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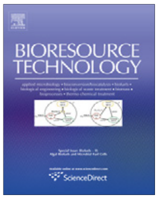

Removal of nutrients from piggery wastewater using struvite precipitation and pyrogenation technology

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ABSTRACT

In this paper, removal of nutrients from piggery wastewater by struvite crystallization was conducted using a combined technology of low-cost magnesium source in struvite precipitation and recycling of the struvite pyrolysate in the process. In the present research, it was found that high concentrations of K^+ and Ca^{2+} present in the solution significantly affected the removal of nutrients. When the struvite crystallization formed at the condition of dosing the magnesite pyrolysate at a Mg:N:P molar ratio of 2.5:1:1, and having a reaction time of 6 h, a majority of nutrients in piggery wastewater can be removed. Surface characterization analysis demonstrated that the main components of the pyrolysate of the obtained struvite were amorphous magnesium sodium phosphate ($MgNaPO_4$) and MgO. When the struvite pyrolysate was recycled in the process at the pH range of 8.0–8.5, the precipitation effect was optimum. When the struvite pyrolysate was recycled repeatedly at pH 8.5 or without any adjustment of pH, the outcome of the removal of the nutrients in both cases was similar. With the increase in the number of recycle times, the performance of struvite precipitation progressively decreased. An economic evaluation showed that the combination of using low-cost material and recycling of struvite was feasible. Recycling struvite for three process cycles could save the chemical costs by 81% compared to the use of pure chemicals.

1. Introduction

Nitrogen is an essential nutrient for living organisms; however, it can provoke water eutrophication when it is present in excess. Therefore, ammonia–nitrogen removal from wastewaters is of importance to prevent environmental pollution. Piggery wastes are considered to be a type of waste with the greatest environmental impact because of the presence of high concentrations of organic matters, nitrogen, and phosphorous in it. Usually, anaerobic digestion is accepted as a principal method of clearing up a majority of organic matters in piggery wastes, but the problem of nutrient enrichment of the digestion liquor still remains (Obaja et al., 2003). The most common and economical method to remove nutrients from wastewater is through the biological process (Cooper et al., 1994). However, high content of ammoniacal nitrogen has a toxic effect on microorganisms (Kim et al., 2008), which may lead to a decrease in the treatment effectiveness of the biological process. Struvite precipitation is a valid alternative for the removal of high ammonia concentrations from the anaerobically digested liquor of piggery wastes due to its high removal effectiveness, reaction rate, and solid–liquid separation capability. Struvite (MAP, $MgNH_4PO_4{\cdot}6H_2O$) is a white crystalline compound composed of magnesium, ammonium, and phosphate in an equal molar ratio (Di Iaconi et al., 2010). It also has a very low solubility.

Removal of ammonia as struvite has been widely investigated on the treatment of wastewaters that is rich in ammonia, such as rare-earth wastewater (Huang et al., 2009), landfill leachate (Di Iaconi et al., 2010), coking wastewater (Chen et al., 2009), semiconductor wastewater (Kim et al., 2009; Warmadewanthi and Liu, 2009), and human urine (Ganrot et al., 2007). The removal rate of ammonia could be reached to 85% within 30 min under a molar ratio of Mg:N:P of 1:1:1 for treating landfill leachate (Ozturk et al., 2003). Since the amount of PO_4^{3-} and Mg^{2+} in wastewaters are usually inadequate, a great amount of phosphate and magnesium salts are required for the effective removal of ammonia. This leads to a high operating cost, which hampers the widespread application of the struvite process. To solve this problem, many researchers have used low-cost materials containing magnesium as magnesium source of struvite precipitation, such as the byproducts generated in the production of magnesium oxide (Chimenos et al., 2003; Quintana et al., 2005; Quintana et al., 2008), the pyrolysate of magnesite (Huang et al., 2010), magnesite mineral (Gunay et al., 2008), bittern (Lee et al., 2003), and seawater (Kumashiro et al., 2001). In addition, process recycling of the struvite pyrolysate for the reduction of operation cost was proposed by some researchers (He et al., 2007; Türker and Çelen, 2007; Huang

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et al., 2009; Zhang et al., 2009). However, the simultaneous use of low-cost materials containing magnesium and the pyrolysate of struvite for ammonia removal has not yet been evaluated.

In earlier published literatures, there are some papers focusing on the pyrogenation and process recycling of struvite. For example, Kenichi et al. (1975) found that an ammonia removal of 86.3% was achieved by recycling the pyrolysate of struvite, which was produced in alkali solution and at 70–80 °C. Huang et al. (2009) introduced a technology of recycling struvite, which could achieve an ammonia removal of 99% and remaining phosphorus of less than 1 mg/L. He et al. (2007) reported that an ammonium-release ratio greater than 96% could be reached when struvite was pyrolyzed in the following conditions: $OH^-:NH_4^+ = 1:1$; decomposition temperature, 90 °C; heating time, 2 h. In addition, Zhang et al. (2009) considered that the optimal condition for struvite pyrolysate production was controlled at an $OH^-:NH_4^+$ molar ratio of 2:1, a heating temperature of 110 °C, and a heating time of 3 h. The pyrogenation of struvite in NaOH solution could be depicted by the following reaction equation:

$$MgNH_4PO_4 \cdot 6H_2O(s) + NaOH(s) \rightarrow MgNaPO_4(s) + NH_3(g) + 7H_2O(g) \quad (4)$$

Zhang et al. (2009) reported that a $NH_4^+–OH^-–Mg^{2+}–Na^+–PO_4^{3-}$ solution system could be formed when struvite was mixed with NaOH solution. As the $NH_4^+–OH^-$ structure was unstable, ammonia could be released according to the Equation $NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O$ when the $NH_4^+–OH^-–Mg^{2+}–Na^+–PO_4^{3-}$ solution system was heated at a given temperature. As a result, the pyrogenation of struvite takes place, leading to the formation of $MgNaPO_4$.

Struvite is an orthorhombic structure consisting of PO_4^{3-} tetrahedral, $Mg(6H_2O)^{2+}$ octahedral and NH_4^+ groups held together by hydrogen bands (Whitaker and Jeffery, 1970). $MgNaPO_4{\cdot}7H_2O$ is an isomorphous analogue with struvite. Besides, a large number of other struvite analogues such as $MgKPO_4{\cdot}6H_2O$, $MgRbPO_4{\cdot}6H_2O$, $MgTlPO_4{\cdot}6H_2O$, and $MgCsPO_4{\cdot}6H_2O$ have been reported (Mathew and Schroeder, 1979; Banks et al., 1975). As the stability of the struvite analogues generally declines with the decrease in the size of the univalent ion (Banks et al., 1975), when $MgNaPO_4$ was added to a solution containing NH_4^+, the Na^+ in the $MgNaPO_4$ could be replaced by NH_4^+ forming more stable $MgNH_4PO_4{\cdot}6H_2O$ because the size of NH_4^+ is larger than that of Na^+. Consequently, the reuse of $MgNaPO_4$ for ammonia removal was achieved.

The objective of this study is to investigate the struvite-precipitation recycle technology with the use of low-cost magnesium sources for ammonia removal, for the purpose of reducing the chemical cost of struvite precipitation. First, the effect of K^+ and Ca^{2+} in solution on struvite precipitation was evaluated by using synthetic swine wastewater. Second, the investigations focused on the conditions of using the pyrolysate of magnesite as the magnesium source and the efficiency of ammonia removal from piggery wastewater by internally recycling struvite pyrolysate. In addition, the solid before and after the struvite pyrogenation were characterized by a scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). Finally, an economic evaluation of the recycle process was performed.

2. Methods

2.1. Raw wastewater

The raw wastewater used in the experiments was the anaerobically digested liquor of piggery wastewater, which was taken from a pig farm located in a city in Guangdong province. Before being used, solid–liquid separation was performed. The composition of the supernatant is shown in Table 1.

2.2. Chemicals for struvite formation

Piggery wastewaters generally contain negligible magnesium and a low concentration of phosphate in comparison to ammonia (NH_3-N) (see Table 1). For the effective removal of ammonia, some phosphate and magnesium salts are required to be added. In this study, the pyrolysate of magnesite that calcined at 700 °C for 1.5 h and with a 53% Mg content was used as a source of magnesium in struvite precipitation (Huang et al., 2010). The original magnesite mineral was purchased from Xinxing Magnesium Powder Plant (Liaoning Province, China). As for the phosphate source, H_3PO_4 (85%) was used. In addition, KCl, $CaCl_2$, $NH_4H_2PO_4$, $MgCl_2{\cdot}6H_2O$, and $Na_2HPO_4{\cdot}12H_2O$ of analytical grade were used in this study.

2.3. Experiments for the influence of K^+ and Ca^{2+}

To study the effect of K^+ and Ca^{2+} on the struvite precipitation of piggery wastewater, synthetic swine wastewater with a NH_3-N concentration of 985 mg/L prepared by dissolving $NH_4H_2PO_4$ into deionized water was used. The experimental procedures are shown in the following. First, 200 mL synthetic wastewater was fed into a jar with an airtight lid. Second, $MgCl_2{\cdot}6H_2O$ was added to the wastewater at the $Mg^{2+}:NH_4^+:PO_4^{3-}$ stoichiometric molar ratio of 1:1:1, and then KCl (or $CaCl_2$) was fed into the wastewater at $K^+:Mg^{2+}$ (or $Ca^{2+}:Mg^{2+}$) molar ratio range of 0–0.75. Third, the reaction solution was stirred by a magnetic stirrer for 15 min at pH 9. Last, the solution supernatant after a precipitation of 10 min was filtered through a 0.45-μm membrane filter for component analysis.

2.4. Experiments for the use of the magnesite pyrolysate

The use of the pyrolysate of magnesite (its main composition was MgO) as the magnesium source of struvite precipitation was performed at different magnesium:ammonia molar ratios (1.5–3.5). Experimental procedures are depicted as follows. 500 mL piggery wastewater and a given dose of magnesite pyrolysate were added to a jar with an airtight lid, and H_3PO_4 was supplemented to the stoichiometric ratio of struvite formation. The pH value of the supernatant was measured after the agitation was intermitted for 1 min, at different time intervals (0.5–8 h). Thereafter, the supernatant of 5 mL was removed and filtered through a 0.45-μm membrane filter for the component analysis. In addition, control experiments using magnesite pyrolysate and H_3PO_4 as magnesium and phosphate sources was conducted by using pure $MgCl_2{\cdot}6H_2O$ and $Na_2HPO_4{\cdot}12H_2O$. The experimental procedures

Table 1
Composition of piggery wastewater supernatant after solid–liquid separation.

Parameters	Average values	Standard deviation
pH	7.8	0.2
COD (mg/L)	2388	238
BOD_5 (mg/L)	1035	164
TN (mg/L)	1212	55
NH_3-N (mg/L)	985	31
TP (mg/L)	182	19
PO_4^{3-}-P (mg/L)	161	11
K (mg/L)	797	27
Ca (mg/L)	135	23
Mg (mg/L)	6.7	3.6
Al (mg/L)	5.8	2.5
Fe (mg/L)	2.1	0.8