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Recycling struvite pyrolysate obtained at negative pressure for ammonia nitrogen removal from landfill leachate

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HIGHLIGHTS

- A magnesium stabilizing agent served as the precursor of struvite precipitation.
- Ammonium was effectively released by pyrolyzing struvite under negative pressure.
- Recycling struvite pyrolysate could achieve approximately 82% of ammonia removal.
- Ammonia removal rate of >68% was maintained during eight recycle cycles.
- The recycling process was economically feasible for the ammonia pretreatment.

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ABSTRACT

Struvite precipitation coupling low-cost materials and recycling was used to remove the total ammonia nitrogen (TAN) from landfill leachate in order to reduce the overall cost of precipitator. Struvite used for recycling was formed using a stabilizing agent (SA) as the precursor, which was formulated by using phosphorus acid and low-grade magnesium oxide (LG-MgO). Results showed that use of SA and LG-MgO for struvite precipitation can achieve TAN removal near that obtained by using pure chemicals. The results of struvite decomposition indicated that maintaining a negative pressure in struvite pyrogenation has a significant effect on the improvement of the ammonium release rate. When struvite pyrogenation was conducted at a vacuum degree of 0.04 MPa and at a temperature of 120 °C for 3 h, the ammonium release rate was >90%. The obtained pyrolysate was recycled for the treatment of landfill leachate without the addition of other chemicals, and the TAN removal efficiency was comparable to that by struvite precipitation using fresh chemicals. When pyrolysate was used repeatedly by supplementing LG-MgO at the MgO:$MgHPO_4$ molar ratio of 0.5:1 and by prolonging the stirring time to 2 h, a TAN removal efficiency >68% could be maintained in the eight-cycle process. Economic analysis revealed that the proposed recycling process could reduce 86% of the cost of struvite precipitation using pure chemicals.

1. Introduction

In the past 20 years, parallel with the rapid urbanization across the world, the production of municipal solid waste (MSW) correspondingly increased quickly. Sanitary landfill is always accepted as the preferred method for the ultimate disposal of MSW owing to its economic advantages and simplicity of operation [1]. In the disposal process, due to the complex function of rainwater percolation and the physical, chemical, and biological processes occurring naturally in wastes, a large amount of leachate is generated from the municipal sanitary landfill sites [2]. These leachates generally contain high amount of total ammonia nitrogen (TAN) and organic matters [expressed as chemical oxygen demand (COD) and biological oxygen demand (BOD)], where humic-type constituents consists an important group as well as a significant amount of inorganic salts [3,4]. Therefore, if landfill leachate is not appropriately collected and treated, it may trigger severe environmental pollution.

Abbreviations: BOD, biological oxygen demand; COD, chemical oxygen demand; FTIR, Fourier transform infrared spectroscopy; LG-MgO, low-grade magnesium oxide; MSW, municipal solid waste; P_T, total orthophosphate; SA, stabilizing agent; SEM, scanning electron microscope; TAN, total ammonia nitrogen; TP, total phosphorus; XRD, X-ray diffraction.

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Biological processes have been shown to be the cost-effective methods for the treatment of landfill leachate [5–7]. However, the high concentrations of TAN present in landfill leachate could significantly affect the performance of conventional biological treatment processes [8]. Therefore, TAN pretreatment is extremely necessary to ensure the smooth performance of biological treatment. Struvite precipitation has been widely considered as the promising pretreatment method to remove TAN in landfill leachate [9–12]. In a previous study, Li et al. [11] precipitated TAN as struvite by using pure $MgCl_2 \cdot 6H_2O$ and $Na_2HPO_4 \cdot 12H_2O$ as magnesium and phosphate sources, respectively, and found that the TAN concentration of landfill leachate was reduced from 5600 to 110 mg/L within 15 min. Although TAN precipitation as struvite is technically attractive, the high economic cost due to the large amounts of chemical consumption significantly hampers its practical application. Consequently, the method to reduce the treatment cost of struvite precipitation is the key issue to promote the practical application of the process.

The chemical cost of struvite precipitation is mainly consisted of three parts: the individual cost of phosphate salts, magnesium salts, and alkali reagent. Using low-cost magnesium materials is an important approach to reduce the struvite precipitation cost [13–18]. For instance, Gunay et al. [14] used low-cost magnesite as a magnesium source of struvite precipitation with a cost saving of 18%. Lahav et al. [13] reported that using NF concentrate as a magnesium source could save 25% of the struvite precipitation cost. However, the treatment cost was difficult to be reduced to the acceptable level for the practical application by solely depending on the use of low-cost magnesium materials. To further decrease the cost of struvite precipitation, another option was to recycle struvite. Until now, various methods for struvite decomposition, such as direct pyrolysis [19–21], NaOH pyrogenation [10,22,23], chlorination decomposition [24], and electrochemical decomposition [25] have been widely reported. Among these methods, direct pyrolysis of struvite does not consume any chemicals, which significantly reduces the recycling cost. Unfortunately, the decomposition method readily results in the generation of magnesium pyrophosphate ($Mg_2P_2O_7$), which has negligible effect on TAN removal. The reported investigations [20,21] revealed that the pyrogenation temperature is an important parameter that influences the formation of $Mg_2P_2O_7$. Huang et al. [21] reported that when the direct pyrogenation temperature of struvite was >150 °C, although the ammonium release rate increased rapidly with increases in the pyrogenation temperature and time, the TAN removal ratio by recycling the corresponding pyrolysate progressively decreased. This observation suggested that a great amount of $Mg_2P_2O_7$ may be formed at a temperature >150 °C. Therefore, lowering the pyrogenation temperature is a crucial approach to reduce the generation amount of $Mg_2P_2O_7$. However, lowering the pyrogenation temperature at the atmospheric pressure would correspondingly decrease the ammonium release rate of struvite. To resolve this problem, we attempted to use a novel pyrolysis process of struvite, wherein struvite was directly pyrolyzed at low temperature and negative pressure.

The main objective of this study was to reduce the struvite precipitation cost for the removal of TAN from landfill leachate. To achieve this aim, the following investigations were performed. First, a stabilizing agent (SA) was formulated by using phosphorus acid and low-grade magnesium oxide (LG-MgO) as the phosphate and magnesium sources to form struvite. Second, the pyrogenation of the formed struvite at negative pressure was investigated. Third, the formed pyrolysate was recycled to investigate its performance for the removal of TAN from landfill leachate. To counter the large amounts of hydrogen ions (H^+) that may be released during the process of pyrolysate recycling, LG-MgO was used as the pH regulator in the experiments. Finally, based on the investigation results, an economic evaluation was conducted.

2. Materials and methods

2.1. Experimental materials

Landfill leachate used in the experiments was collected from a municipal landfill site located at the suburban area of Beijing, China. The landfill leachate was pretreated by filtering through a 0.45-μm membrane filter prior to use. The average properties of the pretreated leachate are shown in Table 1. In this study, LG-MgO generated from the calcination of natural magnesite at 1000 °C (chemical composition: [in mass%]: MgO, 91.5; Al_2O_3, 0.7; CaO, 1.8; SiO_2, 3.9, Fe_2O_3, 0.8; others, 1.5) was used as the dual chemical reagents, i.e., alkali and magnesium sources. All other chemicals used in the study (including humic acid, $MgCl_2 \cdot 6H_2O$, $Na_2HPO_4 \cdot 12H_2O$ and NH_4Cl) were of analytical grade.

2.2. Preparation of the SA used in the experiments

The stabilizing agent (SA) used to form struvite was formulated according to the procedures similar to those described in previous literatures [15,26]. Briefly, LG-MgO powder was slowly added to 14% phosphoric acid solution at a Mg:P molar ratio of 1:1, followed by stirring of the solid–liquid mixture for 10 min. Analyses results showed that the solution pH of SA was approximately 3.5, and the concentration of the dissolved phosphate in the SA was around 10 g/L. It was calculated that approximate 77% of phosphoric acid reacted with LG-MgO to form insoluble solids. XRD analysis showed that the main compositions of the insoluble solids were newberyite ($MgHPO_4 \cdot 3H_2O$), magnesium phosphate ($Mg_3(PO_4)_2$) and magnesium oxide (MgO).

2.3. Struvite precipitation by using SA and LG-MgO

Batch experiments for struvite precipitation by using SA and LG-MgO were performed as follows: briefly, 500 mL of the landfill leachate was first poured into a 1000-mL jar placed in a magnetic stirrer, and then the prepared SA was added to the wastewater at the stoichiometric ratio of struvite formation (i.e. Mg:N:P = 1:1:1). Subsequently, LG-MgO used as an alkali reagent to neutralize the hydrogen ions (H^+) in solution was fed to the wastewater. The mixed solution was stirred at 300 rpm for 120 min. During the stirring reaction, the solution pH was frequently measured and 2 mL samples were removed at different time intervals. The removed samples were filtered through 0.45-μm filter membranes for component analysis. In addition, to compare the effect of

Table 1
The average properties of pretreated landfill leachate.

Parameter	Average value plus standard deviation
pH	7.38 ± 0.05
Alkalinity ($CaCO_3$) (mg/L)	6735 ± 529
COD (mg/L)	4118 ± 383
TAN (mg/L)	1570 ± 87
TP (total phosphorus, mg/L)	17.5 ± 1.7
K (mg/L)	528 ± 63
Ca (mg/L)	48 ± 9.1
Mg (mg/L)	21 ± 3.1
Fe (mg/L)	4.8 ± 1.1
Al (mg/L)	6.8 ± 0.8
Cu (mg/L)	1.2 ± 0.7
Ni (mg/L)	0.6 ± 0.2