Ammonium removal by modified zeolite from municipal wastewater

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Abstract: Ammonium removal by modified zeolite, H-form and Na-form zeolite, were examined by batch-type methods. The adsorption of ammonium on modified zeolite was exothermic process. The saturation adsorption capacity of ammonium on H-form and Na-form zeolite were 21.23 and 41.15 mg/g, respectively. After ten times adsorption-desorption-readsorption cycles the standard deviations of H-form and Na-form zeolite were 6.34% and 6.59%. The zeolite adsorption process has proved cost effective and practical in reducing ammonium by H-form and Na-form zeolite in municipal wastewater from concentration 27.68 mg/L to 2.80 mg/L and 5.91 mg/L.

Keywords: ammonium; modified zeolite; regeneration; municipal wastewater

Introduction

Ammonium produced from agriculture, industry and municipal wastewater mixed into aquatic environment, especially drinking water. The excessive ammonium in receiving water body caused very harmful ecological effects. Concentration of ammonium(about 5 mg/L) in surface water is very toxic for some species of fish(Breck, 1973). These water systems are restricted for human uses, for example, if the water to be used as human drinking water, a costly and difficult treatment process is necessary. Even in this situation, however, the water may remain undesirable (because of taste, odors, and color ration and increased bacteria accumulation). The maximum limit set by the European Association for Drinking Water is 0.5 mg/L (AWWA, 1990). Therefore, raw water containing high concentration ammonium must be treated before reaching the receiving water body. Ammonium removal from wastewater can be achieved by biological nitrification-denitrification, air stripping, and selective ion exchange process. Traditionally, biological systems have provided an economical solution, with the retrofitting of biological ammonium removal facilities to existing organic treatment systems. Whilst often effective, these systems often require large land areas, due to the slowness of biological conversion of ammonium, thus imposing high capital cost. Air stripping at high pH is technically achievable but, given the low concentrations of the ammonium in sewage(bellow 100 mg/L), is economically prohibitive. Selective ion exchange processes is an alternative process for its stable and easy maintenance nature. Zeolite have some capacity and selectivity for removing ammonium (Ames, 1960). The extent of which was dependent on a number of factors(Flood, 1993; Dimova, 1999), such as particle sizes, surface areas, charge and structural characteristics of certain ions, and interference ions. Due to the possibility of reusing the regeneration liquid, the running cost for using zeolite in a municipal wastewater treatment plant would be minor(Booker, 1996).

Recent investigations have focused on zeolite performance within special design and condition of treatment facilities. The idea for the utilization of a combined filter, filled with zeolite and biological activated material with a nitrifying biofilm, had been proposed by a team of German scientists and examined for wastewater. The facility operates in two stages: ion exchange into the zeolite volume; natural desorption of zeolite and biological nitrification(Oldenburg, 1995). Baykal and Guven(Bavkal, 1997) who conducted the experiments to examine the removal of ammonium in domestic wastewater using clinoptilolite only and in sand filters. Columns were set up containing zeolite only, zeolite with sand layers and an aerator. Results revealed that clinoptilolite has comparable ability to take up ammonium regardless of the presence of other filter media or biological activity in its surroundings. Furthermore, Lahav and Green (Lahav, 1998) proposed the process for ammonium removal from secondary effluent by zeolite followed by bioregeneration. The entire process was carried out in a single reactor. The results showed that biological activity actually improve the ammonium removal performance of zeolite. The chemical processes of ammonium removal by modified zeolite will inevitably be accompanied by microbiological activity. This biological activity becomes increasing advantageous to the ion exchange process as time pass due to the behavior of certain bacteria which promote nitrification, followed by denitrification. This assists in renewing the capacity of the zeolite for further ammonium removal(Tsuno, 1994).

A number of processes for the removal of ammonia from wastewater has been explored. This study aimed to realize the value of this natural resource as an efficient alternative to existing treatment process and to determine the most cost effective way that zeolite used with the most critical part being regeneration of it.

1 Materials and methods

1.1 Reagent

All chemicals were of analytical grade. Ammonium chloride was prepared into 1000 mg/L stock solution stored in

polyethylene bottle at 0℃. Deionized water was used throughout the experiments. The zeolite sample used in the experiment was collected from Wuhu, Anhui Province, China. The sample was sieved 200 mesh.

1.2 Ammonium removal

Ammonium removal was carried out with two different form treated zeolite:

Sample 1: natural zeolite was treated with 10% HCl at 25℃ over a period of 24 h. After washing, H-formed zeolite was dried at 105℃ for 2 h.

Sample 2: natural zeolite was treated with 2 mol/L NaCl at 25℃ over a period of 24 h. After washing, Na-formed zeolite was dried at 105℃ for 2 h.

1.3 Batch adsorption experiments

Ion exchange process was carried by using the batch methods. A constant amount of modified zeolite sample(5 g) was mixed with 100 ml ammonium solution of concentration ranging from 10, 30, 50, 100, 500, 5000 to 10000 mg/L. The suspension was shaken for 24 h at 25℃. The suspension was filtered with 0.25 μm membrane and analyzed the ammonium by using spectrophotometer(State Environmental Protection Administration of China, 1997). In the second set of experiment was investigated the influence of temperature change on the uptake of ammonium. 5 g modified zeolite sample was mixed with 100 ml ammonium solution of concentration 100 mg/L. The suspension was shaken for 24 h at 25℃, 45℃ and 65℃, respectively. The suspension was filtered with 0.25 μm membrane and analyzed the ammonium.

1.4 Regeneration

A consideration of practical interest with regard to the application of a new exchanger is its regeneration ability. 5 g H-form or Na-form zeolite exhausted with ammonium was mixed with 100 ml of 10% HCl or 2 mol/L NaCl solution. The suspension was shaken for 24 h at 25℃ then washed with deionized water. After each regeneration cycle, adsorption capacity of the regeneration modified zeolite for ammonium was measured. Ten times adsorption-desorption-readsorption cycles was tested.

1.5 Municipal wastewater treatment

The municipal wastewater was fetched from Quyang Wastewater Treatment Plant, Shanghai, China on September 19th, 2003. The average characteristics of the wastewater during this work were: COD_{Cr} 217.71 mg/L, pH 7.7, ammonium 27.68 mg/L. 5 g H-form or Na-form zeolite was mixed with 100 ml municipal wastewater. The suspension was shaken for 24 h at 25℃ then filtered with 0.25 μm membrane and analyzed COD_{Cr}, pH and the ammonium concentration.

2 Results and discussion

2.1 Characterization of zeolite sample

The chemical analysis of the zeolite is listed in Table 1. Since the sample is rich in Na it was identified as Na zeolite. IR (Fig. 1) showed the constituent of the zeolite was clinoptilolite and mordenite. SEM micrographs gave the

particle size between 10 to 100 μm(Fig.2). The sample has the following properties: cation exchange capacity 130—140 meq/100g; apparent density 1.172 g/ml; suspension pH 9.6—9.8.

Table 1 Chemical analysis of the zeolite sample

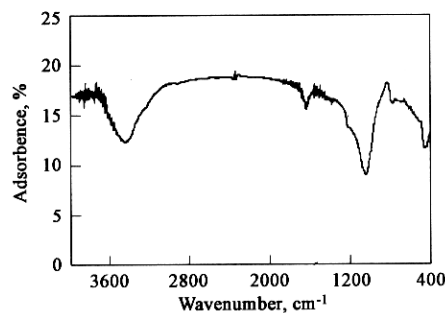| Constituent	Weight, %	Constituent	Weight, %
SiO_2	66.61	TiO_2	0.10
CaO	1.06	P_2O_5	0.44
K_2O	1.73	Fe_2O_3	0.87
SO_3	0.21	Na_2O	4.78
Al_2O_3	13.81	MgO	1.18
MnO_2	0.20	LOI	9.00

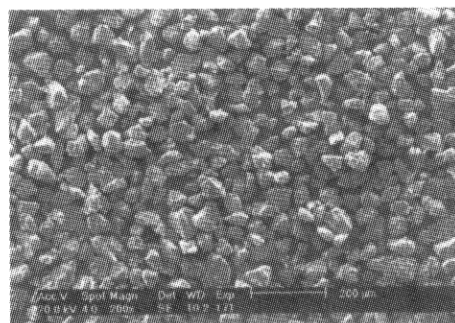Fig.1   IR of zeolite sample

Fig.2   SEM of zeolite sample

2.2 Equilibrium studies

It was clear that ammonium removal efficiencies for H-form zeolite were of about 87.44% to 98.29% and for Na-form zeolite were of about 84.44% to 87.20% at the ammonium concentration less than 100 mg/L. At higher ammonium concentration ranging from 500—10000 mg/L the ammonium removal efficiencies for H-form zeolite decreased from 61.50% to 10.36%, and for Na-form zeolite decreased from 68.33% to 20%. The removal efficiency values indicated that sorption was more favorable for the higher initial ammonium concentration than for the lower ones.

The analysis of isotherm data is important to develop an equation which provided insight into its expected capacity as adsorption media and could be used for design purpose. In order to investigate the sorption isotherm, the Langmuir and Freundlich equation were analyzed.

The Langmuir isotherm is often used to describe sorption of a solute from a liquid solution as

$$\frac{c_e}{q_e} = \frac{1}{q_m \times k_a} + \frac{c_e}{q_m}. \qquad (1)$$

Where c_e and q_e are the equilibrium concentration and

sorption capacity; q_m and k_a are the Langmuir constants and can be obtained from slope and intercept of the plot c_e/q_e vs c_e.

The Freundlich isotherm can be used for heterogeneous sorption, as

$$\log(q_e) = \frac{1}{n}\log(c_e) + \log(k_F). \qquad (2)$$

Where n and k_F are the empirical constants depend on several environmental factors. The parameters of isotherm and experimental data are shown in Table 2 and Fig.3. It was clear that the Langmuir and Freundlich both had best fitted with the sorption of ammonium on the modified zeolite samples. The H-form and Na-form zeolite also had higher saturation adsorption capacity, 21.23 and 41.15 mg/g, respectively. Bolan and Mowatt(Bolan, 2000) found similar evidence that clinoptilolite had a large capacity for ammonium removal, with ammonium retention ranging from 1.63 to 13.05 mg/g. They noted that the removal rates gradually decreased as the amount of effluent input increased. Nguyen and Tanner (Nguyen, 1998) calculated the theoretical saturation capacity of clinoptilolie to be around 15 mg/g of zeolite. It showed that increased capacity could be achieved by converting the ion-exchange sites within the zeolite to the Na-or H-form.
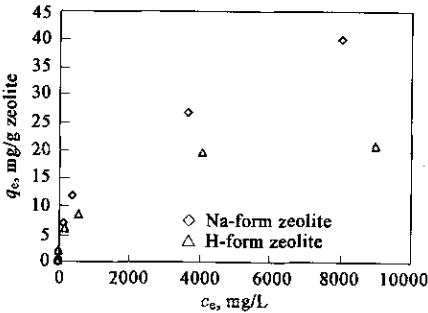

Fig.3   Equilibrium study of modified zeolite

Table 2   Parameters and correlate coefficients of Langmuir and Freundlich

Langmuir	q_m, mg/g	K_a, L/g	R^2
H-form zeolite	21.23	3.49	0.992
Na-form zeolite	41.15	1.29	0.962
Freundlich	n	K_F	R^2
H-form zeolite	2.5	0.72	0.952
Na-form zeolite	1.8	0.33	0.981

2.3 Thermodynamic studies

The effects of the temperature on the ammonium adsorption on the H-form and Na-form zeolite indicated that the adsorption capacity of modified zeolite decreased with the temperature. This phenomenon maybe caused by increasing ammonium desorption from the adsorption sites with temperature.

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what process will occur spontaneously. The free energy of the sorption reaction is given by Arrineus equation

$$\Delta G = - RT\ln K_d. \qquad (3)$$

Where ΔG is the Gibbs free energy change, J/mol; R is the universal gas constant, 8.314 J/(mol·K); T is the

absolute temperature, K; K_d is separation factor q_e/c_e, ml/g.

The Gibbs free energy change can also be represented as

$$\Delta G = \Delta H - T\Delta S. \qquad (4)$$

Substituting Eq.(3) into Eq.(4), the Gibbs free energy change can be represented as follows:

$$\ln K_d = - \frac{\Delta H}{RT} + \frac{\Delta S}{R}. \qquad (5)$$

The plot of $\log K_d$ vs $1/T$ was found to be linear in Fig. 4. The values of ΔH and ΔS were determined from the slope and intercept of the plots. Thermodynamics parameters are listed in Table 3. The negative value of ΔG confirmed that the feasibility of the process and spontaneous nature of sorption with a high preference of ammonium on modified zeolite. The value of ΔH is negative, indicating that the sorption reaction is exothermic. The negative value of ΔS suggested some structural changes of the modified zeolite for ammonium. In addition, negative value of ΔS showed the decreasing randomness at the solid/liquid interface during the sorption of ammonium on modified zeolite.
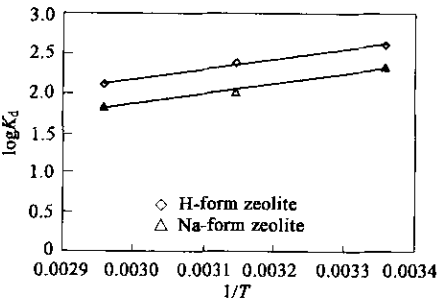

Fig.4   The plot of $\log K_d$ vs $1/T$ of modified zeolite

Table 3   Parameters of thermodynamics of modified zeolite for ammonium

Modified zeolite	T, ℃	ΔH, kJ/(mol·K)	ΔS, J/(mol·K)	ΔG, kJ/mol
H-form	25			- 6.5033
	45	- 10.5455	- 13.5643	- 6.2320
	65			- 5.9608
Na-form	25			- 5.7418
	45	- 10.4366	- 15.7542	- 5.4268
	65			- 5.1117

2.4 Regeneration

A good adsorbent, in addition to its high adsorption capacity, must also exhibit a good regeneration ability for multiple uses. Therefore, the regenerability of modified zeolite must be tested by a series of systematic experiments. The regeneration processes are shown in Table 4 and Fig.5. The results showed that the ammonium was held by the modified zeolite and was not released by flushing with distilled water. For regeneration to occur, the ammonium saturated zeolite must be flushed with a chemical solution containing a high concentration of cations, such as HCl, NaCl, to increase the life span of the zeolite. After ten times adsorption-desorption-readsorption cycles the standard deviations of H-form and Na-form zeolite were 6.34% and 6.59%, respectively. The results showed that the modified zeolite can be regenerated once it approached its saturation capacity, allowing it to be used over a relatively long period of time. Baykal and Guven (Baykal, 1997) found that

clinoptilolite lost only 10% of its total cation exchange capacity after being regenerated 10 times. Bolan and Mowatt (Bolan, 2000) suggested even greater performance when regenerated with HCl. Their research showed that even after 12 times regenerations, the ammonium retention capacity of the clinoptilolite remained the same as that of the original samples.
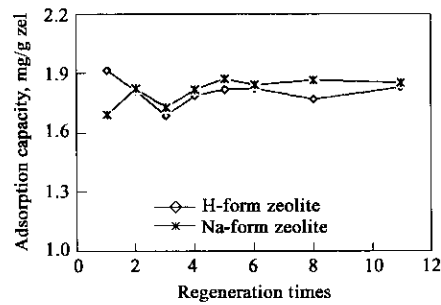

Fig. 5   Relation between repetition times of regeneration and adsorption capacity of modified zeolite

Table 4   The regeneration of the modified zeolite

Regeneration liquid	Modified zeolite	Adsorption capacity, mg/g zeolite								Standard deviation
		1	2	3	4	5	6	8	11	
10% HCl	H-form	1.91	1.81	1.68	1.78	1.82	1.82	1.76	1.83	0.0634
2 mol/L NaCl	Na-form	1.69	1.82	1.72	1.81	1.87	1.84	1.86	1.85	0.0659

2.5   Municipal wastewater treatment

The modified H-form and Na-form zeolite were aim to treat municipal wastewater containing ammonium. After treatment by H-form and Na-form zeolite the ammonium concentration in wastewater decreased from 27.68 mg/L to 2.80 mg/L and 5.91 mg/L (Table 5), separately, far bellowing 15 mg/L(Integrated wastewater discharge standard of China, GB8978-1996). Ammonium removal efficiencies by H-form and Na-form zeolite were 89.88% and 78.65%. Other indexes of effluent also measured up to the GB8978-1996. It showed that modified zeolite was a practical and cost effective adsorbent for ammonium removal from municipal wastewater.

Table 5   Effluent indexes of wastewater treatment by modified zeolite

Modified zeolite	Equilibrium concentration of ammonium, mg/L	Ammonium removal, %	pH	COD_{Cr}, mg/L
H-form	2.80	89.88	7.1	46.32
Na-form	5.91	78.65	7.7	51.54

3   Cost evaluations

If the ammonium concentration in municipal wastewater is 30 mg/L, according to GB8978-1996, the effluent ammonium must below 15 mg/L. 15 g ammonium had to be removed as 1 ton wastewater to be treated. When it came to Na-form zeolite, the saturation adsorption capacity 41.15 mg/g(Table 2), thus 0.364 kg Na-form zeolite is needed to treat 1 ton wastewater in theory.

If 1 ton zeolite costs 200 RMB Yuan, then treatment of 1 ton wastewater will need about 0.072 RMB Yuan in theory. In practice the cost probably slightly higher than that of theory because of other factors.

4   Conclusions

The applied methodology was simple and results showed that the successful performance of the modified H-form and Na-form zeolite can strongly reduce the polluting potential of municipal wastewater with a reduction of ammonium concentration from 27.68 mg/L to 2.80 mg/L and 5.91 mg/L, respectively. Modified zeolite can compete with other adsorbent not only for the efficiency and the low cost but also for the regenerability and possible reuse of final products as fertilizer(Cintoli, 1995).

The chemical processes of ammonium removal by modified zeolite will inevitably be accompanied by microbiological activity. This biological activity becomes increasing advantageous to the ion exchange process as time pass due to the behavior of certain bacteria which promote nitrification, followed by denitrification. This assists in renewing the capacity of the zeolite for further ammonium removal. The function of microorganism, i. e., the nitrification-denitrification on zeolite will be investigated in later works.

Based on the batch experiments results we aim at investigating performance and biological regeneration effect of modified zeolite within a novel and practical minitype process unit, so as to form a complete wastewater treatment process and technological facilities in later works of this research.

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