

REMOVAL OF AMMONIUM ION FROM AQUEOUS SOLUTIONS USING A DOMESTIC NATURAL ZEOLITE

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Abstract : A domestic natural zeolite was pretreated with hydrogen chloride, sodium hydroxide, and sodium chloride to improve the adsorption capacities of ammonium ion from an aqueous solutions. The pretreated natural zeolite was characterized by X-ray diffraction (XRD) and BET experiments. From experimental data, it was shown that the pretreatment with sodium chloride provided the highest capacity for the removal of ammonium ion. Adsorption equilibrium data were correlated with Langmuir, Freundlich, and Sips isotherms. Adsorption and desorption dynamics were investigated in a fixed-bed charged with natural zeolite, that had been pretreated with sodium chloride. A simple dynamic model was formulated in order to describe adsorption breakthrough curves of ammonium ion.

Key Words : adsorption isotherm, ammonium ion, domestic natural zeolite, dynamic model, pretreatment

INTRODUCTION

The municipal, industrial, and population landscape of Korea has experienced significant changes in the past 30 years. The rapidity with which these changes have taken place has created some unexpected negative consequence, particularly increased contamination of livestock wastewater. Livestock wastewater is an organic wastewater containing high concentration of organic matter and nutrients. Without proper treatment, the wastewater of a concentrated livestock farming site is much more polluted with the contamination of ecosystem such as water pollution, soil pollution, and eutrophication in lake or river. Consequently, effective technical methods for the treatment of livestock wastewater are required.¹⁻³⁾

Currently, methods for treatment of livestock waste are classified into two groups, physical and chemical. The most widely used methods include: pretreatment of suspended solids, adsorption by activated carbon, membrane process with solid-liquid separation, and biological treatment.^{4,5)} However, it is the adsorption-based process using activated carbon that is the most commonly used method. But, from both a recyclable and chemical perspective, natural zeolite, when compared to an established process using activated carbon, is an excellent alternative because of its high sorption capacity, special selectivity, good temperature stability, and strong radiation resistance. But a distinction must be made between natural and synthetic zeolite properties. Natural zeolite has an inconsistent composition ratio and irregular pore size, when compared with synthetic zeolite. There has been some important research conducted on the use of natural zeolite for removing heavy metals, radio-

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active metals and ammonium ion from aqueous solutions, including pretreatment methods of natural zeolite. Recently, Lee used natural zeolite to remove heavy metals such as lead, copper, and cadmium.⁶⁾ Rho et al. reported the effects of temperature, pH, and cations on the removal of ammonium ion using natural zeolite.⁷⁾

Adsorption-based processes have usually been performed in a fixed bed through a cyclic operation.⁸⁾ Each cycle involves three main steps; adsorption, desorption, and washing. When and how the breakthrough curves is an important task for the designing, optimization, and scale-up of column adsorbers. Also, the shape and width of the breakthrough curve are crucial in the designing of adsorbers for a cyclic process. Therefore, a mathematical model is required for the simulation of the cyclic operation. The breakthrough curve generally depends on the adsorption isotherm and the transport mechanisms in sorbent particles, as well as in the operating conditions. In order to devise a method of removal for ammonium ion, it is essential to get information in advance, about the adsorption behavior of pure ammonium ion, in a column adsorber charged with natural zeolite.

The aim of this study is to find a pretreatment method with natural zeolite, and to develop a dynamic model to simulate the adsorption-based process. Three kinds of treatments with acidic, basic, and neutral solutions were performed to improve the removal efficiency of ammonium ion. A simple adsorption model was formulated by employing a surface diffusion model in a solid phase and a plug flow model in a fluid phase. Also, adsorption and desorption characteristics were investigated in a fixed-bed adsorber.

THEORETICAL APPROACH

Adsorption Equilibrium

The ion-exchange equilibrium is complex, making it difficult to find a simple and accurate ion-exchange isotherm. Considering that an ion-exchange process is reversible in terms of ionic concentration, one of the conventional adsorption

isotherms could reasonably be used in treating ion-exchange equilibrium data.⁹⁾ There are many kinds of isotherm equations for single-species adsorption systems, but for the purposes of this study, we employed the following three isotherm models: Langmuir, Freundlich, and Sips equation.

$$q = \frac{q_m C}{1 + K_L C} \quad (1)$$

$$q = K_F C^{1/n} \quad (2)$$

$$q = \frac{q_m C^{1/n}}{1 + K_S C^{1/n}} \quad (3)$$

where q is the adsorption amount in solid phase, C is the concentration in liquid phase, and q_m , K_L , K_F , K_S , and n are the isotherm parameters.

Adsorption Model in a Fixed-bed Adsorber

The assumptions made for the development of an adsorption model in a fixed-bed were as follows: (1) the system is isothermal, (2) the shape of NZ particles is spherical, (3) a column is homogeneously packed, (4) pore size distribution is homogeneous, (5) the radial concentration gradient is neglected, (6) the pore structure inside particles is uniform, (7) the fluid physical properties are constant, and (8) the flow pattern is a plug flow with a constant linear velocity along the column. The mass balance equation and the corresponding initial and boundary conditions for the bulk phase in the column are:

$$-D_L \frac{\partial^2 C}{\partial z^2} + \frac{\partial v C}{\partial z} + \frac{\partial C}{\partial t} + \frac{1 - \epsilon_b}{\epsilon_b} \frac{\partial q}{\partial t} = 0 \quad (4)$$

The mass balance equation for the solid phase with initial and boundary conditions is:

$$\frac{\partial q}{\partial t} = D_s \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) \quad (5)$$

where D_L is the axial dispersion coefficient, D_s is the surface diffusion coefficient, v is the

interstitial velocity, ε_b is the bed porosity, t is the time, and z and r are the axial and radial coordinates, respectively.

Numerical Solution

These coupled parabolic second-order partial differential equations can not be solved analytically. Therefore, numerical methods have been generally employed. In this study, partial differential equations were first described by an orthogonal collocation method, in order to form a set of first-order ordinary differential equations.^(10,11) The resulting set of ordinary differential equations was integrated by a subroutine, LSODE, of the International Mathematical and Statistical Library (IMSL).

EXPERIMENTAL

Pretreatment

The domestic natural zeolite was supplied by Han-Doo Co. (Korea). The mesh size was 16×30 (0.59~1.19 mm). The natural zeolite was pretreated with acid (HCl), base (NaOH), and salt (NaCl) solutions, respectively. Pretreatment procedures were as follows: (1) sieve and rinse of the natural zeolite with distilled and ultra-pure water, (2) dry in a vacuum oven at 105°C for 24 hr, (3) storage in a desiccator to be stabilized before pretreatment, (4) create solutions of 1 mol/L hydrogen chloride, sodium hydroxide, and sodium chloride, respectively, (5) pack 100 g of natural zeolite into the column, (6) flow working solutions for pretreatment at a rate of 5 mL/min through the packed column for 24 hr, (7) finally, rinse the treated natural zeolite with distilled and ultra-pure water for 12 hr then dry them in a vacuum oven at 105°C for 24 hr.⁽⁶⁾

Equilibrium and Batch Experiment

Equilibrium data were taken by introducing a given amount of sorbent into a ammonium chloride solution containing 200 mg/L. Equilibrium experiments were carried out at 25°C for 24 hr, using shaking apparatus. After equilibrium was

reached, the excess ammonium ion left in the solutions was analyzed by using UV (Shimadzu 160A, Japan) at 390 nm of wave length. The adsorption capacity of zeolite was determined from the material balance.

Batch experiments were conducted in a Carberry type-batch adsorber with four baffles. The agitation rod was equipped with a four-bladed impeller, 35 mm wide and 50 mm high. This rod was connected to a variable speed motor. The cage, a cross shape of a 50 mesh stainless steel wire screen, was attached around the impeller to sustain the zeolite particles. The vessel had a cooling water circulating jacket in a constant temperature bath to prevent vapor loss and the cover had a 20 mm diameter opening cap for sampling. A 16×30 mesh, granular-type, natural zeolite of 5 g was poured into the cage affixed to the shaft wings. The initial volume of ammonium solution was 2 L with 100 mg/L. All the experiments were carried out at approximately 310~315 rpm and 25°C .

Fixed-bed Experiment

As shown in Figure 1, the adsorption column was made of a glass pipe of 0.02 m inside di-

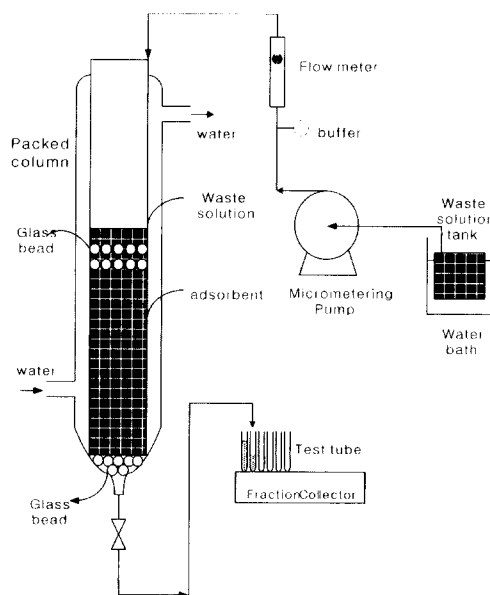


Figure 1. Schematic diagram of experimental fixed-bed system.

ameter and 0.155 m length. The column was lined with a water jacket to maintain the uniform column temperature. The flow was regulated at 9.8 mL/min by a precision FMI pump (model RHODKE). The solution was introduced downward into the column. To prevent channeling and to enhance distribution of the solution through the column, two layers of small glass beads were packed in the top and bottom region of the column. Various breakthrough experiments were carried out under the experimental conditions listed in Table 1. The samples were withdrawn from the effluent line and analyzed using a UV spectrophotometry.

Table 1. Experimental conditions for fixed-bed operation

Variables	Units	Values
Bed length	m	0.155
Bed diameter	m	0.02
Bed porosity	-	0.50
Particle porosity	-	0.37
Particle density	Kg/m ³	1,699
Packing density	Kg/m ³	847
Flow rate	m/sec	5.20×10^{-4}
Temperature	°C	25
Initial concentration of solution	mol/m ³	100

RESULTS AND DISCUSSION

Adsorbent Characterization

To determine the adsorption characteristics of zeolites, such as total pore volume, specific surface area, and pore size distribution, the BET (ASAP-2010, Micromeritics/USA) method was used for both the raw and pretreated samples. XRD analysis was also carried out to examine their structure and mineral type, using Cu K-alpha/30 kV/40 mA (D/MAS-1200, Rigaku/Japan).

As shown in Table 2, the specific surface area of zeolites was followed to the order of HCl-treated > NaCl-treated > untreated > NaOH-

Table 2. Physical properties of natural zeolites treated by different methods

Properties	Natural zeolite	NaCl-treated	NaOH-treated	HCl-treated
Surface area (m ² /g)	106	145	16	272
Total pore volume (cc/g)	0.10	0.12	0.07	0.20
Average pore diameter (Å)	36	31	170	30

treated zeolites. The total pore volume was in the order of HCl-treated, NaCl-treated, untreated, and NaOH-treated zeolites. The HCl-treated zeolite has the smallest average pore diameter among them due to partial breaking of the pore structure. Chemical compositions of the natural zeolite are shown in Table 3. The ratio of Si/Al is an important factor in the zeolite structure. When the ratio is over 4.0, the zeolite is a clinoptilolite-type. On the contrary, if the ratio is less than 4.0, the clinoptilolite-type zeolite would be somewhat shifted to a heulandite-type. The ratio of Si/Al for natural zeolite used in this study is about 4.67, which means that clinoptilolite and heulandite types are mixed together. Although the commonly occurring sedimentary mineral, clinoptilolite, is generally considered to be an isostructural variant of heulandite, there is no sufficient evidence for this conclusion.¹²⁾ Figure 2 shows the results of the XRD analysis for raw and pretreated natural zeolites. Even some minor changes are observed, there is no significant change in XRD peaks to identify the structural change before and after pretreatment.

Adsorption Equilibrium

Figure 3 shows the concentration decay curves of ammonium ion of 100 mg/L on various adsorbents in a batch adsorber in order to investigate adsorption capacity and equilibrium time. The adsorbed amounts on samples pretreated with

Table 3. Chemical compositions of natural zeolite used in this study

Components	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O(+)
Content(%)	66.5	14.7	1.67	1.26	1.80	1.92	3.25	0.04	8.04

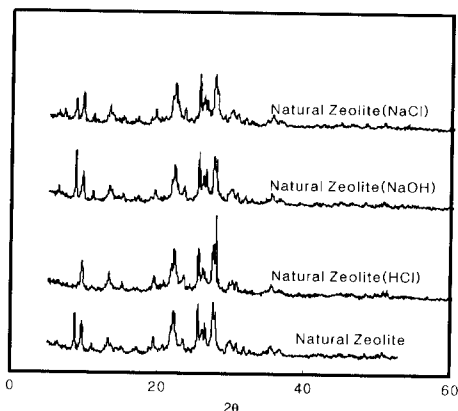


Figure 2. X-ray patterns of natural zeolites after pretreatment.

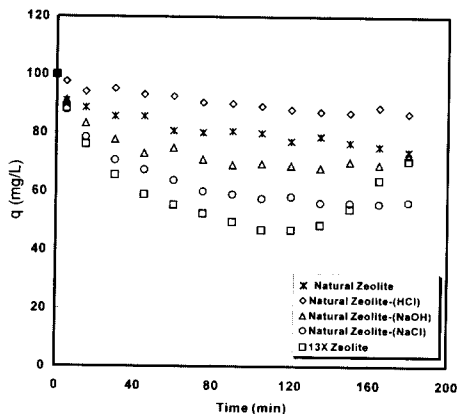


Figure 3. Concentration decay curves of ammonium ion on sorbents in a batch adsorber.

sodium chloride were much more than those on samples pretreated with hydrogen chloride and sodium hydroxide. According to BET adsorption data, the hydrogen chloride-treated natural zeolite has the largest surface area, but the adsorption amounts of ammonium ion are low. From this result, it can be concluded that the structure of the zeolite was partially collapsed by a strong acid, hydrogen chloride. Also, this result implies that the removal of ammonium ion by zeolites is not a physical adsorption, but a chemical adsorption, namely an ion-exchange process. In case of 13X zeolite, which is a kind of commercial molecular sieve adsorbents, namely X-type zeolite, and is composed of twelve-membered

rings with fairly large windows, the adsorbed amount was greater than zeolite treated with sodium chloride. However, the adsorption capacity was reduced from 120 min to 180 min, because of the breakage of 13X in an aqueous solution. Considering that natural zeolite is cheaper and more abundant than commercial zeolites, and that it can be easily modified by simple treatments, it is a promising medium for the removal of ammonium ion from aqueous solutions.

Experimental equilibrium data are important when judging the feasibility of the adsorption process for a given application. Moreover, the isotherm plays a crucial role in the predictive modeling procedure for the analysis and design of ammonium removal processes. Adsorption isotherm data of ammonium ion on zeolite treated with sodium chloride are shown in Figure 4. The experimental equilibrium data were correlated with the Langmuir, Freundlich equation with two parameters, and Sips equation with three parameters. The parameters of adsorption isotherms were determined by least squares methods with experiment data, and the results were listed in Table 4. The mean errors between experimental and calculated values were determined as follows:

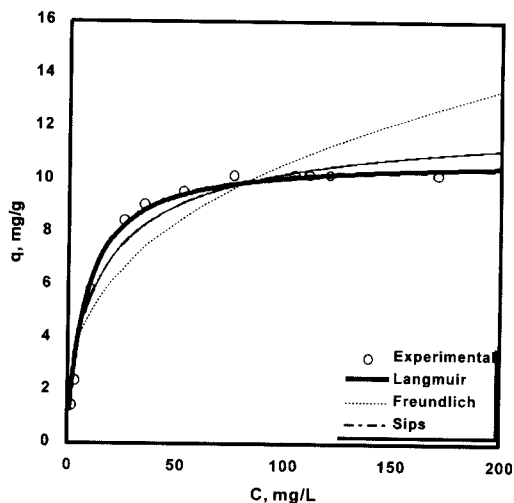


Figure 4. Adsorption isotherms of ammonium ion on natural zeolite treated with sodium chloride at 25°C.

Table 4. Isotherm parameters estimated for ammonium ion on natural zeolite at 25°C

Isotherms	Parameters	Value
Langmuir	q_m	10.906
	b	0.123
	E(%)	9.43
Freundlich	K	2.241
	n	2.963
	E(%)	17.00
Sips	q_m	13.00
	b	0.140
	n	1.406
	E(%)	10.02

$$E(\%) = \frac{100}{N} \sum_{k=1}^N \left\{ \frac{(q_{\text{exp}} - q_{\text{pre}})}{q_{\text{pre}}} \right\} \quad (6)$$

The experimental data were well correlated with the Langmuir equation as shown Figure 4.

Determination of Mass Transfer Coefficients

In the separation processes of mass by adsorbent, the diffusion process into intraparticle becomes the rate-determining step. Determination of the diffusion coefficient is the fundamental problem of adsorption processes analysis. There are several methods used to determine the diffusion coefficient. The most common method is to determine by comparison between concentration decay curve calculated by the diffusion model, and that measured by experiment. The determined value becomes an effective diffusion coefficient to represent composite resistance including pore diffusion, surface diffusion, and steric effect by mass transfer concerned. As seen in Figure 5, there is no difference between surface and pore diffusion models for simulated concentration decay curves of ammonium ion in a batch adsorber. This implies that the choice of diffusion model depends on the researcher.¹³⁾

Figure 6 shows the experimental and predicted concentration decay curves for 20, 40, 80, and 100 mg/L of ammonium ion, respectively. The solid lines are the predicted result from the surface diffusion model at a fixed value of $k_f =$

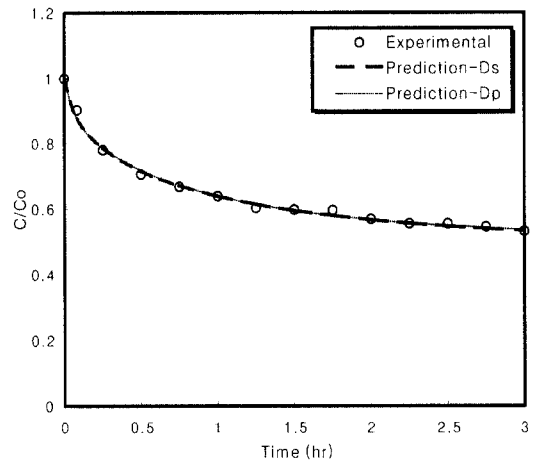


Figure 5. Comparison of pore and surface diffusion model in a batch adsorber.

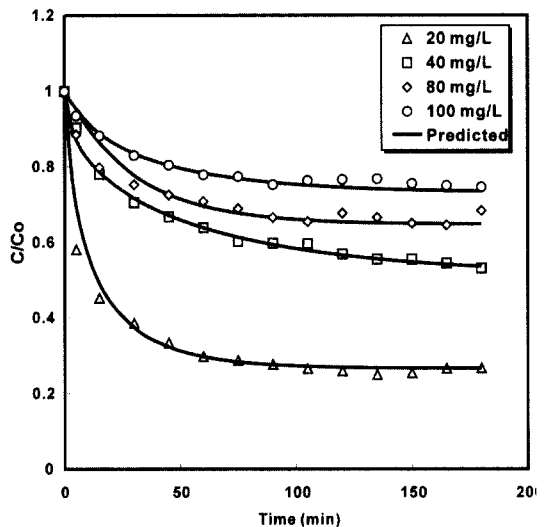


Figure 6. Observed and predicted concentration decay curves in a batch adsorber.

Table 5. Kinetic parameters determined in a batch adsorber

Concentration (mg/L)	$D_p \times 10^9$ (m ² /sec)	$D_s \times 10^{11}$ (m ² /sec)
20	13.368	4.370
40	7.235	1.964
80	5.280	5.690
100	3.740	3.536

2.27×10^{-5} m/sec. This film mass transfer coefficient was determined according to the method detailed in the literature.⁸⁾ In Table 5, the determined diffusion coefficients, based on two

different pore and surface diffusion models, are listed. The estimated values are in the range of $D_p = 3.740\sim 13.368 \times 10^{-9} \text{ m}^2/\text{sec}$ and $D_s = 1.964 \sim 5.69 \times 10^{-11} \text{ m}^2/\text{sec}$, respectively.

Adsorption and Desorption Dynamics in a Fixed-bed

In commercial equipment for adsorption separation, a fixed-bed adsorber has been used. It gives a sharp breakthrough curve by the difference in affinity between adsorbed particles and sorbent particles. In general, the breakthrough curve depends on adsorption equilibrium, interparticle and intraparticle mass transfer, and hydrodynamic conditions in the column. Figure 7 shows the experimental and predicted breakthrough curves of ammonium ion, in a fixed-bed, charged with zeolite treated sodium chloride. The predicted breakthrough curve was obtained by using the proposed adsorption model, without any manipulation of model parameters estimated from the correlations given in the previous section. Results between experimental and simulated were consistent with each other. The effect of pH on column dynamics of ammonium ion is shown in Figure 8 without simulation. The ad-

sorption capacity was greater and the breakthrough curves were sharper as increasing the concentration of hydrogen ions, in other words, low pH. In order to simulate the influence of pH on column dynamics, the adsorption equilibrium should be explained based on ion-exchange

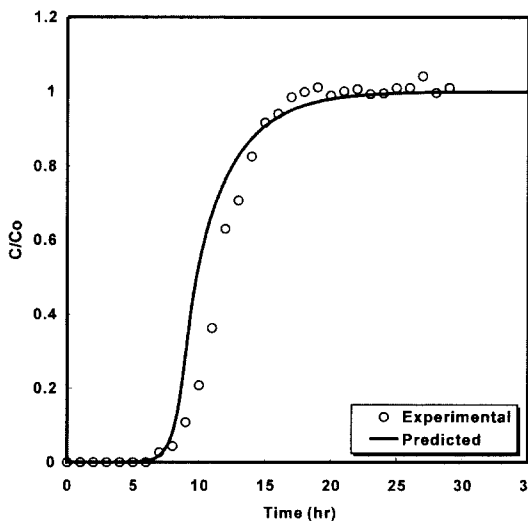


Figure 7. Experimental and predicted adsorption breakthrough curves of ammonium ion in a fixed-bed (L : 0.155 m, C_0 : 100 mg/L, v : 9.60 mL/min, w : 30 g).

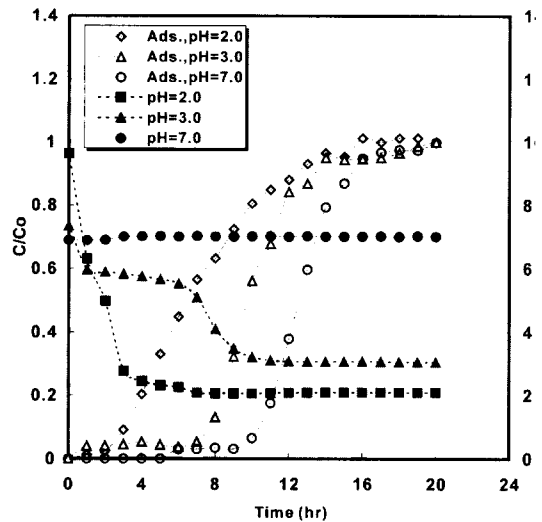


Figure 8. Effect of pH on adsorption breakthrough curves of ammonium ion (L : 0.14 m, C_0 : 100 mg/L, v : 9.60 mL/min, w : 30 g).

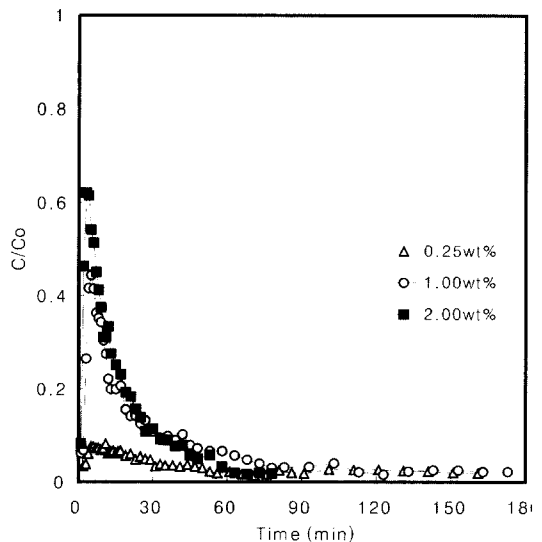


Figure 9. Desorption breakthrough curves of ammonium ion as a function of the concentration of sodium chloride (L : 0.115 m, v : 9.28 mL/min, w : 30 g).

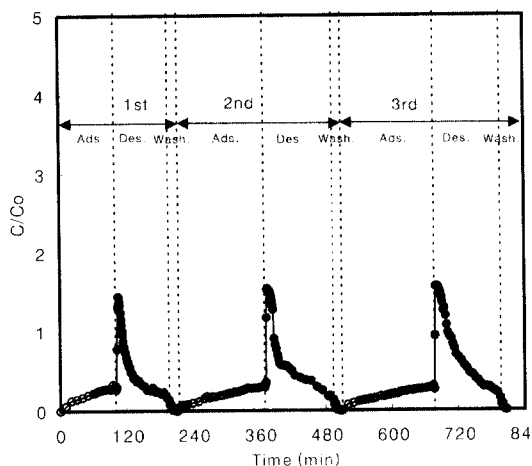


Figure 10. Cyclic operation of repeated adsorption, desorption, and washing in a fixed-bed (L : 0.115 m, C_0 : 100 mg/L, v : 9.28 mL/min, w : 30 g).

equilibria, considering competitive adsorption between hydrogen and ammonium ions within the zeolite phase.

Desorption breakthrough curves are obtained by allowing the desorbent, sodium chloride, to flow after saturation of ammonium ion in the fixed-bed. Figure 9 shows desorption breakthrough curves by examining the effective concentration of sodium chloride with 0.25, 1.0, and 2.0 wt% for the regeneration of spent sorbent. Desorption profiles of ammonium ion are sharper with an increase of the concentration of sodium chloride. Figure 10 shows the cyclic operation of repeated adsorption, desorption (or regeneration), and washing. Regardless of repeated regeneration of spent sorbent, the adsorption capacity was almost the same as the fresh sorbent. This result implies that a domestic natural zeolite with pretreatments can be applicable to the effective removal of ammonium ion.

CONCLUSIONS

The adsorption and desorption of ammonium ion in a fixed-bed adsorber charged with natural zeolite, was examined to determine its relevance as a technology for removing dissolved ammonium ion in aqueous solutions. To enhance the adsorp-

tion capacity of zeolite, the pretreatment was conducted through three kinds of chemical methods, acid (HCl), base (NaOH), and salt (NaCl) treatment. In doing so, it was determined that zeolite pretreated with sodium chloride was superior to other pretreatments. A simple but practical model was also proposed for predicting adsorption breakthrough curves. The formulated model was based on the surface diffusion model for intraparticle mass transfer, and Langmuir equation for adsorption isotherm. In spite of this simplification, it successfully simulated adsorption behavior. However, further works should be conducted to take into account the influence of pH on column dynamics and desorption behaviors. The ammonium ion adsorbed on zeolite was desorbed effectively with a low, 1.0 wt% sodium chloride solution, and the sorbent had nearly the same adsorption capacity as the fresh one, even after repeated regenerations. This result confirms that domestic natural zeolite pretreated seems to be promising sorbents for the removal of ammonium ion by means of a cyclic adsorption process.

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