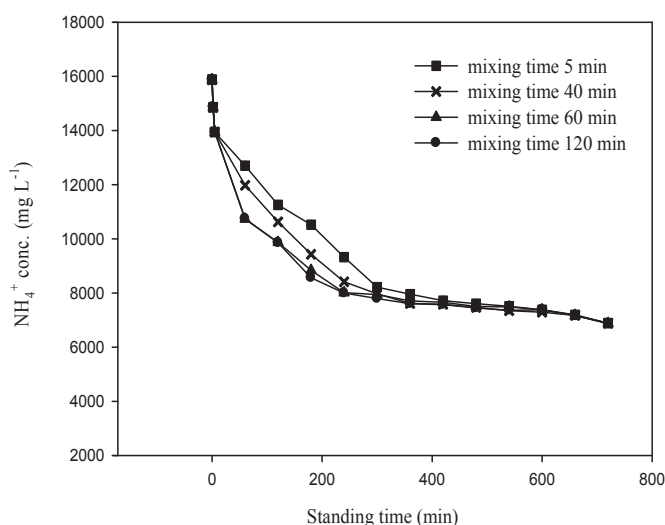


Fig. 5. The relationship between ammonium ion concentration and standing time under various mixing time.

Table 5

The crystal amount of ammonium alum at different mixing speed.

G value (s ⁻¹)	Dry weight ammonium alum (g)	Residual concentration NH ₄ ⁺ (mg L ⁻¹)	Theory weight (g)	Actual weight ammonium alum (g)	Residual concentration Al (mg L ⁻¹)	Recovery ratio (%)
50	225.11	7860	244.16	179.45	9460	73
100	236.53	8960	214.72	193.73	9400	90
200	220.43	9130	210.21	177.37	9350	84
300	203.55	9300	205.57	147.87	9310	71
400	197.55	9280	206.19	137.69	9300	66
500	182.16	9110	210.80	132.60	9260	63

The initial concentration of NH₄⁺ in wastewater is 17,010 mg L⁻¹.**Table 6**

The crystal amount of ammonium alum at different temperature.

Temp. (°C)	Dry weight ammonium alum (g)	Residual concentration NH ₄ ⁺ (mg L ⁻¹)	Theory weight (g)	Actual weight ammonium alum (g)	Residual concentration Al (mg L ⁻¹)	Recovery ratio (%)
10	293.32	2980	346.50	290.19	5980	84
30	219.44	4780	298.45	214.99	8360	72
50	104.98	9100	183.23	99.57	12,060	54
70	65.67	11,570	117.33	60.20	13,650	51

The initial concentration of NH₄⁺ in wastewater is 16,100 mg L⁻¹.

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