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Simultaneous removal of nutrients from simulated swine wastewater by adsorption of modified zeolite combined with struvite crystallization

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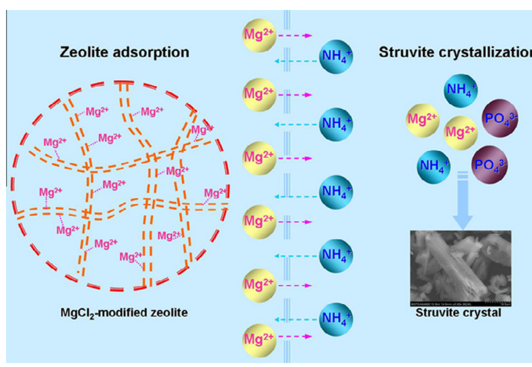
HIGHLIGHTS

- $MgCl_2$-modified zeolite was used as adsorbent material and magnesium source.
- 82% TAN and 98% P_T in synthetic swine wastewater were simultaneously removed.
- K^+, Ca^{2+}, Na^+ and Mg^{2+} had a significant effect on the proposed process.
- The presence of citric acid had a significant effect on the proposed process.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper proposes a novel process for the simultaneous removal of ammonia–nitrogen and phosphate from simulated swine wastewater using modified zeolite. The natural zeolite was modified by magnesium salts as the adsorbent material for ammonia–nitrogen from wastewater. Mg^{2+} released from the adsorption process served as the magnesium source in struvite crystallization. The treatment of simulated swine wastewater using modified zeolite at pH 8–9.5 showed much better efficiencies of ammonia–nitrogen and phosphate removal than those by natural zeolite at the same pH. The high nutrient-removal efficiencies were mainly achieved because of cooperation between adsorption by modified zeolite and struvite crystallization. When the reaction condition was controlled at 110 g/L of modified zeolite and 40 min of reaction time, the ammonia–nitrogen and phosphate-removal efficiencies reached 82% and 98%, respectively. The individual presence of K^+, Ca^{2+}, Na^+, and Mg^{2+} had a significantly negative effect on the removal of ammonia–nitrogen in the order of preference of $Ca^{2+} > Mg^{2+} > K^+ > Na^+$ at identical molar concentrations. Nevertheless, the presence of these ions, except for Na^+, had a positive influence on the removal of phosphate. In addition, investigation of the effects of organic acids on the process showed that the removal of nutrients could be significantly reduced by inhibiting struvite crystallization by citric acid present in the simulated swine wastewater. However, the presence of acetic acid had no effect on the proposed process. An economic evaluation revealed that the treatment cost of the proposed process was 3.65 $/m^3 of simulated swine wastewater.

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1. Introduction

In recent years, with the rapid economical development in developing countries, the demand for pork is also increasing, resulting in the generation of enormous amounts of swine wastewater, which generally contains high concentrations of the total ammonia–nitrogen (TAN) and the total orthophosphate (P_T). When these compounds are present in substantial quantities in the receiving water bodies such as lakes and rivers, algae and other microorganisms breed excessively in these water bodies. As a consequence, the eutrophication phenomenon occurs, which increases the depletion of dissolved oxygen in the water, making the water toxic to fish [1]. Thus, rigorous removal of nitrogen and phosphorous nutrients from swine wastewater is of critical importance to prevent pollution of surface water around livestock farms.

Usually, biological process is accepted as the most common and economical method to treat wastewater [2]. However, the activity of microorganisms in the biological treatment system can be significantly inhibited by high concentrations of ammoniacal nitrogen (NH_3) in swine wastewater [3,4], leading to a decrease in the treatment performance of the biological process. It is therefore necessary to lower the concentration of ammonia prior to the biological processing. To resolve this issue, some physical–chemical methods such as ammonia stripping [5], struvite precipitation [6], zeolite adsorption [7], membrane separation [8], and microwave radiation [9] have been proposed. Among these methods, the formation of struvite has been widely proven to be effective for the simultaneous recovery of TAN and P_T from swine wastewater [10]. Due to the special characteristic of the simultaneous presence of TAN and P_T in the wastewater, Mg^{2+}, NH_4^+ and PO_4^{3-} can crystallize to form struvite ($MgNH_4PO_4{\cdot}6H_2O$) when an appropriate amount of magnesium salts is added into swine wastewater, whereby its pH increases to 8–9 [11]. However, since the amount of TAN in swine wastewater far exceeds that of P_T [12], TAN removal by crystallization of Mg^{2+}, NH_4^+ and PO_4^{3-} in equal-molar concentrations is very low [13]. To achieve a high TAN removal, addition of external phosphate salt is required, but this process can significantly increase the treatment cost of struvite precipitation.

In separate consideration of TAN removal, adsorption of TAN on zeolites is gaining attention because of its low market price and relative simplicity of application and operation [7]. Zeolites are crystalline, microporous aluminosilicate minerals consisting of three-dimensional frameworks of SiO_4^{4-} and AlO_4^{5-} tetrahedra linked through shared oxygen atoms [14,15]. It generally exhibits a high selectivity for ammonium and metallic ions and can often be used as ion exchanger in domestic and commercial water purification, softening, and other applications [16,17]. Because natural zeolites have a lower adsorption capacity, they usually need to be modified before use to improve their adsorption capacity and purity. Conventionally, these modification/regeneration methods often include treatments of acid, alkali, and salts of alkaline metals [18–20], integrated calcination [21], microwave pretreatment [22], and electrochemical treatment [23]. For example, Lin et al. [17] prepared modified zeolite by immersing 5 g of natural zeolite in the flask containing 100 mL of sodium chloride (NaCl; 2 M) solution under 35 ± 1 °C in a thermostatic shaker at 100 rpm for 24 h. The ammonium adsorption capacity of NaCl-modified zeolite (17.3 mg-N/g) was greater than that of natural zeolite (11.0 mg-N/g). Unfortunately, regardless of modified zeolites or natural zeolites, their efficiencies for simultaneous removal of TAN and P_T were quite limited, despite their high TAN-removal potential. Generally, the combination of a cation exchanger and an anion exchanger or that of a cation exchanger and an inorganic cohesion precipitation is considered for the simultaneous removal of TAN and P_T [24]. However, the operation of this combination is complicated and expensive. Although it is difficult to use only one adsorption material to simultaneously remove TAN and P_T from swine wastewater, we can use a material that triggers two reaction mechanisms (adsorption reaction and struvite crystallization) for the removal of both simultaneously. In other words, we can use zeolite modified with magnesium salts as the adsorbent material for TAN removal and the magnesium ions released from zeolite as the source of struvite precipitation for the removal of TAN and P_T from swine wastewater.

The main objective of this study was to investigate the mechanisms for simultaneous removal of TAN and P_T from simulated swine wastewater using $MgCl_2$-modified zeolite. The influence of different pH, reaction time, and reagent dosage of the zeolite on the process was evaluated. The composition of actual swine wastewater is complicated; it generally contains various types of cations (K^+, Ca^{2+}, Na^+ and Mg^{2+}) and high concentrations of organic matter besides TAN and P_T. In the process of anaerobic digestion, the organic matter in swine wastewater can be converted to various organic acids such as acetic acid, propionic acid, and succinic acid [25,26]. In addition, some feed additives such as citric acid and fumaric acid which remain in the pig house during feeding enters the swine wastewater during cleaning of the pig house [26]. Hence, we also investigated the effect of individual presence of such species of cations and organic matters (acetic acid and citric acid) on the removal of TAN and P_T.

2. Materials and methods

2.1. Materials

The natural zeolite media used in this study were supplied by a mineral processing plant located in the Henan province, China. The media was ground and sieved to a particle size range of 0.18–0.35 mm. The chemical composition of zeolite was specified by the supplier (listed in Table 1). Prior to the modification process, the natural zeolite was washed with distilled water to remove impurities such as salinity, ash, and sand specimen, and then dried at 100 ± 5 °C for 12 h. Subsequently, 100 g of the dried zeolite was taken in a 1-L solution with a magnesium chloride ($MgCl_2$) concentration of 2 mol/L and then stirred for 12 h. The obtained sample was collected with filter paper and washed with distilled water thrice. Finally, the sample was dried in an oven at 100 ± 5 °C for 12 h. The raw wastewater used in the study was simulated swine wastewater with TAN and P_T concentrations of 35 and 5 mM, respectively, which were prepared by dissolving NH_4Cl and $(NH_4)_2HPO_4$ of analytical grade into distilled water. In addition, the working solutions for the control experiments were prepared by only dissolving NH_4Cl or $Na_2HPO_4{\cdot}12H_2O$ of analytical grade in distilled water; their individual concentrations were identical to that of the corresponding

Table 1
Chemical composition of the natural zeolite (wt.%).

Constituent	Value (%)
SiO_2	67.52
Al_2O_3	12.78
Fe_2O_3	2.01
TiO_2	0.25
CaO	3.26
MgO	1.33
Na_2O	1.93
K_2O	1.68
MnO	0.04
Loss of ignition	10.8