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Recovery and removal of ammonia–nitrogen and phosphate from swine wastewater by internal recycling of struvite chlorination product

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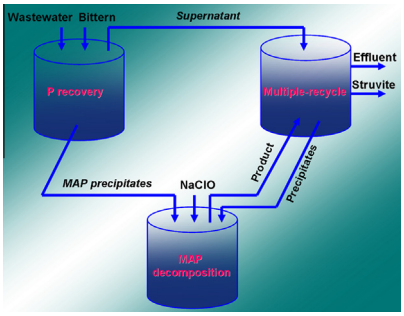
HIGHLIGHTS

- Recovery of phosphate was significantly influenced by the solution pH.
- Purity of struvite was mainly determined by the solution pH and Mg:P molar ratio.
- Nitrogen in struvite could be completely oxidized to N_2 gas by NaClO.
- High NH_4-N removal was achieved using the chlorination decomposition product.
- 84.5% of NH_4-N can be removed from the swine wastewater by the proposed process.

GRAPHICAL ABSTRACT



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ABSTRACT

The recovery of the total orthophosphate (P_T) and removal of the total ammonia–nitrogen (TAN) from swine wastewater were investigated through a combined technology of using bittern as the magnesium source in struvite precipitation along with internal recycling of the chlorination product of the recovered struvite. Results revealed that the P_T recovery efficiency and the struvite purity was mainly depended on the wastewater pH and the Mg:P_T molar ratio. Co-precipitations of $Mg_3(PO_4)_2$, $MgKPO_4$, $Ca_3(PO_4)_2$, and $Mg(OH)_2$ (pH > 9) were confirmed to be responsible for the decrease in the purity of struvite. The decomposition of recovered struvite by sodium hypochlorite (NaClO) was feasible. The TAN concentration of the swine wastewater was decreased to 63 mg/L by internal recycling of the chlorination decomposition product for seven cycles. An economic evaluation showed that 37% of the treatment cost of the proposed process could be saved as compared with struvite precipitation using pure chemicals.

1. Introduction

Nitrogen (N) and phosphorus (P) are the indispensable elements for all living organisms. They play an irreplaceable role in the breeding, growth, and development of organisms. Nitrogen is abundant in the nature, and its resource is sufficient and hence not a cause for concern. However, the resource amount of P is rather limited; it has been estimated that the phosphate rock reserves in the world that can be mined in the form of P_2O_5 is 7×10^9 metric tons (MT) (Shu et al., 2006). Phosphate rock (apatite) is mainly used as a raw material in fertilizer manufacturing. With the increasing world population, the demand for P fertilizer has been estimated to increase from 34.3×10^6 MT in 2000 to 47.6×10^6 in 2020 and to 83.7×10^6 in 2050 (Tilman et al., 2001). Given the current rate of consumption, it can be predicted that the P resource in the world would last for a maximum of 200 years more. Therefore, it is of great importance to recover the used P from the society for sustainable development of P resource.

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Swine wastewater is a wastewater type that contains abundant N and P, which are major pollutant source to water bodies if discharged without adequate treatment. Pollution problems related to the N and P discharge of swine wastewater commonly include eutrophication and dissolved oxygen depletion in water bodies as well as toxicity to the aquatic life and increase in the chloride dose for drink water disinfection due to the presence of ammonia (Dong and Reddy, 2012; Huang et al., 2010). In order to avoid the appearance of these problems, more stringent water quality standards have been established to decrease the levels of P and N entering surface water resources (Adnan et al., 2003). Therefore, the recovery of P from swine wastewater is not only an available means to realize sustainable development of P resource but also an essential measure for maintaining the water environment quality. For P recovery, various physical–chemical and biological methods such as metal ion (e.g., Al, Fe, and Ca) precipitation (Xu et al., 2014), adsorption (Alshameri et al., 2014), biological nutrient removal process (Bassin et al., 2012), and struvite (magnesium ammonium phosphate, MAP) crystallization (Huang et al., 2014) have been reported. Among these processes, struvite crystallization is a promising and feasible method to recover nutrients from swine wastewater as the total ammonia–nitrogen (TAN) and the total orthophosphate (P_T) content can rapidly react with magnesium (Mg) to form white struvite crystal, the solubility of which is only 0.023 mg per 100 g water (Li et al., 1999).

Swine wastewater generally contains several hundreds milligram per liter of TAN, less than 200 mg/L of P_T, and small amount of Mg (Liu et al., 2011). To obtain a high recovery efficiency of P_T, addition of external Mg source is required in the process of struvite crystallization. Pure Mg salts such as magnesium chloride ($MgCl_2$) and magnesium sulfate ($MgSO_4$) are often selected as the Mg source of struvite crystallization, but owing to their high cost price, their use tends to increase the recovery cost of P_T. Therefore, using low-grade Mg-containing materials such as brucite mineral (Huang et al., 2012), magnesite pyrolysate (Chen et al., 2009), magnesite mineral (Gunay et al., 2008), and seawater (Liu et al., 2013) as alternatives of Mg is a good strategy to decrease the recovery cost. Bittern is the remaining mother liquid in the process of seawater salt manufacturing and contains mostly $MgCl_2$, $MgSO_4$, sodium chloride, and small amounts of other inorganic compounds (Lee et al., 2003). With an increase in the degree of seawater enrichment, the maximum Mg^{2+} content in bittern is near 60,000 mg/L. In a previous study (Lee et al., 2003), bittern has proved to be an effective Mg source for struvite crystallization.

Although, in the process of P_T recovery by struvite crystallization, some proportion of the TAN in swine wastewater can be removed, but the removed amount is small as the amount of TAN in swine wastewater is much more than that of P_T. High contents of TAN remaining in the swine wastewater may inhibit the activity of microorganisms in the biological treatment system, thereby lowering the treatment efficiency of wastewater (Vadivelu et al., 2007). Therefore, there is a need to decrease the TAN concentration of swine wastewater before biological processing. Generally, under this condition, additional phosphate has to be added to the wastewater if high removal of TAN is desired. Nevertheless, this operation would significantly increase the treatment cost. To overcome this issue, recycling of struvite pyrogenation product is often considered to be an alternative process (Sugiyama et al., 2005; Türker and Çelen, 2007). However, with an increase in the recycling time, the removal ratio of TAN by this process decreased progressively due to the accumulation of byproducts such as $Mg_2P_2O_7$ and $Mg_3(PO_4)_2$ during struvite pyrogenation and the loss of phosphate and Mg in during pyrolysate reuse (Huang et al., 2011; Türker and Çelen, 2007).

In this study, in order to simultaneously recover P_T and remove TAN from swine wastewater, a novel treatment process that included the recovery of P_T and the reuse of recovered struvite was proposed. In this process, bittern as the external Mg source in struvite precipitation was added to the swine wastewater for the recovery of P_T. The recovered struvite was decomposed by sodium hypochlorite (NaClO), and its product was continuously reused for the removal of TAN from the supernatant after P_T recovery. The effects of pH and Mg dose on the recovery efficiency of P_T and the purity of struvite were first explored. Subsequently, the influences of pH and Cl/N weight ratio on the chlorination decomposition efficiency of struvite were investigated. Finally, multiple recycling of the chlorinated product was performed and an economic evaluation of the proposed process was performed.

2. Methods

2.1. Materials

Swine wastewater used during this study was collected from a pig farm located in Beijing. Before use, the swine wastewater was filtered through filter paper to remove the suspended solids and then stored in a 30-L plastic bucket at 5 ± 1 °C. The chemical characteristics of the filtered wastewater are given in Table 1. The bittern used in the experiments was collected from a solar salt field in Tianjin, and its main components are listed in Table 1.

2.2. Experimental methods

The flow chart of the proposed process is shown in Fig. 1. As seen in Fig. 1, the flow chart was divided into three stages: phosphate recovery, struvite decomposition, and product multiple recycling. (a) Swine wastewater was poured into the phosphate recovery reactor (PRR), and the phosphate in the wastewater was recovered with bittern as Mg source of struvite crystallization, followed by the addition of the recovered struvite and the supernatant into the struvite decomposition reactor (SDR) and multiple-recycle reactor (MRT), respectively. (b) The recovered struvite was decomposed using NaClO as an oxidant, and the resulting decomposition product was added to the MRT for the removal of the remaining TAN in the supernatant. (c) The struvite formed in MRT was returned to SDR and step (b) was repeated. (d) After several repetitions of steps (b) and (c), the supernatant after solid–liquid separation was discharged to the next treatment process and the formed struvite was recovered.

Here, batch experiments were conducted to optimize the operating conditions of each stage. The specific experiment procedures were as follows:

1. *P_T recovery:* For the first-stage recovery of phosphate, 1000 mL of swine wastewater was added into the PRR (a 1500-mL jar with an airtight lid). Subsequently, bittern was added to the swine wastewater at different Mg/P_T molar ratios, and the

Table 1
Compositions of filtered swine wastewater and bittern used in this study.

Swine wastewater		Bittern	
Parameter	Value and S.D.	Parameter	Value and S.D.
pH	7.5 ± 0.2	Ca^{2+} (mg/L)	90 ± 20
Alkalinity (as $CaCO_3$) (mg/L)	2939 ± 193	Mg^{2+} (mg/L)	44,000 ± 2100
COD (mg/L)	3298 ± 276	K^+ (mg/L)	12,300 ± 600
TAN (mg/L)	406 ± 28	Na^+ (mg/L)	58,000 ± 1800
P_T (mg/L)	128 ± 13	Cl^- (mg/L)	202,000 ± 13,000
K^+ (mg/L)	338 ± 21	SO_4^{2-} (mg/L)	60,000 ± 3000
Ca^{2+} (mg/L)	58 ± 9	Br^- (mg/L)	5300 ± 400
Mg^{2+} (mg/L)	28 ± 5		
Fe^{3+} (mg/L)	1.2 ± 0.3		
Zn^{2+} (mg/L)	0.6 ± 0.2		
Al^{3+} (mg/L)	0.5 ± 0.1		