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Feasibility of physicochemical recovery of nutrients from swine wastewater: Evaluation of three kinds of magnesium sources

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ABSTRACT

In this study, two physicochemical methods (struvite precipitation and ammonia stripping) were coupled for the recovery of nutrients from swine wastewater. Recovering phosphate (PO_4-P) as struvite was first performed using three different types of magnesium (Mg) sources: Mg alloy, low-grade magnesium oxide (LG-MgO), and Mg-containing supernatant, followed by the removal of total ammonia nitrogen (TAN) by ammonia stripping using LG-MgO as the pH adjustor. The results indicated that the PO_4-P in swine wastewater can be recovered as struvite with high purity through chemical corrosion of Mg alloy, whereas a very low-purity struvite was obtained using LG-MgO as the Mg source for struvite precipitation. Approximately >94% of TAN could be removed from the effluent generated from the phosphate-recovery stage by ammonia stripping at an aeration rate of 5 L air/l wastewater · min, LG-MgO dosage of 8 g/l, and a temperature of 25 °C for 180 min. Recycling the supernatant after ammonia stripping as the Mg source of struvite precipitation could recover PO_4-P as struvite with a purity of 85.8% at pH 9.5 and Mg:P molar ratio of 1.2:1. The comparison analysis indicated that the optimal Mg source for the recovery of phosphate was Mg-containing supernatant.

1. Introduction

Phosphorus (P) and nitrogen (N) are the essential nutrients for all living organisms, and they play an important role in the agricultural and industrial development. In the recent years, with the increase in the population and economy in the world, the amount of exploited P rock has risen every year, resulting in the rapid decrease in the reserves of P rock, which is a limited and non-renewable mineral resource [1]. Shu et al. [2] forecasted that all reserves of P mineral will be exhausted by 2090, unless some countermeasures are enforced. Therefore, it is extremely necessary to recover P from wastes to achieve the sustainable development of P resources. Generally, swine wastewater contains high concentrations of organic matters, N and P. To avoid the eutrophication of the receiving water bodies such as rivers and lakes, swine wastewater need to be strictly treated in compliance with the law standards, prior to being discharged into the environment.

At present, the methods applied for the recovery and removal of N and P from wastewaters mainly include biological processes, ammonia stripping and struvite precipitation [3–7]. Usually, biological processes are accepted as the most economical method to treat swine wastewater [8], although the treatment stability and performance of biological processes are seriously influenced by the high concentration of ammoniacal nitrogen present in swine wastewater, which can significantly inhibit the activity of microorganisms [9]. Therefore, before biological treatment is initiated, the N and P nutrients in swine wastewater require pretreatment by physiochemical processes such as struvite precipitation and ammonia stripping. Struvite precipitation is a promising method for the simultaneous recovery of total ammonia nitrogen (TAN; NH_3, and NH_4^+) and phosphate (PO_4-P) [10], and the resultant struvite can be used as a slow-release fertilizer in agriculture. Due to the lack of Mg^{2+} in swine wastewater, there is a necessity to supplement some Mg^{2+} to the wastewater for the simultaneous recovery of TAN and PO_4-P by struvite precipitation. For this purpose, various magnesium (Mg) sources such as pure $MgCl_2$ and $MgSO_4$ salts [11], bittern [12], seawater [13], brucite [14], MgO [6], seawater nanofiltration concentrate [15], and magnesite [16] are widely used. Among these Mg sources, MgO is the most favorable owing to its low cost. However, using MgO as a Mg source has generally resulted in a decrease in the purity of the recovered struvite, which would influence its further application in agriculture. To obtain high purity of struvite, in recent years, some researchers have proposed the recovery of phosphate by struvite precipitation using Mg sacrificial anode [17,18], which can be rapidly dissolved through

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external electric current. Actually, in aqueous environments, the corrosion of Mg alloys occurs spontaneously at a high rate due to their poor corrosion-resistance [19], which could release Mg^{2+} ions for struvite crystallization. As a consequence, an external electric source supply for the electric current of the dissolution of Mg electrode may be completely unnecessary. Therefore, in this study, we aimed to investigate the feasibility of providing Mg^{2+} for struvite crystallization by the spontaneous chemical corrosion of Mg alloy.

For the treatment of swine wastewater, if only considering the recovery of PO_4-P, approximately 100% of the PO_4-P recovery efficiency could be achieved by struvite precipitation. However, since the TAN concentration in swine wastewater generally far exceeds that of PO_4-P, only a small amount of TAN can be removed by struvite precipitation. Hence, to reduce the influence of TAN in the subsequent biological process, TAN needed to be further pretreated by other processes. The ammonia-stripping process is a relatively low-cost method for TAN removal, and it is often applied to the treatment of wastewaters containing ammonia [20]. In the process of ammonia stripping, sodium hydrate (NaOH) and slaked lime ($Ca(OH)_2$) are usually used to adjust the pH value of wastewater [21,22]. Nevertheless, the use of NaOH readily leads to a high treatment cost. Although the use of lime for adjusting pH could significantly reduce the cost of chemicals, the high concentrations of Ca^{2+} ions remaining in the wastewater after ammonia stripping may result in difficulties in the operation of subsequent biological treatments such as the fouling of the pipes for the transfer of wastewater and sludge. To the best of our knowledge, researches on the application of ammonia stripping with MgO as the pH adjustor for TAN removal from swine wastewater are extremely limited. The biggest benefit in the use of MgO as the pH adjustor of ammonia stripping may be that the resultant supernatant after ammonia stripping contains high concentration of Mg^{2+}, which can be recycled as the Mg source of struvite precipitation for the recovery of phosphate.

Thus, in this study, we investigated a process involving coupling of struvite precipitation and ammonia stripping for the simultaneous recovery and removal of TAN and PO_4-P from swine wastewater. To search the optimal Mg source for struvite precipitation, three different types of Mg sources—Mg alloy, low-grade Mg oxide (LG-MgO) generated from the magnesite calcination, and the Mg-containing supernatant after ammonia stripping—were used for the struvite precipitation of swine wastewater. In addition, the performances of these Mg sources on the purity of recovered struvite as well as the cost involved were evaluated and compared. To further remove the high concentration of TAN from the effluent after the recovery of phosphate by struvite precipitation, ammonia stripping with LG-MgO as the pH adjustor was conducted.

2. Material and methods

2.1. Materials

The raw swine wastewater used in the study was collected from a pig farm located in the suburb of Beijing, China. Before use, to eliminate the possible effect of suspended solids on the struvite crystallization, the swine wastewater was pretreated by filtering through a filter paper with an aperture of 30–50 µm. The specific characteristics of the filtered wastewater are listed in Table 1. In the experiments, the magnesite mineral used as the raw materials of LG-MgO was purchased from Xinxing Mg Powder Plant (Yingkou, China), with $MgCO_3$ content of 94% (*i.e.*, Mg: 268.6 mg/g), along with other main compositions of Si 14.2 mg/g, Fe 10.2 mg/g, Ca 5.1 mg/g and Al 5 mg/g. Before the experiments, the magnesite mineral was ground to a particle size less than 0.12 mm, and then was calcined in a muffle furnace at 700 °C for 1.5 h [23]. The residues (LG-MgO) generated from the magnesite calcinations contained approximately 91% of MgO (wt. %), and was used as the Mg source of struvite precipitation and as the alkali reagent for ammonia stripping. The Mg alloy used in the experiments (AZ91 type) was purchased from an Mg Alloy Plant located in the Hangzhou city, China; it was cut into a rectangular plate of size 13 cm × 8 cm (thickness: 1.5 mm). The active surface area of the alloy plate was 208 cm^2 as both its sides could be used.

Table 1
The characteristics of the pretreated swine wastewater used in the experiments.

Parameter	Average values plus standard deviation
pH	7.7 ± 0.05
SS (suspended solids, mg/l)	45 ± 6.4
COD (mg/l)	3532 ± 231
PO_4-P (mg/l)	110 ± 4.5
TAN (mg/l)	730 ± 51
Na (mg/l)	357 ± 28
K (mg/l)	301 ± 37
Ca (mg/l)	53 ± 7.5
Mg (mg/l)	15.9 ± 4.2
Fe (mg/l)	2.8 ± 0.7

2.2. Operational procedures and experimental methods

To simultaneously recover TAN and phosphate from swine wastewater, a process involving a combination of struvite precipitation and ammonia stripping was designed. The schematic diagram of the combined process is described in Fig. 1. As seen in the figure, phosphate present in the swine wastewater was first recovered in a phosphate recovery reactor (PRR) with an effective volume of 1500 ml. Next, the resulting supernatant was transferred to an aeration reactor (AR, 1500 ml) for the further removal of TAN. The AR was airtight and linked with two absorption bottles by a glass tube. For the mixing of solution and the ammonia stripping, a coarse air bubble diffuser and a mechanical agitator were mounted at the bottom and top of the reactor, respectively. The stripped ammonia was passed through the two absorption bottles (containing 100 ml of H_2SO_4, 1 mol/l), and was absorbed by the sulfate acid solution.

In the experiments of phosphate recovery, to obtain a high purity of struvite, three kinds of Mg sources (Mg alloy, LG-MgO, and Mg-containing supernatant) were used for the formation of struvite. The experimental procedures involved in the application of the three kinds of Mg sources were as follows: (1) for the use of Mg alloy, 1000 ml of swine wastewater was first added to the PRR and then the Mg alloy plate was directly immersed into the wastewater, followed by the recovery of phosphate at different NaCl doses (0–0.15 mM) for 150 min at a stirring rate of 300 rpm; (2) for the use of LG-MgO, 1000 ml of swine wastewater was first poured into the PRR; next, LG-MgO was added to the solution at different MgO:P molar ratios (1:1–5:1), followed by stirring for 90 min; (3) as for the Mg-containing supernatant, it was the effluent after ammonia stripping in the AR (containing high concentrations of Mg^{2+}). The operational procedures for the use of the supernatant were identical to those for the use of the LG-MgO. Briefly, the supernatant was added to the swine wastewater at different Mg:P molar ratios (1:1–1.5:1), with a stirring time of 30 min at a pH range of 8–10 (solution pH was adjusted with 1 M NaOH).

After the recovery of phosphate, the remaining supernatant was fed to the AR for TAN recovery. In the reactor, the LG-MgO used as an alkali reagent was added to the solution at a given dosage (6–10 g/l); next, the mixture was aerated by an air pump at a certain aeration rate (3.3–6.7 L air/l wastewater · min; this unit means that a certain volume of air is supplied for 1 liter wastewater per minute) and temperature (25–45 °C) for 180 min.