Removal of ammonium from rare-earth wastewater using natural brucite as a magnesium source of struvite precipitation

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ABSTRACT

This paper presents a study regarding ammonium removal from rare-earth wastewater by struvite precipitation with natural brucite mineral as a source of magnesium. Experimental results indicated that a pH ranging from 8.5 to 9.5 was the optimum for the removal of ammonium using the soluble form of brucite as a magnesium source. Additionally, when solid brucite was used as a magnesium source as well as an alkali reagent, the initial ammonium concentration of 4,535 mg/L decreased to 239–317 mg/L after an reaction time of 12 h in wastewater treated with the S/L (solid brucite/liquid wastewater) ratios ranging from 31.2 to 63.2 g/L. Furthermore, as some non-reacted brucite still remained in the precipitates obtained at the end of reaction, the precipitates were subjected to reuse. The reuse results demonstrated that the reuse of the precipitates obtained with 63.2 g/L was feasible, and almost half of the brucite dose could be saved.

Key words | ammonium, brucite mineral, phosphorus, rare-earth, struvite precipitation

INTRODUCTION

The wastewater produced from the separation process of rare-earth elements usually contains high concentrations of ammonium. It is known that substantial quantities of ammonium in water can induce problems related to the toxicity to aquatic organisms. Hence, ammonium removal from wastewater is of great importance. With more stringent standards imposed regarding nutrient removal, many varied processes have been progressively developed to remove the compounds containing nitrogen and phosphorus from wastewater (Jaffer et al. 2002). Among alternative treatment methods, struvite precipitation has been considered to be an effective method for the removal of ammonium and phosphate (Li et al. 1999; Barnes et al. 2007).

Up to now, removal of ammonium from various wastewaters through the formation of struvite (MgNH4PO4·6H2O) has been widely investigated (Kabdaslı et al. 2000, 2002; El Diwani et al. 2007; Ryu et al. 2008; Huang et al. 2009). Literatures published indicated that, although removal of ammonium as struvite is technically feasible, it is not economically viable because of the high cost of the magnesium and phosphate salts (Giesen 1999; He et al. 2007). Therefore, in order to facilitate the application of struvite precipitation, its treatment cost is required to be lowered. Employing comparatively inexpensive magnesium sources was thought to be an effective approach to lower the treatment cost. Many researchers have investigated various low-cost materials containing magnesium, such as by-products generated in the production of magnesium oxide (Chimenos et al. 2003; Quintana et al. 2005), bittern (Lee et al. 2003), and magnesite (MgCO3) mineral (Gunay et al. 2008; Chen et al. 2009). It was reported that using above-mentioned materials as magnesium sources in struvite precipitation could achieve a high removal of ammonium.

The natural brucite is one of the minerals containing magnesium and its deposits are abundant in nature. Its main composition is magnesium hydroxide. There are many advantages in the use of brucite as magnesium source. To be precise, natural brucite is comparatively inexpensive, and has a high alkalinity, as well as very low concentrations of heavy metals. In addition, brucite has a higher solubility (pKsp = 11.1) in comparison to other magnesium sources such as magnesia and magnesite, which could shorten the reaction time of struvite precipitation.
The objective of this study was to investigate the feasibility of using natural brucite as a magnesium source of struvite precipitation for the removal of ammonium from rare-earth wastewater. For this purpose, the present work focused on the following. First, the effect of solution pH on struvite precipitation was investigated by using the soluble form of brucite as magnesium source. Secondly, the use of solid brucite as a dual function chemical (i.e., magnesium source and alkali reagent) was conducted, and a mechanism of struvite formation involving the natural brucite was proposed. Finally, the precipitates containing the non-reacted brucite were collected and further reused.

MATERIALS AND METHODS

Wastewater used in this study was taken from a rare-earth separation plant located in the Guangdong Province in China, and its composition is shown in Table 1. The natural brucite used as magnesium source was provided by Dandong Tianci Flame-retardant Materials Co. (Dandong of the Liaoning Province in China), and was pulverised to a grain size of less than 25 μm. Its chemical composition is given in Table 1.

Additionally, phosphoric acid (85%) was used as a phosphate source, and 5 M HCl was used to obtain the soluble form of brucite. The solution pH value was adjusted by first using 10 M NaOH and then 1 M NaOH.

To investigate the effect of solution pH on the struvite precipitation of using the soluble form of brucite, 1.54 g of brucite dosed at a Mg:N:P molar ratio of 1:1:1 was added to a jar (250 mL) with airtight lid, and was dissolved by adding 5 M HCl at a Mg(OH)₂:HCl molar ratio of 1.2. Then, 100 mL of wastewater was fed into the jar and the required phosphoric acid was added. The experiments were conducted at pH values ranging from 5.0 to 10.5, having a reaction time of 30 min and a precipitation time of 10 min. A supernatant of 5 mL was removed and filtered through a 0.45 μm membrane filter, for the analyses of the components.

To study the effect of using solid brucite as a dual function chemical, batch experiments were conducted on different solid (brucite)/liquid (wastewater) (S/L) ratios (23.2–63.2 g/L); that is, brucite was added at Mg:N molar ratios ranging from 1.5 to 4.0. In the experiments, wastewater of 500 mL was added to a jar (1,000 mL), and phosphoric acid was added at a P:N molar ratio of 1:1. During the reaction, the pH value of the supernatant was measured after the stirring was stopped for 30 s at different time intervals (0.5–12.0 h). Thereafter, the supernatant of 5 mL was removed and filtered through a 0.45 μm membrane filter for the analysis of phosphorus and ammonium. As excessive brucite may still remain in the precipitates obtained at the end of the reaction, the precipitates obtained with 47.2, 55.2, and 63.2 g/L were collected and washed thrice with ultra-pure water, and were then reused according to the experimental procedure entailed in the fresh use of brucite presented earlier. In the present study, all experiments were carried out at the room temperature (20–25°C), with a stirring rate of 300 rpm. All of the experiments were performed in triplicate.

The concentration of ammonium ions was analysed through the conventional Nesslerisation method by employing a spectrophotometer (752N, China). The concentration of phosphorus was measured using the ascorbic acid method, and the pH value of the solution was measured using a pH meter (pHS-3D, China). The morphology of the struvite precipitates was observed by employing the Scanning Electron Microscope–Energy Dispersive X-Ray (SEM-EDX) (FEI Quanta 400, America) and its composition was characterised by X-ray diffraction (XRD) (Philips Model PW1830).

RESULTS AND DISCUSSION

Optimum pH of using the soluble form of brucite as magnesium source

pH is an important factor controlling the species in the struvite crystallisation system. Mijangos et al. (2004) reported that $\text{H}_3\text{PO}_4$, $\text{H}_2\text{PO}_4^-$, $\text{HPO}_4^{2-}$, $\text{MgOH}^+$, $\text{MgNH}_4\text{PO}_4$, $\text{Mg}^{2+}$, $\text{NH}_4^+$, ...
MgPO$_4^-$, MgH$_2$PO$_4^+$ and MgHPO$_4$ can be formed in the system involving Mg$^{2+}$, PO$_4^{3-}$, NH$_4^+$ aqueous solutions, when the pH varied. At pH range of 2.15–7.2, H$_2$PO$_4^-$ ions are the predominant species. At pH range of 7.2–12.35, the predominant species are HPO$_4^{2-}$. At pH $>$ 12.35, the phosphate is present predominately as PO$_4^{3-}$ (Saidou et al. 2009). Consequently, in the process of struvite precipitation different compounds could be produced with the change of pH. For example, when pH values increased from 4 to 10, magnesium species changed from MgHPO$_4$ in an acidic medium to Mg$_3$(PO$_4$)$_2$ and MgNH$_4$PO$_4$ in a slightly alkaline medium (Saidou et al. 2009).

In this study, the results of experiments to determine the optimum pH are shown in Figure 1. It is observed that the concentrations of remaining ammonium and phosphorus decreased at the pH ranging from 5 to 8 and kept stable at the minimum values of around 420 and 220 mg/L, respectively, at the pH range of 8.5–9.5. When the pH was higher than 9.5, the remaining ammonium concentration rose slightly, but there was a comparatively small influence on the removal of phosphorus. Under an alkaline condition, Mg$_3$(PO$_4$)$_2$ may be formed instead of struvite; additionally, the metal ions in the wastewater, as well as the aluminium, iron and calcium contained in the brucite, could react with phosphate. All these could inhibit the formation of struvite.

In Figure 1, it is found that, although certain variations have been recorded to appear in the concentrations of ammonium at the pH range of 6.5–10.5, just a slight change has occurred in the variations in relation to its initial concentration. This may be attributed to the fact that the solution is significantly saturated in terms of struvite-forming ions; the effect of an increase in the pH value becomes insignificant during the removal of ions from the solution (Uludag-Demirer & Othman 2009). According to the results reported in other literatures, it was concluded that, by using the soluble form of brucite, a ammonium removal equivalent to that obtained with pure magnesium salts, such as MgCl$_2$·6H$_2$O and MgSO$_4$·7H$_2$O (Huang et al. 2009; Zhang et al. 2009), could be achieved.

**Effect of solid brucite acting as a dual function chemical**

Although a high removal of ammonium was achieved by using the soluble form of brucite as a magnesium source, this process consumed a large amount of acid and alkali reagents. Thereby, it was considered that solid brucite be used as a magnesium source as well as the required alkali reagent in the struvite precipitation. According to the composition described in Table 1, the stoichiometric amount of brucite necessary to neutralise the protons in the phosphoric acid added was 23.2 g/L. However, considering the fact that the optimum value of pH entailed in the formation of struvite was 8.5–9.5, a brucite dose over the stoichiometric amount was necessary to attain a higher pH value.

The results of the experiments performed with different S/L ratios are shown in Figure 2. Figure 2a reveals that pH values greater than 8 were never achieved with the tested S/L ratios, for 12 h. This may be attributed to the inability of Mg(OH)$_2$ to attain an equilibrium solubility. The pH values were observed to increase slowly in the range of 5.05–5.6, for a reaction time between 0.5 and 12 h in wastewater treated with 23.2 g/L, whereas the pH values tended to rapidly reach 8 after 0.5 h in wastewater treated with S/L ratios over 47.2 g/L.

Figure 2b shows that remaining ammonium concentrations reached between 235 and 309 mg/L after 12 h, excluding the experiment performed with 23.2 g/L. In addition, it was observed that for S/L ratios over 39.2 g/L the concentration of remaining ammonium rapidly reached close to a minimum value after 0.5 h. When wastewater was treated...
with 23.2 g/L, the remaining ammonium concentration decreased within 2 h, and increased slightly between 2 and 8 h, and then decreased again after 8 h. This could be because newberyite (MgHPO$_4$·3H$_2$O) could precipitate significantly in solution media of lower pH values (6) containing high concentrations of magnesium and phosphate (Musvoto et al. 2000), and its formation might result in undersaturation with respect to struvite, which led to the dissolving of struvite to restore saturation (Bhuiyan et al. 2008). Nevertheless, as the solution pH increased (5.35–5.6), the predominant solid species might gradually change from newberyite to struvite. This could be a reason for the phenomenon where a wave profile appeared in the curve of the ammonium concentration for 23.2 g/L. This fact will be further corroborated in the subsequent analysis results.

Figure 2c indicates that remaining phosphorus concentration decreased with an increase in the S/L ratio and reaction time. For S/L ratios greater than 39.2 g/L the phosphorus concentrations entailed short reaction times. For example, the remaining phosphorus concentration quickly decreased to a minimum value of 10 mg/L after 0.5 h in wastewater treated with 55.2 g/L.

The results of the SEM-EDX and XRD analysis conducted on the precipitates obtained with an S/L ratio value of 23.2 g/L and a reaction time of 12 h are shown in Figure 3a and b. The SEM picture (Figure 3a) shows that a small amount of the unshaped crystal, with a relatively larger grain size, interspersed among a large amount of fine amorphous solids that were present in the precipitates. The X-ray diffractogram (Figure 3b) reveals that the peaks of struvite as well as of newberyite were the main phases. The peaks of brucite, dolomite, and cristobalite were identified as the minor phases present in the precipitates. The presence of newberyite could further corroborate the experimental results obtained with 23.2 g/L. The X-ray diffractogram with regard to the precipitates obtained with 47.2 g/L for 12 h and the SEM picture of the polished section of the particle present in it are shown in Figure 3c and d, respectively. In Figure 3c, the peaks of struvite and brucite were identified as the main phases; in addition, other minerals, such as cristobalite, dolomite, and newberyite, were also identified and constituted the minor phases. This suggested that the large quantities of the brucite added did not react. Moreover, a SEM picture of the present precipitates (that remained unattached) revealed that large quantities of the struvite crystal and very small amounts of the amorphous solid were observed to be present in this. Therefore, it was reckoned that struvite could have been formed on the surface of the brucite particle, wrapping all around it, which led to the disappearance of a large amount of the amorphous solid in the SEM picture. The fact could be additionally corroborated by the SEM picture of the polished section of the precipitate particle shown in Figure 3d. An obvious interface was revealed between the interior (A) and exterior (B) surfaces of the precipitate particle. The EDX analysis of the interior surface indicated that the compositions mainly contained oxygen and magnesium, but did not contain any phosphorus. Furthermore, the EDX analysis of the exterior surface demonstrated that a large amount of oxygen, magnesium, and phosphorus were found therein.
These results confirmed that struvite was formed on the surface of brucite; therefore, it hindered the diffusion process of the magnesium, phosphate, and ammonium ions.

In the process of conducting the experiments, it was found that the brucite added to the wastewater rapidly agglomerated; nevertheless, the amount and size of the agglomeration gradually diminished with an increase in the pH value of the solution. Finally, the brucite agglomeration completely disappeared, excluding the experiment performed with 23.2 g/L, after 12 h. According to the results obtained, the phenomenon presented, and the investigations conducted by previous researchers (Chimenos et al. 2003; Chen et al. 2009), a mechanism was proposed for the removal of ammonium through the process of struvite precipitation using brucite as the magnesium source and alkali reagent and phosphoric acid as the phosphate source.

In this study, the mechanism is depicted as follows: (1) first, brucite neutralises the protons of phosphoric acid, resulting in an increase in pH value from 1.42 to around 5 at the beginning of the reaction; simultaneously, brucite rapidly agglomerates due to its huge surface absorbability; (2) the dissolution of magnesium hydroxide takes place on the surface of the produced agglomeration, and the Nernst interface is formed, following which the concentration levels of the hydroxyl and magnesium ions increase in the interface; (3) the hydroxyl and magnesium ions diffuse into the bulk solution; simultaneously, the phosphate and the ammonium ions present in the bulk solution diffuse into the interface; and (4) the struvite is produced and it eventually grows on the exterior surface of brucite.

**Reuse of the obtained precipitates**

As the precipitates collected at the end of the reaction contained a large amount of non-reacted brucite, the precipitates...
obtained with 47.2, 55.2, and 63.2 g/L were reused. Experimental results similar to those obtained with the fresh brucite were obtained and are shown in Figure 4. Figure 4a shows that the higher the amount of brucite added initially, the higher would be the pH values entailed in the reuse of the precipitates obtained. Figure 4b and c demonstrate that the concentrations of ammonium and phosphorus remaining in the solution decreased with an increase in the initial S/L ratio and the reaction time. The concentrations of ammonium and phosphorus reached around 180 and 30 mg/L, respectively, after 2 h in wastewater treated with the precipitates obtained with 63.2 g/L.

In the experiment of the reuse of the obtained precipitates, similar results were obtained in the reuse of the precipitates obtained with 63.2 g/L in comparison with those obtained in the experiment performed with fresh brucite of 39.2 g/L. Nevertheless, the reused precipitates contained the produced struvite crystals, which could be used as the seeding material in the struvite precipitation (Kim et al. 2007) to reduce the nucleation time and initiate the rapid growth of the crystal. Therefore, in the reuse of the precipitates, ammonium and phosphorus concentrations could reach their minimum values after 2 h, revealing a faster rate of reaction, in comparison with that obtained with the initial S/L ratio of 39.2 g/L, which reached the minimum values after 3 h. Thereby, on the basis of the obtained results and the conducted analysis, it could be suggested that the process of reusing the obtained precipitates with 63.2 g/L was feasible. By undertaking this process, the average brucite dose required for treating 1 L of wastewater was 31.6 g (i.e., Mg:P = 2:1); in other words, this method required a comparatively low dose of brucite. Moreover, it was also recorded that this process optimised the removal of ammonium and phosphorus, and that, too, within a considerably short reaction time.

In this work, the heavy metal contents of the precipitates obtained by the reuse process were measured. It was found that the contents of Zn, Mn, Cu and Ni were 163, 32, 37 and 45 mg/kg, respectively, which were greater than the requirements of Chinese Soil Quality Criterion (Zn: 100; Cu: 35; Ni: 40 mg/kg; GB 15618-1995). That means the obtained precipitates could not be used as agricultural fertiliser; in addition to this, the market for struvite as agricultural fertiliser was never founded in China. Under this condition, the precipitates obtained could only be used as industrial chemicals instead of agricultural fertiliser.

CONCLUSIONS

The feasibility of using the natural brucite mineral as the magnesium source of struvite precipitation for the removal of ammonium from rare-earth wastewater was investigated, and the following conclusions could be obtained.

(1) When the soluble form of brucite was used as a magnesium source, the optimum pH value for struvite precipitation of rare-earth wastewater is at 8.5–9.5.
When brucite was used as a dual function chemical, 47.2 g/L of brucite and a reaction time of 0.5 h were required to remove considerable amounts of ammonium ions and phosphorus as struvite compounds.

With the increase in the S/L ratios, the solution pH value rapidly reached a maximum value of 8; nevertheless, in the tested S/L ratios the solution pH value was not found to be higher than 8 after a reaction time of 12 h.

The formation of struvite took place on the surface of the brucite, rather than in the bulk solution.

Reusing the precipitates obtained with 63.2 g/L was feasible, and the actual dose of brucite decreased to 31.6 g (Mg:N or Mg:P molar ratio = 2:1) for the treatment of 1 L wastewater.

On the basis of the results above-mentioned, it can be concluded that using the natural brucite mineral as the magnesium source of struvite precipitation is feasible for the removal of ammonium from rare-earth wastewater.

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