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Ammonia nitrogen removal from aqueous solution using functionalized zeolite columns

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ABSTRACT

In this study, a functionalized zeolites column was developed to remove ammonia nitrogen with a low concentration (50 mg/L) from aqueous solution. The absorption properties and regeneration capacity were investigated. Through breakthrough and elution curve for dynamic adsorption, we found the wastewater with 50 mg/L ammonia nitrogen took 7 h to flow 10 g modified zeolites column with diameters of 24 to 64 meshes at a flow rate of 2 mL/min. The saturated extent of adsorption was up to 7.95 mg/g, and the saturated adsorption time was 22 h. The process of dynamic adsorption could be fitted by the Thomas Model. The regeneration ability was optimized by 0.1 M Na_2CO_3 as a regenerant. With excellent absorption ability for removing ammonia nitrogen with a low concentration, the functionalized zeolites could be potentially used a high-performance adsorbent for removing ammonia nitrogen.

Keywords: Functionalized zeolites; Ammonia/nitrogen; Dynamic adsorption; Thomas model; Recycling

1. Introduction

Water eutrophication is a worldwide environmental issue in recent years, and can cause serious harm to human health, ecological system, and water [1,2]. The major nutrient elements on water eutrophication are nitrogen and phosphorus. Bio-treatments have been one of the major technologies in the field of wastewater [3–6]. It is a challenge to ensure that the total nitrogen and ammonia nitrogen can keep stable and reach discharge standard by the wastewater nitrogen removal process. Adsorption method has received considerable attention in the physicochemical treatment of wastewater due to their advantages such as efficiency, simple and robust process. The key to adsorption method is to choose cheap and high-performance adsorbents [7–9]. Zeolites are abundant nonmetallic minerals with a

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low-cost, high surface area, and profound adsorption capability, which can be a excellent candidate in the removal of ammonia nitrogen, organic compound, turbidity, heavy metal and oxyanion from water [9–14]. Compared with static adsorption, the dynamic adsorption will better approach in water treatments. Even dynamic adsorption on the removal of fluorine, methylene blue by using zeolites has been reported recently [15,16], and there are few reports on the dynamic adsorption of ammonia nitrogen.

In this study, dynamic adsorption for ammonia nitrogen from aqueous solution by functionalized zeolites column was investigated. We found that functionalized zeolites were excellent adsorbents for the removal of ammonia ions from aqueous solution. The experimental results of dynamic adsorption could be analyzed by Thomas model, and also large adsorption capacity can be obtained through regeneration of the saturated zeolite columns. This study provides a new method for the development of cheap, renewable, and cycle using in the ammonia wastewater treatment.

2. Experimental sections

2.1. Synthesis of functionalized adsorbents

Natural zeolites of Clinoptilolite (Wenshan, Yunnan province, China) with a particle size of 0.25 mm to 0.70 mm was used as adsorbent. It was baked in DL402 electric blast oven (Tianjin Experiment Instrument Factory, China) at 110 °C for 2 h. According to solid/liquid ratio of 1:2 (zeolites weight to volume of sodium chloride, g:mL), then put into 0.1 M sodium chloride solution and finally stirred in a constant temperature digital display waterbath Pot (HH-2, Jiangsu province) at 90 °C for 3 h. And then it was collected by vacuum filtration. It was washed to remove chloride ions and dried at 110 °C for 3 h.

2.2. Analytical methods

The concentration of ammonia concentration in the aqueous solution was determined by a spectrophotometer (UNICO 7200 type, Shanghai) using the method of Nessler's Reagent Spectrophotometry (GB7479–87) [17].

2.3. Dynamic adsorption experiments

Modified zeolites (10 g) were packed into the glass column with an inner diameter of 12 mm and a height of 250 mm. Ammonia nitrogen (50 mg/L) passed through the glass column from top to down until the adsorbent in column was saturated. The dynamic adsorption experiments were conducted at a flow rate of 2 mL/min at a room temperature. The concentration of outlet was measured each hour until it began to remain unchanged. Subsequently, the saturation column was eluted by 1.0 M sodium carbonate. The weight ratio of sodium chloride to sodium hydroxide is 3:7 (g:g).

2.4. Data analysis by dynamic adsorption

The formula of dynamic adsorption capacity is as follows [18]:

$$q_t = \frac{10^{-3}V\int_0^t (C_0 - C_t)\mathrm{d}t}{X} = \frac{10^{-3}V(C_0 t - \int_0^t C_t \mathrm{d}t)}{X} \quad (1)$$

where q_t is adsorption capacity of the column (mg/g), X is the amount of sorbent in the adsorbent column (g). C_0 is initial concentration of ammonium ion and C_t is effluent concentration of ammonium ion, respectively (M). V is outflow rate (mL/min), and t is adsorption time (min), respectively. Breakthrough curve is obtained by C_t versus time. $(\int_0^t C_t \mathrm{d}t)$ is an integral area below the adsorption curve that can be calculated numerical integration by origin 8.5 software.

Thomas model is one of the most widely used as analytical method in the column performance [19], which can be used to determine the adsorption capacity and adsorption rate constant. Thomas model is applied to fit the dynamic adsorption data. The following equation is the mathematical expression of Thomas model:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp(\frac{K_{Th} q_0 X}{V} - 10^{-3} K_{Th} C_0 t)} \quad (2)$$

where K_{Th} is Thomas constant (L/(mg min)), q_0 stands for equilibrium adsorption after fitting Thomas model (mg/g).

Thomas model of linear equation is as follows:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{Th} q_0 X}{V} - 10^{-3} K_{Th} C_0 t \quad (3)$$

A straight line is obtained by $\ln\left(\frac{C_0}{C_t} - 1\right)$ vs. t. Parameters of Thomas model (K_{Th}, q_0) can be calculated from the straight line of slope and intercept.

3. Results and discussion

3.1. Characterization of adsorbents

The structure was analyzed by a scanning electron microscopy (XL30ESEM-TMP, Philips-FEI, Holland) and X-ray Diffraction (XRD) (D/max-3b, Rigaku Corporation Japan). Fig. 1 shows SEM images of original zeolites and modified zeolites. The differences between crystal size and shape were also shown in the figure. The shape of the functionalized zeolites changed from rough cylinder shape to much smaller one. This change increased the specific surface area and provided more capacity space. As shown in Fig. 1 (b), chemical modification mainly processed on the surface of zeolites. The structure of interspaces had been improved. The appearance characteristic of the modified zeolite's surface was important to improve the adsorption capacity of ammonia nitrogen.

XRD was used for analyzing the sample's composition. In Fig. 2(a), compared with standard spectrogram (PDF2-2004), the natural zeolites diffraction peaks mainly consist of clinoptilolite (2 θ=9.81°, 11.14°, 12.98°, 22.34°, 23.5°, 26.82°, 29.92°, 32.76°). As shown in Fig. 2(a) and (b), the mainly peaks were unchanged, but a few impurity peaks of modified zeolites were disappeared or weakened. The diffraction peak of natural zeolites was much stronger than that of the modified zeolites in 2-theta 2°–2.9°, 8.08–8.58°. It displays that the impurities of natural zeolites had been removed by the modified treatment. The diffraction peaks of modified zeolites were significantly higher than those of natural zeolites at 2 θ = 8.86 and 26.62. As shown in Fig. 2, the mainly peaks were unchanged, but a few impurity peaks of functionalized zeolites disappeared or weakened. The results indicated that the functionalization process did not affect the structure of zeolites, but concentration of adsorption sites was increased, which could improve the adsorption capacity of functionalized zeolites [20].

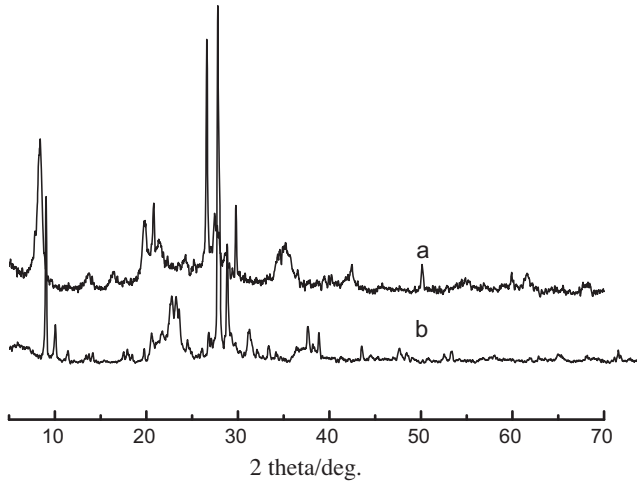

Fig. 2. XRD spectra of natural zeolites (a) and modified zeolites (b).

3.2. Dynamic adsorption analysis

The breakthrough curve is plotted versus time in Fig. 3 through normalized concentration as measured concentration, which showed ammonia nitrogen in the solution was removed by functionalized zeolites, which were immobilized in columns. The S shape and the appearance of the breakthrough point described a typical behavior of modified zeolites inside fixed bed column systems. With the adsorption sites of zeolites constantly to be covered by ammonium ion, the saturated zone was enlarged constantly and the adsorption zone decreased gradually at the same time [21]. The breakthrough point is a parameter that can be measured for adsorption property of the column. The effluent concentration took a value of 0.1 times of initial concentration as the breakthrough point [22]. At the breakthrough point, the breakthrough time of the adsorption column was 7 h. Meanwhile, the effluent volume and concentration were 885 mL and 6.92 mg/L, respectively. The saturated time was

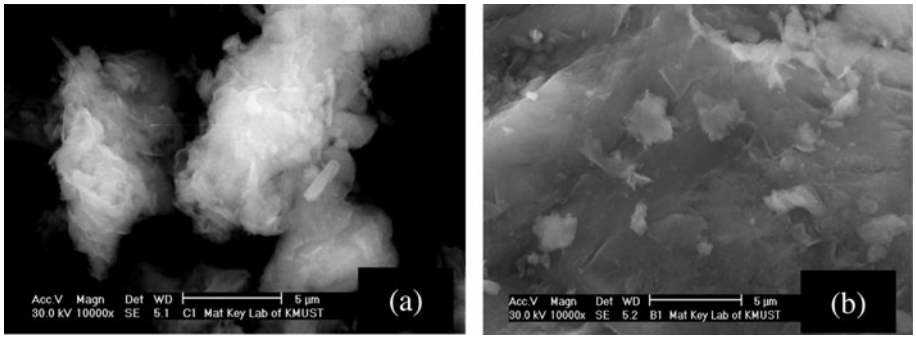

Fig. 1. SEM images of natural zeolites (a) and modified zeolites (b).

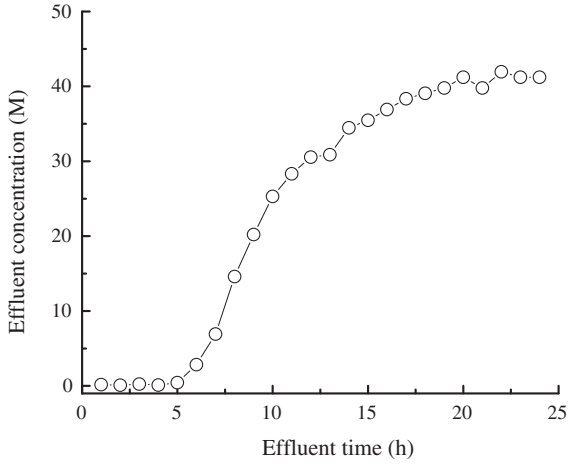

Fig. 3. Breakthrough curve of modified zeolites column on ammonia-nitrogen ($C_0 = 50$ mg/L, $V = 2$ mL/min).

around 22 h. All of them showed good adsorption performance for ammonia ions removal from aqueous solution by functionalized zeolites. Consequently, the zeolites could be used as a practical adsorbent material in treatment of wastewater [23,24].

3.3. Regeneration cycling

The saturation adsorbent was selected from the column and then regenerated by the variety of sodium salts in the beaker. Fig. 4 shows that the regeneration of sodium carbonate was better than mixture of sodium chloride and sodium hydroxide. The regeneration effect was depended on the concentration of sodium ion exchanged in adsorption sites.

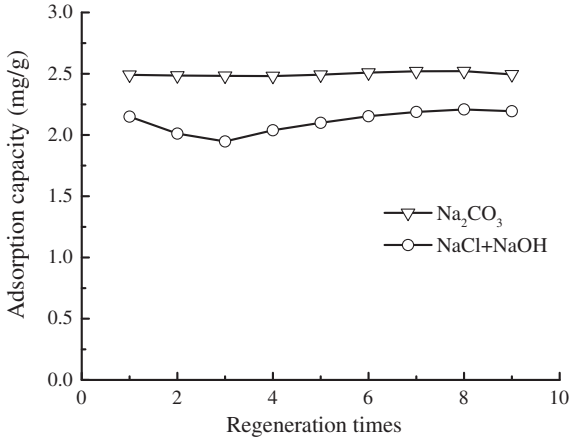

Fig. 4. Effect of regeneration capacity for the saturated zeolites.

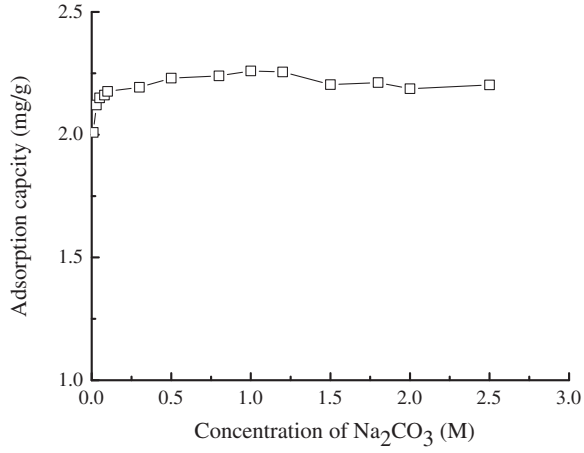

Fig. 5. Effect of Na_2CO_3 concentration on regeneration capacity for the saturated zeolites.

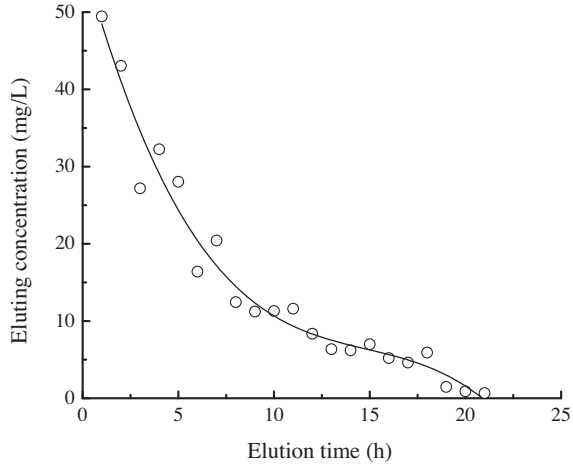

Fig. 6. Elution curve for saturated zeolites column (regenerants: 0.1 M Na_2CO_3, $v = 1$ mL/min).

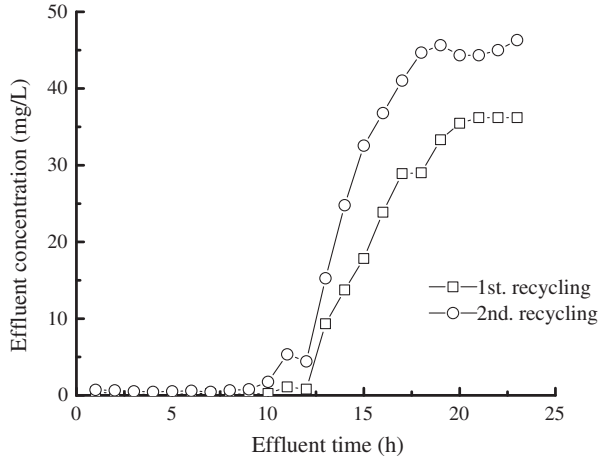

Fig. 7. Recycling times of modified zeolites columns.

Table 1
Dynamic adsorption and dynamic adsorption model fitting parameters

Adsorption times	C_0 (mg/L)	V (mL/min)	Saturated time (min)	q_t (mg/g)	K_{Th} (mL/(min mg))	q_0 (mg/g)	R
1	50.00	2	1,320	7.95	0.118	8.97	0.9038
2	49.64	2	1,290	10.67	0.129	11.48	0.9327
3	51.28	2	1,290	10.21	0.121	10.59	0.9488

Fig. 5 shows the effect of Na_2CO_3 concentration on regenerating capacity for saturating zeolites. The regenerative capacity of zeolites column was improved with increasing the concentration of sodium carbonate. When the concentration of sodium carbonate was 0.1 M, the adsorption capacity of regeneration reached 2.176 mg/g which closed to the optimal adsorption capacity 2.256 mg/g. Therefore, low concentration of regenerants was enough to exchange more ammonium ions, and 0.1 M sodium carbonate was optimized as the best regeneration agent based on the cost, time, and effect of regeneration.

About 0.1 M sodium carbonate solution was continually injected into saturation adsorbent column at a rate of 1 mL min^{-1}. The eluting process of the adsorption column was completed when outflow concentration reached the lowest point or a constant value. Fig. 6 is the elution curve for saturating zeolites column. The eluting at the beginning was faster than late stage because ammonia on the surfaces of zeolites was mainly eluted when it started. With the increase of elution time, ammonia nitrogen of internal active sites was eluted. Based on the regeneration and efficiency of column, 20 h was optimized as adsorption column elution time.

In order to study regeneration performance of adsorption columns, dynamic adsorption of 0.1 M sodium carbonate solution was investigated. Fig. 7 shows the breakthrough points remained 21.5 h with two cycles closed to one cycle. Regeneration column still kept excellent adsorption performance. The adsorption capacities are 10.67 and 10.21 mg/g, respectively, at breakthrough points by two cycles. Functionalized zeolites were regenerated by increasing active sites in zeolites structures. Therefore, the adsorption performance can be improved by regeneration. Regeneration did not destroy the structure of zeolites as shown in Fig. 7, which demonstrates good recycling capacity from the adsorbent column.

3.4. Dynamic adsorption isotherm

Thomas model was used to fit the ammonia/nitrogen dynamic adsorption on zeolites column. The Thomas rate constant (K_{Th}) and maximum adsorption quantities (q_0) were calculated by Eq. (3) of linear regression, and the results are shown in Table 1. In addition, q_t was actual maximum column capacity obtained from Eq. (1). The correlation coefficient R was ranging from 0.9038 to 0.9488 which indicated that dynamic adsorption processes were suitable for Thomas dynamic model. The adsorption capacity of zeolites adsorption column was in accordance with the experimental data, so it could be used for predicting adsorption of ammonia ions in aqueous solution. With regeneration, the column capacity was up to 10.67 mg/g. On increasing regeneration time, the values of q_t and k_{Th} decreased slowly. Han et al. [25] obtained maximum adsorption quantities (q_0) with 4.47 mg/g at initial concentration of methylene blue. So, the functionalized zeolite column showed a stronger adsorption capacity than pre-functionalized zeolite column. It can be reused with low cost.

4. Conclusions

In this paper, we demonstrated the dynamic adsorption of modified zeolites was an excellent adsorbent for the removal of ammonia ions from aqueous solution. The zeolites column could prolong its service life when 0.1 M sodium carbonate solution was chosen as regeneration agent. The process of dynamic adsorption could be fitted by Thomas Model which further indicated the modified zeolites is an excellent adsorbent for the removal of ammonia ions from aqueous solution.

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