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Capture and recycling of ammonium by dolomite-aided struvite precipitation and thermolysis

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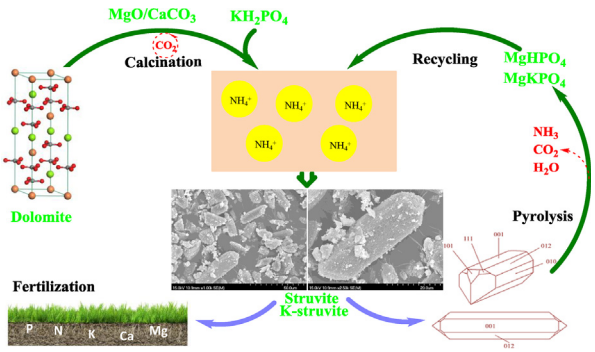
HIGHLIGHTS

- Dolomite can be a cost-effective Mg source for struvite formation.
- Competition between formation of $MgNH_4PO_4 \cdot 6H_2O$ and $MgKPO_4 \cdot 6H_2O$ occurred.
- Hydrolyzed $MgO/CaCO_3$ was an active Mg source and alkali for struvite reaction.
- $CaCO_3$ facilitated the thermolysis of struvite to release ammonium.
- Use of Recycled $MgHPO_4$ and $MgKPO_4$ for forming struvite led to a high NH_4^+ removal rate.

GRAPHICAL ABSTRACT



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ABSTRACT

The capture and reuse of NH_4^+ is an ideal solution to treat NH_4^+-containing wastewater. The capture and reuse process needs to be clean and cost-effective. Currently, however, there are many obstacles, particularly in the availability, cost, and recovery of the chemical sources required. Here, we demonstrate a clean and efficient method to capture and recycle NH_4^+ by a dolomite-aided struvite precipitation process. Dolomite calcined carefully in CO_2 atmosphere was used as a Mg source to react with PO_4^{3-} (KH_2PO_4) and NH_4^+ in model wastewater (2000 mg L^{-1} NH_4^+). The precipitation was performed at $nMg^{2+}:nNH_4^+:nPO_4^{3-} = 1:1:1.2$ and pH = 8.0 for 2 h; 89.7% of NH_4^+ was recovered in the form of struvite precipitate. The competition between K^+ and NH_4^+ in the model wastewater led to the formation of K-struvite ($MgKPO_4 \cdot 6H_2O$) and struvite ($MgNH_4PO_4 \cdot 6H_2O$). The formation of K-struvite resulted in a decrease in the NH_4^+ removal rate. When struvite was heated at 110 °C for 4 h, the NH_4^+ release rate from the thermolysis reached 75.7%. Thermolysis readily occurred as an unstable Ca^{2+}-CO_3^{2-}-NH_4^+ system formed in the mixture of $MgNH_4PO_4 \cdot 6H_2O$ and $CaCO_3$. The elements Mg and P that were obtained during the struvite precipitation–thermolysis–reprecipitation process can be repeatedly used. After 6 cycles,

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under the conditions pH = 9.0, nMg^{2+}:nNH_4^+:nPO_4^{3-} = 1:1:1 and reaction time of 2 h, up to 78.3% of NH_4^+ was removed from the model wastewater.

1. Introduction

Ammonium (NH_4^+) is a typical cation present in agricultural, municipal, and industrial wastewater. The improper treatment and mismanagement of such cations can lead to the eutrophication of water and cause a negative disturbance to microorganisms in soil (Liu et al., 2012; Chen et al., 2017). The biological process of nitrification–denitrification has commonly been used to remove NH_4^+ from wastewater (Escudero et al., 2015). However, this process is not very suitable for treating wastewater with a high concentration of NH_4^+ (e.g., anaerobic digestion solution, landfill leachate, and piggy wastewater) because of the toxicity of NH_4^+ to microorganisms (Kim et al., 2008). To minimize NH_4^+-related toxicity in the biological process, long hydraulic residence times and large reaction volumes are required (Kim et al., 2008; Di Iaconi et al., 2010). Furthermore, as NH_4^+ is a useful chemical, particularly as a fertilizer for crops, its removal, recovery, and reuse from wastewater is desirable.

Chemically capturing NH_4^+ by reacting with equimolar magnesium and phosphate ions to form magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$, struvite), a precipitate that can be separated from water, appears to be an alternative for the removal of high concentrations of NH_4^+ from wastewater (Karabegovic et al., 2013; Zhou et al., 2015). Moreover, the resultant struvite proved to be a high-quality slow-release fertilizer, providing both nitrogen and phosphorous nutrients simultaneously. It has long been known that struvite as fertilizer causes little damage to plant roots even at high application rates (Lu et al., 2016). For wastewater, however, the molar ratio of nMg^{2+}:nNH_4^+:nPO_4^{3-} in NH_4^+-containing wastewater needs to be stoichiometrically adjusted to meet the composition of struvite (nMg^{2+}:nNH_4^+:nPO_4^{3-}=1:1:1). Namely, additional magnesium and phosphate are required for NH_4^+ removal (Romero-Güiza et al., 2015) and particularly more magnesium (Huang et al., 2011a). The cost of magnesium was estimated to be 75% of the overall cost of struvite precipitation (Kumar and Pal, 2015), and this high cost is one of the limiting factors that hampers the application of struvite precipitation in practice. Hence, low-cost magnesium sources such as seawater (Crutchik et al., 2013; Liu et al., 2013), MgO-saponification wastewater (Huang et al., 2014), bittern (Liu et al., 2013; Siciliano and Rosa, 2014), wood ash (Sakthivel et al., 2012), brucite (Huang et al., 2011b), magnesium hydroxide (Münch and Barr, 2001), and magnesite (Gunay et al., 2008) have been used to produce struvite.

Dolomite, $CaMg(CO_3)_2$, is a double carbonate of calcium and magnesium that is cheap, abundant, and ubiquitous worldwide. For example, the proven reserves of dolomite in China are above four billion tons (Wu and Ma, 2007). Dolomite has been merely used as low-value-added products such as refractories and fluxing agents. The present study aims to use light-burnt dolomite ($MgO/CaCO_3$) as a low-cost magnesium source and an alkali reagent for the struvite precipitation to remove and recover NH_4^+ from wastewater. As such, dolomite can convert into a slow-release fertilizer of struvite.

The objective of this work is to investigate struvite precipitation using low-cost dolomite and struvite pyrolysate recycling technology by direct thermolysis for NH_4^+ removal. First, struvite precipitation was evaluated using hydrolyzed $MgO/CaCO_3$ suspension and NH_4^+ model wastewater. Second, direct thermolysis was used to treat struvite precipitate, and the resultant struvite pyrolysate was recycled for the removal of NH_4^+. To the best of our knowledge, the depositing process of struvite followed by light-burnt dolomite and hydrolyzed $MgO/CaCO_3$ suspension is reported here for the first time. $CaCO_3$ can also be a useful source for soil. When applied to soil, the soil pH can be buffered by the addition of $CaCO_3$ and the amelioration of the sodic soils (Magdoff and Bartlett, 1985; Tyler and Olsson, 2001; Choudhary et al., 2011).

2. Materials and methods

2.1. Materials

The original dolomite was purchased from the Xingtang Powder Plant (Hebei Province, China). The elemental analysis was performed using an atomic absorption spectrometer (AAS, AAnalyst, Perkins Elmer), which indicated that the original dolomite had 21.8% MgO. A 2000-mg L^{-1} NH_4^+ aqueous solution as model wastewater was prepared by dissolving 0.5944 g NH_4Cl in 100 mL distilled water. KH_2PO_4 was used as the phosphate source and directly added to the model wastewater. Both materials were stored separately and mixed only in the model wastewater just prior to the experimental run. The pH of the suspension was adjusted using 1 M aqueous sodium hydroxide (NaOH) solution. All the chemicals used were of analytical grade and purchased from No. 4 Reagent & H.V Chemical Co., Ltd, Shanghai, China.

2.2. Pretreatment of raw dolomite

Raw dolomite (30 g) in a crucible was placed in a furnace and calcined under a constant CO_2 flow of 100 mL min^{-1} from room temperature to 750 °C at a heating rate of 10 °C min^{-1}. The dolomite sample was then maintained at 750 °C for 2 h. Thereafter, the sample was cooled down naturally to yield a solid product $MgO/CaCO_3$.

The $MgO/CaCO_3$ suspension was prepared by dispersing 1.6025 g $MgO/CaCO_3$ in 100 mL deionized water. The mixture was stirred (840 rpm) in a batch beaker (0.5 L) at room temperature. The hydrolysis of $MgO/CaCO_3$ in the suspension was detected and monitored using a glass electrode connected to a pH meter (pHS-3C, Bante, China). The average pH value was obtained by measuring three identical $MgO/CaCO_3$ suspensions for each sample. Hydrolysis was conducted over a period of 12 h to determine the time at which the pH remained almost unchanged. The $MgO/CaCO_3$ in 100 mL deionized water treated as above for 10 h was used as the magnesium source for the following struvite precipitation process.

2.3. Struvite precipitation

nMg^{2+}:nNH_4^+:nPO_4^{3-} at a ratio of 1:1:1.2 was used for struvite precipitation by adding the magnesium source (the above-mentioned $MgO/CaCO_3$ suspension) and PO_4^{3-} (KH_2PO_4) to a beaker containing 100 mL model wastewater with an NH_4^+ initial concentration of 2000 mg L^{-1}. Struvite formed according to the following equation:

$$Mg^{2+} + NH_4^+ + H_nPO_4^{3-n} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + nH^+ \ (n = 0, 1, \text{or } 2) \quad (1)$$