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Simultaneous removal of ammonia nitrogen and recovery of phosphate from swine wastewater by struvite electrochemical precipitation and recycling technology

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ABSTRACT

The removal of phosphorus and nitrogen from wastewater has been a matter of great concern for several decades. In this study, a coupled electrochemical process, involving the electrochemical recovery of phosphate as struvite, electrochemical decomposition of the struvite recovered, and removal of the ammonia nitrogen by recycling the struvite electrolysis product, was tested to simultaneously recover phosphate and remove the ammonia nitrogen from swine wastewater. The results demonstrated that when a magnesium alloy was electrolyzed as the magnesium source of struvite crystallization, the recovery efficiency of the phosphate was 99%, at a current density of 2 mA/cm^2 for 45 min. When the struvite recovered was electrolyzed using seawater as a supporting solution, the ammonium in the struvite could be completely removed. The characterization analysis revealed that the active component of the electrolysis product was present as dissolved phosphate and magnesium and insoluble cattiite. An efficiency of >90% of ammonia nitrogen removal could be achieved by recycling the electrolysis product of struvite. A pilot-scale test performed for 30 recycle cycles demonstrated that approximately 93% of the recovery/removal efficiencies of the phosphate and ammonia nitrogen from swine wastewater could be achieved stably by the process proposed, which implied the presence of an important application value in the water eutrophication control and recovery of the phosphorus resources.

1. Introduction

In recent years, the pig industry in the world has witnessed rapid growth in the global demand for red meat. According to the statistical data of the Food and Agricultural Organization (FAO), the amount of swine produced in the world reached 963,044,187 heads in 2012 (Lim and Kim, 2015). On the one hand, since large quantities of swine wastewater containing high concentrations of total orthophosphate (P_T), total ammonia nitrogen (TAN), and organic substances was generated from the feeding process of pigs (Ye et al., 2010), the serious effect of wastewater on the ecological environment is of great concern. On the other hand, the phosphorus (P) element in swine wastewater is a valuable resource. P is an important non-renewable resource in the nature, which is essential to maintain the development of societies (Zhang et al., 2013). Unfortunately, the exploitable reserves of phosphate rock are progressively decreasing since large amounts of P are utilized as the fertilizers in agriculture and the raw materials in some industries. It has been reported that the available accessible reserves of clean phosphate rock would be exhausted in the next 50 years unless some effective measures are taken (Gilbert, 2009). Therefore, based on the consideration of the sustainable development of P resource, recovery of P from wastewaters has received great attention worldwide (Cardoso et al., 2015; Ichihashi and Hirooka, 2012; Zhang et al., 2013).

Currently, several techniques are available such as the osmotic membrane bioreactor (Qiu and Ting, 2014), selectrodialysis/crystallization (Tran et al., 2014), amorphous calcium silicate hydrates adsorption (Okano et al., 2013), biosorption (Rathod et al., 2014) and struvite crystallization (Romero-Güiza et al., 2015) for the recovery of phosphate. Among these processes, struvite precipitation has been proven to be a promising technique for the removals of P_T and TAN. Struvite ($MgNH_4PO_4 \cdot 6H_2O$) is an insoluble double salt that can be potentially used as a slow-release fertilizer as it contains

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both P and N (Hao et al., 2013). Precipitating struvite in the form of stable white orthorhombic crystals should be of a suitable pH, with the required concentrations of Mg^{2+}, NH_4^+, and PO_4^{3-}. Although swine wastewater is rich in P_T and TAN, its magnesium content is scarce. Hence, a large amount of magnesium needs to be added to swine wastewater for the crystallization of struvite. Soluble salts such as $MgCl_2$ and $MgSO_4$ are the most frequently used magnesium sources for such processes. Besides, other low-grade magnesium sources such as seawater (Crutchik and Garrido, 2011), bittern (Lee et al., 2003), and seawater nanofiltration concentrate (Lahav et al., 2013) have also been used. Nonetheless, when these magnesium sources are used to prepare struvite, a large amount of NaOH is required for pH adjustment, which may significantly increase salt concentration in the wastewater, which in turn is highly inhibitory toward the microbial activity in the following biological treatment process (An and Gu, 1993; Demirer et al., 2008; Long et al., 2007). Although the use of $MgO/Mg(OH)_2$ as a magnesium source can resolve the problem of increased salinity, it significantly decreases the purity of recovered struvite due to the excessive dosing of alkali compounds. To resolve this issue, Ben Moussa et al. (2006) and Wang et al. (2010) used electrolytic cell with inert anodes to provide hydroxide anions for struvite crystallization to obtain pure struvite. In addition, Kruk et al. (2014) and Hug and Udert (2013) used magnesium sacrificial anode to simultaneously provide magnesium ions and hydroxide anions for the formation of high-purity struvite. Kruk et al. (2014) reported that struvite with purity of >90% can be obtained by struvite precipitation using magnesium sacrificial anode and by controlling the pH at the range of 7.5–9.3.

Although phosphate could be completely recovered from swine wastewater by struvite precipitation with magnesium sacrificial anode, only a very small proportion of TAN was removed as the amount of TAN in swine wastewater was much higher than that of phosphate (Liu et al., 2011). To achieve greater TAN removal, it is necessary to supplement additional phosphate salt to swine wastewater; however, this process is not economical for TAN removal. Recycling of struvite is a highly feasible method to reduce the dosage of phosphate salt and the cost of struvite precipitation. At present, direct pyrolysis (Huang et al., 2011a; Sugiyama et al., 2005) and NaOH pyrogenation (He et al., 2007; Türker and Çelen, 2007; Zhang et al., 2009) have been used most often for struvite decomposition. However, both the methods readily result in the generation of byproducts of magnesium pyrophosphate ($Mg_2P_2O_7$), which has no contribution to TAN removal. Moreover, the amount of $Mg_2P_2O_7$ in the decomposition product increased with the increase in the number of times of recycling (Türker and Çelen, 2007). $Mg_2P_2O_7$ is favorably produced from the further dehydration of magnesium hydrogen phosphate ($MgHPO_4$) at temperatures of >80 °C (Sugiyama et al., 2005; Türker and Çelen, 2007). Therefore, given that struvite was decomposed in the water solution at room temperature, $Mg_2P_2O_7$ should not be formed. Electrolysis oxidation is a simple and cost-effective technique for the removal of ammonium, which has been widely used for the treatment of various types of ammonium-containing wastewaters (Pérez et al., 2012; Vanlangendonck et al., 2005; Xie et al., 2006). Therefore, removal of ammonium in struvite by the electrolysis process is completely feasible.

The main objective of the present study was to achieve the simultaneous recovery of P_T and removal of TAN from swine wastewater by a coupled electrochemical process. The specific investigations involve the following aspects: 1) effectiveness of electrochemically dissolved magnesium as a precipitant for the recovery of P_T from swine wastewater and the purity of the struvite recovered; 2) optimal conditions for the electrochemical decomposition of the struvite recovered and the decomposition mechanism involved; 3) recycling process of the product of decomposition for TAN removal; and 4) evaluation of the stability and feasibility of the combined process proposed.

2. Materials and methods

2.1. Raw wastewater

The swine wastewater used in the lab-scale experiments was collected from a pig farm located in a Beijing suburb and stored in a refrigerator at 5 °C. Prior to use, the wastewater was pretreated by filtering it through a 0.45-μm filter membrane to remove the suspended solids. The characteristics of the pretreated wastewater are given in Table 1. In this study, the raw seawater collected from a bathing beach in the Qinhuangdao city was the supporting solution used in the experiments of the electrochemical decomposition of struvite. It was filtered through a filter paper prior to use, and the main features of the filtrate are shown in Table 2.

2.2. Analytical methods

The pretreated swine wastewater was analyzed according to the standard methods (APHA, 1998) to identify the concentration of the relevant P_T, TAN, COD, alkalinity, and other cations. The TAN and P_T constituents were analyzed by Nessler's reagent spectrophotometry and Mo–Sb anti-spectrophotometry (752 N-spectrophotometer, JINGKE, China), respectively. The cation concentrations were determined using an Atomic Absorption Spectrophotometer (AA-6800; Shimadzu, Japan). The solution pH was recorded with a pH meter (pHS-3C, JINGKE, China). The morphology and composition of the solid components were investigated using an SEM-energy dispersive spectrometer (SEM-EDS; SUPRA 55 SAPPHIRE; Germany) and an XRD (DMAX-RB; Rigaku, Japan), respectively. In this study, all the tests were performed in triplicate, and the average value was recorded. The purity of the struvite precipitates was determined according to the following method. At first, 0.5 g of the struvite precipitates was dissolved in 0.5% nitric acid solution and this solution was then diluted with ultrapure water to 100 ml. Finally, the solution pH was adjusted to around 4 by employing NaOH solution (1 M) prior to determining the ammonium concentration. The quantity of struvite in the precipitates could be calculated based on the result of the ammonium determination. Therefore, the struvite purity (P_s) can be calculated according to the equation given,

$$P_s = \frac{Q_s}{Q_p} \times 100\% \quad (1)$$

where Q_s and Q_p represent the struvite mass in the precipitates and the total mass of the precipitates, respectively.

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

Parameter	Average values plus standard deviation
pH	7.8 ± 0.06
COD (mg/L)	4105 ± 327
Alkalinity (as Na_2CO_3) (mg/L)	3135 ± 293
P_T (total orthophosphate, mg/L)	103 ± 9.8
TAN (total ammonia nitrogen, mg/L)	426 ± 21
K (mg/L)	293 ± 18
Ca (mg/L)	64 ± 7.2
Mg (mg/L)	13 ± 2.5
Fe (mg/L)	1.6 ± 0.5
Cu (mg/L)	0.8 ± 0.1
Zn (mg/L)	0.5 ± 0.1