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Research article

Removal of ammonium from swine wastewater by zeolite combined with chlorination for regeneration

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ABSTRACT

This study investigated a process using ammonium ion (NH_4^+) exchange on zeolite in combination with chlorination regeneration for the safe treatment of simulated swine wastewater. Two stages i) 120-min zeolite ion-exchange and ii) 10-min exchanged zeolite regeneration facilitated NH_4^+ ion removal from wastewater. Solution pH, contact time, adsorbent dosage, and competitive cations were the significant factors influencing the entire process. The effect of competitive cations on NH_4^+ removal effectively followed the order of preference as $Na^+ > K^+ > Ca^{2+} > Mg^{2+}$ at equivalent concentrations. The chlorination method experimentally removed approximately 99% of the NH_4^+ exchanged on the zeolite, without remaining NH_4^+ in the regeneration solution. Our analysis revealed that, in this process, the NH_4^+ exchanged on the zeolite was first replaced by Na^+ and then oxidized to nitrogen gas. Reuse of the regenerated zeolite (GZ) indicated that the removal efficiency of NH_4^+ ions was equal to that of the fresh zeolite modified with NaCl. Results of kinetic analysis revealed that the NH_4^+ exchange on the GZ followed the pseudo-second-order model and the intraparticle diffusion model only for the first 60 min. The ion-exchange isotherm results demonstrated that the Langmuir model provided a slightly more consistent fit to the equilibrium data as compared with the Freundlich model. Repetitive experimental results confirmed that the proposed zeolite recycling process was stable and usable in simulated swine wastewater treatment.

1. Introduction

With the rapid increase in the world population and economy, the demand for meat is also rising fast. Pork, one of the largest meat sources, accounts for about 40% of the world's total meat consumption (Lahav et al., 2013). The worldwide pork production was estimated at 111.8 million metric tons in 2015, with an increase of 1.1% from 2014 (USDA, 2014). This large-scale pork production directly results in the generation of huge amounts of wastewater containing high concentrations of nitrogen and phosphorus. Although nitrogen is essential for nucleic acid and protein synthesis, the two most important polymers of life (Canfield et al., 2010), the presence of excessive amounts of nitrogen in water bodies can cause serious ecological and environmental backlashes such as algal bloom in lakes and rivers, depletion of dissolved oxygen (DO), and toxicity in aquatic fauna. Nitrogen in swine wastewater mainly occurs in the form of NH_4^+. Therefore, it is very significant to remove the NH_4^+ from swine wastewater for prevention of the nitrogen pollution. The most widely used traditional NH_4^+-removal processes from swine wastewater are air stripping, ion-exchange, and biological nitrification–denitrification process. Among these, air stripping and biological nitrification–denitrification processes involve complicated configuration and are significantly influenced by the low temperatures in winter. Therefore, ion-exchange is an attractive method for NH_4^+ removal since it is not influenced by temperature variations with relatively simple operation.

Zeolites, which are microporous aluminosilicate minerals, have a three-dimensional framework structure, making them usable as an excellent ion-exchange material due to their ability to preferentially remove NH_4^+ from wastewater (Lin et al., 2013). The general

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formula of zeolites is expressed as follows (Saltalı et al., 2007):

$$\left(M_x^+,\ M_y^{2+}\right)\left(Al_{(x+2y)}Si_{n-(x+2y)}\right)\cdot mH_2O$$

where, M^+ and M^{2+} represent the monovalent and divalent cations, respectively (including Na^+, K^+, Ca^{2+}, and Mg^{2+}). These are called exchangeable cations as they can be easily exchanged by other surrounding cations in a contact solution (Lin et al., 2013). Factors such as particle size, solution pH, temperature, initial ammonium concentration, competitive cations, and zeolite dosage significantly affect the NH_4^+-exchange capacity of the zeolites (Karadag et al., 2006; Lei et al., 2008a,b; Huang et al., 2010; Alshameri et al., 2014). In general, before using natural zeolites (NZ) for NH_4^+ removal, they should be pretreated to improve their purity and NH_4^+-exchange capacity. Several methods including integrated calcination (Liang and Ni, 2009), NaCl solution treatment (Lin et al., 2013), acid (HCl) or alkali (NaOH) treatment (Wang et al., 2011), and microwave pretreatment (Lei et al., 2008a,b) have been used for zeolites modification. Although the natural or modified zeolites possess several advantages including good selectivity on NH_4^+, availability, and lower price, they have not been widely used in a commercial scale for domestic or industrial wastewater treatments, which probably because the exchanged zeolites require further disposal or regeneration process.

Currently, some methods have been applied for zeolite regeneration, including the use of brine solutions of varying compositions (Dryden and Weatherley, 1989; Booker et al., 1996; Demir et al., 2002; Du et al., 2005), NaOH regeneration (Jorgensen et al., 1976), biological regeneration (Green et al., 1996; Lahav and Green, 1998; Jung et al., 2004; Wu et al., 2008), and electrochemical regeneration (Lei et al., 2009; Lahav et al., 2013). However, the brine and NaOH (or HCl) regeneration process normally requires great quantities of chemical reagents, which immediately produces NH_4^+ as a secondary pollutant requiring further treatment. Although biological regeneration could effectively remove NH_4^+ exchanged on zeolites, avoiding the secondary NH_4^+ pollution, the activated sludge in the regeneration process led to rapid fouling of the zeolites, which further reduced their NH_4^+ ion-exchange capacity. In addition, biological regeneration requires rigorous monitoring and management to maintain various parameters (such as the solution temperature, pH, carbon source supplementation, and the aeration rate) in optimum condition. It also necessitates the further removal of byproducts such as nitrites (Li et al., 2010). In recent years, some researchers have utilized electrochemical method to regenerate exchanged zeolites and have reported that the NH_4^+ exchanged by zeolite can be effectively oxidized to nitrogen gas in the presence of chloride ions (Lei et al., 2009; Li et al., 2010; Lahav et al., 2013). However, complex equipment and relatively high-energy consumption are needed for zeolite electrochemical regeneration, which may increase the costs of project operation and wastewater treatment. In this study, based on the electrochemical regeneration mechanism, we have proposed a simpler method of zeolite regeneration that involves the chlorination of the NH_4^+ with the addition of sodium hypochlorite (NaClO). Zeolite regeneration by NH_4^+ chlorination has the following advantages: (i) the NH_4^+ exchanged by the zeolite can be rapidly (within few minutes) oxidized to nitrogen gas without any generation of secondary NH_4^+ pollution, (ii) the equipment and operation required for zeolite chlorination regeneration are simple, and (iii) the chlorination regeneration of zeolite is unaffected by the solution temperature and the quantity of NH_4^+ exchanged.

The main objective of this study was to investigate the feasibility of NH_4^+ removal from swine wastewater by zeolite ion-exchange in combination with chlorination regeneration of the zeolite-exchanged NH_4^+. Therefore, a series of experiments was first conducted to determine the optimal conditions for NH_4^+ removal by using natural and modified zeolites. In these experiments, the effects of pH, contact time, adsorbent dosage, and competitive cations on NH_4^+ removal by the zeolites were studied. Besides, experiments for the regeneration of the exchanged zeolite by chlorination reaction were also carried out. Finally, the reuse performance of the regenerated zeolite (GZ) for NH_4^+ removal was investigated, and the stability and adaptability of the proposed zeolite recycling process were evaluated.

2. Materials and methods

2.1. Materials

The NZ used in this study was obtained from Zhejiang Yatai Zeolite, Ltd, Zhejiang province, China. X-ray diffraction (XRD) used to perform mineral characterization of the NZ revealed the presence of mainly clinoptilolite. Its specific chemical composition is as follows: SiO_2 65.81%, Al_2O_3 12.49%, K_2O 2.63%, Na_2O 2.7%, TiO_2 0.29%, CaO 1.83%, Fe_2O_3 1.82%, and MgO 1.81%, with loss of ignition (LOI) 10.62%. The NZ used in the study had a 0.3–0.5 mm particle size range. Before use, the NZ was washed thrice with distilled water to remove impurities such as salinity, ash, and sand, followed by oven drying at 80 ± 1 °C for 24 h. The chemical modification of the 50 g dried NZ was performed by adding 500 mL NaCl solution (1 M) in a 1-L beaker and stirring the mixture for 24 h at room temperature. After the chemical modification, the modified zeolite (MZ) was thoroughly washed with distilled water and dried for 24 h at 80 ± 1 °C. In this study, the working solutions included the simulated swine wastewater (Table 1), which was prepared by dissolving NH_4Cl, $(NH_4)_2HPO_4$, KCl, $MgCl_2$, NaCl, $CaCl_2$, Na_2SO_4, and $NaNO_3$ in distilled water. All chemicals used in this study were of analytical grade.

2.2. Experimental methods

2.2.1. Ion-exchange experiments

The experiments were performed to determine the effects of pH, contact time, adsorbent dosage, and competitive cations on NH_4^+ removal from simulated swine wastewater by NZ and MZ. The experimental procedures involved the following steps: First, 100 mL simulated swine wastewater was taken in a 250-mL beaker placed on a magnetic stirrer. A pre-decided dose of zeolite (NZ or MZ) was then added into the solution and the solid–liquid mixture was stirred at the rate of 300 rpm. In the ion-exchange reaction, the desired pH was controlled by the addition of 0.1 M NaOH or 0.1 M HCl. After the ion-exchange reaction, the supernatant was passed through a 0.45-μm filter membrane for composition analysis.

2.2.2. Regeneration experiments

Under optimal conditions, the zeolite with exchanged NH_4^+ was

Table 1
Characteristics of the simulated swine wastewater.

Parameters	Value
NH_4^+ (mg/L)	322
$P-PO_4^{3-}$ (mg/L)	87
Cl^- (mg/L)	823
SO_4^{2-} (mg/L)	38
NO_3^- (mg/L)	6
Na^+ (mg/L)	90
K^+ (mg/L)	191
Ca^{2+} (mg/L)	31
Mg^{2+} (mg/L)	20

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