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Optimization for zeolite regeneration and nitrogen removal performance of a hypochlorite-chloride regenerant

Wei Zhang, Zhen Zhou*, Ying An**, Silu Du, Danian Ruan, Chengyue Zhao, Ning Ren, Xiaoce Tian

College of Environmental and Chemical Engineering, Shanghai University of Electric Power, 2588 Changyang Road, Shanghai 200090, China

HIGHLIGHTS

- NaClO-NaCl solution was effective for zeolite regeneration and nitrogen removal.
- NaClO-NaCl regeneration condition was optimized by response surface method.
- The regeneration improved NH_4^+ removal of zeolites by increasing microporosity.
- The regeneration had insignificant effect on composition and morphology of zeolites.

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ABSTRACT

Simultaneous zeolites regeneration and nitrogen removal were investigated by using a mixed solution of NaClO and NaCl (NaClO-NaCl solution), and effects of the regenerant on ammonium removal performance and textural properties of zeolites were analyzed by long-term adsorption and regeneration operations. Mixed NaClO-NaCl solution removed more NH_4^+ exchanged on zeolites and converted more of them to nitrogen than using NaClO or NaCl solution alone. Response surface methodological analysis indicated that molar ratio of hypochlorite and nitrogen (ClO^-/N), NaCl concentration and pH value all had significant effects on zeolites regeneration and NH_4^+ conversion to nitrogen, and the optimum condition was obtained at ClO^-/N of 1.75, NaCl concentration of 20 g/L and pH of 10.0. Zeolites regenerated by mixed NaClO-NaCl solution showed higher ammonium adsorption rate and lower capacity than unused zeolites. Zeolites and the regeneration solution were both effective even after 20 cycles of use. Composition and morphological analysis revealed that the main mineral species and surface morphology of zeolites before and after NaClO-NaCl regeneration were unchanged. Textural analysis indicated that NaClO-NaCl regeneration leads to an increased surface area of zeolites, especially the microporosity. The results indicated that NaClO-NaCl regeneration is an attractive method to achieve sustainable removal of nitrogen from wastewater through zeolite.

1. Introduction

Large quantity of nitrogen present in wastewater is one of the main causes of eutrophication that negatively affects natural water bodies. Nitrogen contamination consumes dissolve oxygen, generates offensive odors and hinders disinfection process of water supplies (Sarioglu, 2005; Huang et al., 2015a). Therefore, nitrogen removal from wastewater is obligatory in many countries (Wang et al., 2006; Liao et al., 2015). Various methods, such as nitrification-denitrification, air stripping and struvite precipitation, have been successfully used for ammonium nitrogen (NH_4^+-N) removal from wastewater, but their effectiveness are constrained by temperature, NH_4^+-N concentration, pH and impurity substances (Li et al., 2009; Huang et al., 2014, 2015b; Zhou et al., 2015). Ion exchange process opens opportunities for effective NH_4^+-N removal as it is almost unaffected by temperature and pH fluctuations, suitable for low NH_4^+-N concentration, and easy to operate (Li et al., 2010). Zeolites, which are micro- and mesoporous hydrated crystalline aluminum-silicate materials with a three-dimensional

* Corresponding author.
** Corresponding author.
E-mail addresses: zhouzhen@shiep.edu.cn (Z. Zhou), anying007@163.com (Y. An).

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framework structure, are considered as an excellent ion-exchange material for their high selectivity on NH_4^+, high exchange capacity, availability and safety (Guaya et al., 2015; Huang et al., 2015b). Many researchers have investigated the NH_4^+-N removal performance by natural zeolites and modified zeolites, and found that both zeolites achieved effective NH_4^+-N removal (Jung et al., 2004; Li et al., 2010; Huang et al., 2014, 2015b; Guaya et al., 2015). To date, commercial application of zeolites in NH_4^+-N removal was limited, probably attributed to concerns of short life service span and the deficiency of regeneration methods.

Many approaches have been applied for exchanged zeolites regeneration to achieve sustainable NH_4^+-N removal. NaCl solution effectively exchanged adsorbed NH_4^+-N from zeolite (Rahmani and Mahvi, 2004), and the alkaline condition further enhanced the regeneration efficiency (Du et al., 2005). However, NaCl regeneration requires periodical replacement due to the accumulation of NH_4^+-N in the regenerant solution, which resulted in secondary pollution that needs further treatment (Lei et al., 2009). Alkaline regeneration by NaOH solution successfully avoided NH_4^+-N accumulation by air stripping, but was restrained by its high cost in regenerant and gaseous pollution control. Compared to chemical approaches, the biological regeneration method was developed to remove NH_4^+-N from zeolite through nitrification and/or denitrification process, and shows advantages in an environmental-friendly and economical manner (Lahav and Green, 1998; Jung et al., 2004; Zheng et al., 2015; Vitzthum von Eckstaedt et al., 2016). Conventional biological regeneration requires external alkalinity to control pH, carbon source for denitrification, proper temperature and long reaction time. Vitzthum von Eckstaedt et al. (2016) reported a novel biofilter for air streams converted ammonia into N_2 via nitrite by using zeolites as adsorbent and catalyst, which saved external alkalinity and dissolved oxygen for biological regeneration of zeolite. In recent years, hypochlorite ion, which can be generated by dosing NaClO (Huang et al., 2015b) or electrochemical method (Lei et al., 2009; Li et al., 2010; Gendel and Lahav, 2013; Lahav et al., 2013) was used to oxidize adsorbed NH_4^+ to N_2, and thus achieved effective and rapid zeolites regeneration without secondary pollution. To confirm the stability and adaptability of hypochlorite regeneration, more detailed research is needed to investigate regeneration kinetics and optimal condition, and the effects of hypochlorite on composition and textural properties of regenerated zeolite (RZ) in long-term operation.

In this study, three regenerants, including NaCl, NaClO and their mixture (NaClO-NaCl solution), were firstly used to investigate their effects on zeolites regeneration efficiency (ZRE) and terminal species of nitrogen after regeneration. Then the regeneration condition of zeolites was optimized using response surface methodology (RSM). Effects of hypochlorite regeneration on NH_4^+-N removal performance, composition and textural properties of RZ were also investigated in long-term adsorption and regeneration operation.

2. Materials and methods

2.1. Materials

Zeolites used in this study are commercial products from Jinyun County, Zhejiang Province, China. The ore is mainly clinoptilolite type composed of quartzes, which is the most common and abundant type of zeolites with widespread industrial and environmental applications. Its specific chemical compositions are as follows: O 42.2%, Si 37.6%, Al 8.8%, C 5.0%, Ca 3.5%, K 1.5%, Na 0.9% and Mg 0.5%. The particle size of natural zeolites used in this study is 0.3–0.5 mm. Before use, zeolites were washed thrice with distilled water to remove non-adhesive impurities and small particles, and then dried at 60 °C in oven for 12 h to remove moisture.

2.2. Experimental methods

2.2.1. NH_4^+-N removal by zeolite

Ammoniacal solution with initial NH_4^+-N concentration of 25 mg/L was prepared by analytical grade ammonium chloride. The NH_4^+-N removal experiment was performed in a 250 ml beaker placed on an agitator by dosing 200 ml solution and 8 g of zeolites. The solid-liquid mixture was stirred at 150 rpm for pre-decided time, and then settled for solid-liquid separation. The supernatant was filtered through a 0.45 μm filter membrane for analyzing NH_4^+-N concentration. More than 50 batch tests were conducted under the same condition mentioned above to prepare exchanged zeolites for the regeneration experiment.

2.2.2. Zeolite regeneration

The zeolites were regenerated by three different regenerants, including 5 g/L NaCl, NaClO with molar ratio of hypochlorite and nitrogen (ClO^-/N) of 2.25, and NaClO-NaCl solution with above-mentioned dose, respectively. Six tests were conducted for each regenerant in the 250 ml beaker with dried zeolites immersed in 200 ml regenerant for 2.5, 5, 10, 20, 30 and 40 min, respectively. Then the solid-liquid mixture was settled, and the supernatant was filtered to analyze NH_4^+-N, nitrate nitrogen (NO_3^--N) and total nitrogen (TN). The RZ was added into 250 ml beaker with 50 ml HCl at pH of 0.5–0.6 to release residual NH_4^+-N from RZ after stirring for 2 h (Huang et al., 2015b). The concentration of released NH_4^+-N was measured with samples filtered through a 0.45 μm filter membrane.

ZRE is calculated according to Eq. (1).

$$ZRE = \left[1 - \frac{V_a AN_a}{V_w (AN_i - AN_e)}\right] \times 100\% \tag{1}$$

Where, AN_i and AN_e are NH_4^+-N concentrations in the ammoniacal solution before and after zeolite adsorption, mg/L, respectively; V_w is the volume of the ammoniacal solution, L; AN_a is the NH_4^+-N concentration in HCl solution for the determination of residual NH_4^+-N after regeneration, mg/L; V_a is the volume of HCl solution, L. The nitrogen removal efficiency (NRE) after zeolite adsorption-regeneration process is calculated as

$$NRE = \left[1 - \frac{V_a AN_a + V_r TN_r}{V_w (AN_i - AN_e)}\right] \times 100\% \tag{2}$$

Where, TN_r is the TN in the regenerant solution after regeneration, mg/L; V_a is the volume of regenerant solution, L. The difference between NRE and ZRE is the ratio of NH_4^+ converted to NO_3^- in the regeneration process.

2.2.3. Optimization for zeolite regeneration by NaClO-NaCl solution

The experiments were operated to determine effects of ClO^-/N, NaCl concentration and pH on ZRE and NRE in the process of zeolite adsorption combined with NaClO-NaCl regeneration. The single factor tests with different levels of ClO^-/N, NaCl concentration and pH were performed in advance to ascertain the appropriate range of the factors. Then RSM with Box-Behnken design was used to optimize the effective parameters for NaClO-NaCl regeneration. The experiments were designed against a three-level three factorial trial, which required a total of 17 tests. ClO^-/N (1.8–3.0), NaCl concentration (0–20 g/L) and pH (4–10) were selected as the three factors, and ZRE and NRE were selected as the response variable. In all the regeneration experiments, zeolites were immersed in