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

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ABSTRACT

This study applies a process to treat ammonium-rich wastewater using alum-generated sludge form water purification plant, and gain economic benefit by producing ammonium alum ($Al(NH_4)(SO_4)_2 \cdot 12H_2O$). 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.

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 Protect 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 ($Al_2(SO_4)_3$) 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 ($NH_4Al(SO_4)_2 \cdot 12H_2O$, 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 $Al_2(SO_4)_3$ is added to ammonium-rich wastewater, the dissolved $Al_2(SO_4)_3$ reacts with ammonium to form ammonium alum crystal. Therefore, ammonium alum precipitation process can reduce the

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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 ($Al(OH)_3$), 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 form 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.