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Nutrients removal from swine wastewater by struvite precipitation recycling technology with the use of $Mg_3(PO_4)_2$ as active component

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ABSTRACT

The recovery and removal of nutrients from swine wastewater was investigated by employing a struvite recycling process, which used magnesium phosphate (MP) as the active component. In this study, the effect of organic matters (sodium alginate, bovine albumin and acetic acid) in swine wastewater on the crystallization of struvite and the feasibility of MP as the phosphate and magnesium sources of struvite precipitation were first evaluated. The results demonstrated that sodium alginate and bovine albumin could slightly influence the crystallization of struvite while acetic acid did not. Using MP as the phosphate and magnesium sources of struvite precipitation could achieve a removal efficiency of the total ammonia nitrogen (TAN) close to that of using pure chemicals ($MgCl_2·6H_2O$ and $Na_2HPO_4·12H_2O$). The results of struvite pyrgenation revealed that the optimal pyrogenation condition of struvite was at $Mg(OH)_2:NH_4^+$ 1:1 and temperature 150 °C for 3 h, at which the main pyrogenation product was MP. Recycling the pyrolysate at pH 8.5 could achieve a TAN removal of 78%. When the pyrolysate was recycled for six cycles, the TAN removal efficiency could be maintained above 70%, and 67% of the struvite precipitation cost could be reduced compared to using pure chemicals.

1. Introduction

The total ammonia nitrogen (TAN) is one of the compounds containing nitrogen, the harm of which to water bodies is more extensive and complex compared with other forms of nitrogen. Swine wastewater is a typical wastewater that simultaneously contains high concentrations of TAN and total orthophosphate (P_T). In recent years, with the rapid rise in China's economy, the corresponding increase in the demand for pork resulted in the generation of large volumes of swine wastewater. This would bring about a high pollution risk to the water bodies around the pig farm if no rigorous treatment was performed. For the removal of TAN and P_T from swine wastewater, struvite precipitation has been technically proven to be an effective process, and has received extensive attention (Ichihashi and Hirooka, 2012; Kumar and Pal, 2013; Capdevielle et al., 2013; Lahav et al., 2013; Huang et al., 2014; Romero-Güiza et al., 2015). However, since swine wastewater is commonly short of magnesium and phosphate used for the effective removal of TAN by struvite precipitation, large amounts of magnesium and phosphate salts and alkali reagents needs to be supplemented to the wastewater, resulting in a high treatment cost. This would significantly affect the economic feasibility of struvite precipitation. Hence, to promote the further development and application of the process in the field of ammonia nitrogen wastewater treatment, it is of great importance to develop highly cost-effective struvite precipitation technology.

The recycling use of struvite is a significant approach to reducing the cost of struvite precipitation. This process is mainly achieved by direct pyrolysis (Yang et al., 2004; Iqbal et al., 2008), or NaOH pyrogenation of struvite (He et al., 2007; Zhang et al., 2009). The active product in the direct pyrolysis of struvite is $MgHPO_4$. However, at high temperatures, the product of the direct pyrolysis process is complex and commonly contains high contents of $Mg_2P_2O_7$, which has no capacity to remove TAN (Sugiyama et al., 2005). Additionally, the recycling of $MgHPO_4$ needs to consume large amounts of alkali reagent (NaOH) for the formation of struvite. Although the NaOH pyrogenation could effectively lower the decomposition temperature of struvite, the process needs a large quantity of NaOH. For example, Zhang et al. (2009) reported that the optimal $NaOH:NH_4^+$ molar ratio in the NaOH pyrogenation of struvite was required to

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be controlled at 2:1. In fact, the NaOH pyrogenation process cannot entirely avoid the formation of the byproducts [e.g., $Mg_3(PO_4)_2$ and $Mg_2P_2O_7$]. Through the analysis of published literatures, it was found that the large consumption of NaOH and the formation of byproducts may be the main obstacles to the further development of struvite recycling technology. To avoid the formation of $Mg_2P_2O_7$ in the pyrogenation of struvite, Huang et al. (2014) proposed the chlorination decomposition process of struvite, and found that the main components of the decomposition process were newberyite, dissolved HPO_4^{2-} and Mg^{2+}, and magnesium phosphate (MP). Although this process well resolved the problem of the formation of $Mg_2P_2O_7$, unfortunately, it only reduced a small amount of the struvite precipitation cost (34%) due to the large consumption of sodium hypochlorous. As for how to reduce the consumption of NaOH, to the best of our knowledge, there is no study dealing with this problem.

On the basis of our previous investigations and the summary of the published literatures, we found that the reported struvite recycling technologies were significantly affected by the habitual thinking of researchers. They commonly considered that only when struvite was decomposed to $MgHPO_4$, $MgNaPO_4$, or dissolved magnesium and phosphate salts, the recycling could be well accomplished. To the best of our knowledge, there was few investigation focused on the feasibility of using MP as the active component of the struvite pyrolysate for the formation of struvite. Indeed, under identical reaction conditions, $Mg_3(PO_4)_2$ has a low capacity for the removal of TAN compared to $MgHPO_4$ and $MgNaPO_4$. However, there was no detailed investigation data demonstrating the capacity of $Mg_3(PO_4)_2$ for the removal of TAN under different reaction conditions. Therefore, in this study, we proposed a novel recycling process of struvite, which was achieved by pyrolyzing struvite to $Mg_3(PO_4)_2$.

The main objective of this study was to investigate the simultaneous removal of TAN and P_T from swine wastewater by the proposed struvite recycling process. Owing to the presence of some organic matter in swine wastewater, the influence of organic matter on the crystallization of struvite was first studied by using simulated swine wastewater. Second, the investigations were focused on the performance of MP as the phosphate and magnesium sources of struvite precipitation. Third, to effectively reduce the cost of struvite precipitation, natural brucite mineral was used as the alkali reagent for the pyrogenation of struvite at different $Mg(OH)_2$:NH_4^+ molar ratios and pyrogenation times, and then the obtained pyrolysate was recycled for the simultaneous removal of TAN and P_T from swine wastewater. Lastly, the economic evaluation of the proposed recycling process was undertaken.

2. Materials and methods

2.1. Experimental materials

The swine wastewater used in this study was taken from a pig farm located in a suburb of Beijing. Prior to use, the swine wastewater was pretreated by passing it through a 0.45 μm filter membrane for the removal of suspended solids. The characteristics of the pretreated swine wastewater are shown in Table 1. The chemical reagents used in the experiments, including $MgCl_2·6H_2O$, $Na_2HPO_4·12H_2O$, NH_4Cl, $Mg_3(PO_4)_2·8H_2O$, acetic acid, sodium alginate and bovine albumin were purchased from Tianjing Chemical Reagent Plant, China. Additionally, in this study, the natural brucite powder used in the pyrogenation of struvite was obtained from Dangdong Tianci Flame-retardant Materials Co., China, and its chemical composition is identical to that in our previous investigation (Huang et al., 2012).

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

Parameter	Value and S.D.
pH	7.9 ± 0.1
Alkalinity (as $CaCO_3$) (mg/L)	1423 ± 108
COD (mg/L)	2985 ± 213
TAN (mg/L)	386 ± 19
P_T (mg/L)	97 ± 5.8
K^+ (mg/L)	298 ± 17
Ca^{2+} (mg/L)	35 ± 4.6
Mg^{2+} (mg/L)	28 ± 3.3

2.2. Effect of organic matter on the struvite crystallization

To investigate the influence of organic matter on the crystallization of struvite, three kinds of organic matter, including acetic acid, sodium alginate and bovine albumin were chosen. Moreover, in the experiments, simulated swine wastewater with the same concentrations of TAN and P_T to the actual swine wastewater was prepared by dissolving NH_4Cl and $Na_2HPO_4·12H_2O$ into pure water. The specified procedures of the experiments are described as follows: (1) 100 ml simulated wastewater was added to a 200 ml jar with an airtight lid, which was placed on a magnetic stirrer; (2) the desired amount of organic matter was fed to the wastewater for preparing different concentrations of organic matter (0–1000 mg/L), followed by 10 min rapid mixing to dissolve the organic matter; (3) external $MgCl_2·6H_2O$ and $Na_2HPO_4·12H_2O$ were added to the mixed wastewater at the Mg:N:P molar ratio of 1:1:1; (4) the mixed solution was stirred for 30 min at pH 9, and then was precipitated for 30 min; (5) 5 ml of the supernatant was taken and filtered through a 0.45 μm filter membrane for the composition analysis.

2.3. The use of MP as the phosphate and magnesium sources of struvite precipitation

The effects of the solution pH (7.5–9.5) and reaction time (10–120 min) on the removal of TAN from swine wastewater were first investigated by adding MP as the phosphate and magnesium sources of struvite crystallization at the P:N molar ratio of 1:1. Subsequently, based on the optimal conditions obtained, batch experiments were further conducted to investigate the effect of P:N molar ratio (1:1–1.8:1). The experimental procedures are shown in the following. First, 250 ml swine wastewater was fed to a jar with an airtight lid, followed by the addition of MP at the desired P:N molar ratio. Second, the mixed solution was stirred at 300 rpm, and the pH value was adjusted once every 2 min (1 M NaOH or HCl), and was controlled at a designed value. Third, 2 ml of solution was taken from the jar at 10 min intervals (within 120 min) and filtered through a 0.45 μm membrane filter for component analysis.

2.4. The decomposition and recycling of struvite

First, the struvite used in the experiments was formed by adding $MgCl_2·6H_2O$ and $Na_2HPO_4·12H_2O$ to swine wastewater at the stoichiometric ratio, with a reaction time of 60 min at pH 9. The formed struvite was washed thrice with pure water and dried in an oven at 35 ± 1 °C for 48 h. Second, 1 g dried struvite was mixed with brucite powder at a given $Mg(OH)_2$:NH_4^+ molar ratio (1:1–1.4:1), and then the mixed powder was heated at 150 °C for a given reaction time (30–240 min) to release ammonium. Third, the pyrolysate obtained under optimal conditions was added to swine wastewater at the active P (including MP in the pyrolysate and P_T in the swine wastewater) to TAN molar ratio of 1.6:1, and was recycled for the removal of TAN. The experimental procedures were similar to that mentioned in Section 2.3. Last, under the optimal conditions, the precipitates obtained at the third step were collected and