Korean J. of Chem. Eng., 4(2) (1987) *149-153*

REMOVAL AND RECOVERY OF AMMONIUM ION FROM WASTEWATER BY ADSORPTION ON NATURAL ZEOLITE

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(Received 2 December 1986 • accepted 24 February 1987)

Abstract—The Removal test of ammonium ion from cokes wastewater by natural zeolite was performed in two point of view. One is to examine the adsorption capacity stability for ammonium ion in recyclic adsorption-desorption. The other is to find out the effective chemical regeneration process used by experiments and mathematical method in connection with regeneration cost and the recovery of ammonium ion.

INTRODUCTION

Recently, the removal of ammonium ion from wastewater either by natural clinoptilolite or by phillipsite has been noted in several papers because of high ammonium ion selectivity and low cost [1,2,3,]. Most of those papers have used the artificial wastewater in removal test of ammonium ion by zeolite.

There are many types of effluents containing ammonium ion, such as municipal wastewater, coke furnace wastewater, pulp industry wastewater and etc. Generally, these effluents contain several kinds of ions and organic substances except ammonium ion. The adsorption of ammonium ion by zeolite can be influenced by those substances. And the process of ammonium ion removal including regeneration operation can be changed by the kind of wastewater.

Also when the recovery of ammonium ion in high concentration is desired, the choice of regeneration process is very important factor because of recovery concentration of ammonium ion and cost. In this meaning, the coke furnace wastewater which finished 2ndary biological treatment was used in this experiment.

We have discussed here from two points of view in removal test of ammonium ion from the coke furnace wastewater by natural clinoptilolite. One is to examine the adsorption capacity stability for a ammonium ion in recyclic adsorption-desorption in case of the coke furnace wastewater. The other is to find out the effective chemical regeneration process used by experiments and mathematical model calculation in connection with regeneration cost and the recovery of ammonium ion in high concentration from wasted regenerant.

MODEL DEVELOPMENT

To research the effective chemical regeneration process in removal of ammonium ion from the coke furnace wastewater, the mathematical model is constructed for the regeneration of spent clinoptilolite by concentrated NaCl solution in the fixed bed on the basis of following assumptions;

1) Total cation concentration in the fixed bed consists of ammonium and sodium ions; that is, $C_T = C_{NH4} + C_{Na}$
2) Intraparticle diffusion is expressed by solid phase diffusion in spherical particle.
3) The rate of exchange reaction is much faster than the rate of diffusion, hence local equilibrium is maintained between the ammonium and sodium ions in the bed and the surface of the particle.
4) Cation exchange capacity of zeolite is constant and thus cation in the particle is preserved.

Differential mass balance of total ion for the fluid phase in the fixed bed is described in the one-dimensional dispersion model.

$$u\frac{\partial C_T}{\partial z} + \varepsilon\frac{\partial C_T}{\partial t} = E_z\,\varepsilon\frac{\partial^2 C_T}{\partial z^2} \tag{1}$$

Sodium mass balance in the bed

$$u\frac{\partial C_{Na}}{\partial z} + \varepsilon\frac{\partial C_{Na}}{\partial t} + k_f\,av\,(C_{Na} - C_{Na,s}) = E_z\,\varepsilon\frac{\partial^2 C_{Na}}{\partial z^2} \tag{2}$$

And sodium ion mass balance in the particle is written as

$$\frac{\partial q_{Na}}{\partial t} = D_s\left(\frac{\partial^2 q_{Na}}{\partial r^2} + \frac{2}{r}\frac{\partial q_{Na}}{\partial r}\right) \tag{3}$$

Equilibrium relation between ammonium and sodium ions at the surface of the particle is given in the previous papers as [4]

$$C_{Na,s}/C_{T,0} = \frac{K_c \frac{q_{Na,s}}{q_0}}{1 - \frac{q_{Na,s}}{q_0} + K_c \frac{q_{Na,s}}{q_0}} \quad (4)$$

$$K_c = (11.75)\ 10^{-0.52\ (1-(q_{Na,s}/q_0))^3}$$

Boundary conditions and initial conditions are

$$C_{Na} = q_{Na} = 0\ ;\ t=0,\ z>0$$
$$C_{T,0} = C_{Na}\ ;\ t>0,\ z=0 \quad (5)$$

$$\frac{\partial q_{Na}}{\partial t} = k_f av (C_{Na} - C_{Na,s}) = \rho_s D_s av \left(\frac{\partial q_{Na}}{\partial r}\right)_{r=R} \quad (6)$$

The solid-phase diffusion coefficient of sodium ion in clinoptilolite particle, also cited from the previous paper, is 5.6×10^{-12} m^2/s [4].

Basis equations (1) and (6) are converted to non-dimensional form. And numerical calculation was excuted. Since ammonium ion is exchanged with an equivalent amount of sodium ion in the zeolite particle, the concentration of ammonium ion can be determined from the mass balance of total cation and sodium ion in the same calculation step and time.

The liquid-to-particle mass transfer coefficient in the fixed bed was calculated by Wilson's equation [5]. The dispersion coefficient in L-direction in the fixed bed was determined from separate experiment in the same column.

The pulse response was measured by introducing, in the water flowing through the same bed as was used for regeneration studies, a small pulse of 0.3% aqueous phenol solution, which is an inert solution to the clinoptilolite. The detailed precedure can be found elsewhere [6].

Table 1. Physical properties of sample zeolite.

Origin	Kyeongbuk, Korea
Particle density	$1.8 \times 10^3 kg/m^3$
C.E.C.	1.95 Eq./kg
Crystal Type	Clinoptilolite

EXPERIMENTAL

Materials

Korean natural zeolite was used as the sample zeolite in this experiment. The sample was found to be mainly composed of clinoptilolite crystal by X-ray diffraction diagram. The physical properties of zeolite are given in Table 1. All cations contained in the original zeolite were replaced by the sodium ion in order to extend the effective adsorption capacity for ammonium ion.

The detailed preparation procedure of sodium form zeolite can be found elsewhere [4].

As a chemical regenerant for spent clinoptilolite from ammonium treatment, sodium chloride, sodium hydoxide, and calcium chloride have been reported in the literature [7,8]. In this work, 2×10^3 mol/m^3 sodium chloride solution was used since it has low cost, high selectivity against ammonium, stability on zeolite, and higher exchange rate with ammonium.

Apparatus and Procedure

A series of cyclic adsorption-desorption runs were carried out with 1.05×10^{-2}m $\phi \times$ 0.24m glass column. 1.7×10^{-2} Kg of sodium form 24/32 mesh zeolite was filled in the column, which formed a bed volume of 2.1×10^{-5} m^3.

The cokes furnace wastewater of steel and iron mill finished secondary biological treatment was provided form S company. The composition of the wastewater is presented in Table 2.

Column studies on stability of adsorption capacity of clinoptilolite for ammonium ion in cyclic adsorption-desorption operation at fixed bed used by the above wastewater were performed as below. The influent solution was introduced at SV of 10 and the effluent was analyzed for every 5cc to obtain ammonium breakthrough curve.

After the 10 bed volumes of $2 \times 10^3 mol/m^3$ sodium chloride solution as regenerant was introduced to regenerate the spent clinoptilolite in the bed. After the regeneration operation has been finished, above wastewater was introduced again to obtain the ammonium 2nd run breakthrough curve under the same

Table 2. Composition of cokes furnace wastewater used in this experiment.

Run No.	NH_4	Na^+	Ca^{++} me/l	K^+	Mg^{++}	TC	IC	TOC mg/l	BOD	COD	SS	PH
R-1	22.8	1.3	0.65	0.12	0.65	152	78	76	78	14	17	8.0
R-2	32.4	1.6	0.54	0.14	0.67	196	58	75	14	16	16	8.1
R-3	20.6	1.6	0.65	0.12	0.63	135	73	73	14	14	17	8.0

TC = Total Carbon, TOC = Total Organic Carbon, IC = Inorganic Carbon, BOD = Biochemical Oxygen Demand, COD = Chemical Oxygen Demand, SS = Suspended Solid

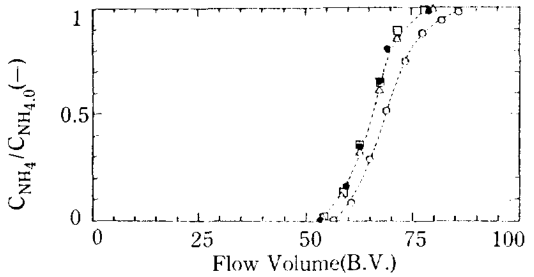

Fig. 1. Experimental results of cyclic adsorption-desorption of ammonium ion from cokes wastewater by Na-form clinoptilolite.

Key	Recyclic time	Key	Recyclic time
○	1st run	△	2nd run
□	3rd run	●	4th run

conditions as before. Like this 4 time of cyclic adsorption-desorption runs have been repeated.

Experimental on the effectiveness study of regeneration was performed through the reuse of regenerant solution. Two cases of, that is 100% and 80% recyclic use were carried out.

RESULTS AND DISCUSSION

The Stability of Adsorption Capacity of Clinoptilolite for Ammonium

Typical experimental results on the stability of adsorption capacity of natural clinoptilolite for ammonium ion with recyclic use are plotted in Fig. 1. In case of the cokes furnace wastewater there are many kinds of ions and organic substances as listed in Table 2. Therefore, it is generally expected any degradation of adsorption capacity of clinoptilolite with increase of repetition.

As shown in Fig. 1 the effective adsorption amount of ammonium which expressed as adsorption amount at breakpoint, $C_{NH4}/C_o = 0.05$ was calculated as 1.75 eq./Kg-zeolite for the first adsorption run. In case of the single component of ammonium, that of the sample was reported as 1.80 eq./Kg-zeolite. This small difference was caused by coexisting ions such as K, Na, Ca and Mg.

The ammonium elution curve of the 1st regeneration run was plotted in Fig. 2 with fractional regeneration of the bed. Solid lines in this figure illustrate the results of model calculation. A slight difference between the results of experiment and that of model calculation in elution curve of ammonium and fractional regeneration of the bed appears. From the experiment and the model calculation, the fractional regeneration by introducing 10 bed volumes of $2 \times 10^3 mol/m^3$ sodium chloride solution was calculated as 95%.

From the second run to fourth run, the breakthrough curve of ammonium ion and elution curve of ammonium were also plotted in Fig. 1 and 2 respectively. From the Fig. 1 any change of adsorption capacity for ammonium of the clinoptilolite was not shown in spite of the increasing number of repetition. The difference of adsorption amount of ammonium between first run and other runs may be caused by incomplete regeneration of the bed as mentioned above. From the results of this experiment we can conclude that clinoptilolite used in this experiment can be used without any degradation of exchange capacity in recyclic use.

Recyclic Use of Regenerant

The cost of ammonium removal from wastewater by natural clinoptilolite can be varied by operating conditions of adsorption as well as that of regeneration. The cost of regeneration of spent clinoptilolite by a chemical regenerant such as sodium chloride and sodium hydroxide is mainly decided by its amounts used in regeneration operation.

As shown above, stable regeneration operation which means keeping the same fractional regeneration is possible by introducing the same bed volume of fresh regenerant every time. From the Fig. 2 total amount of sodium chloride introduced into column to regenerate the spent clinoptilolite was calculated as 405 miliequivalent, but total amount of ammonium desorbed by this regenerant was calculated as only 29.7 milliequivalent. The efficiency of regenerant which expressed as eq. of regenerant applied per kg of zeolite is merely 7.3%. From this fact it is hard to say desirable regeneration process.

Here we investigated the useful way of reuse through experiments and computer simulation in con-

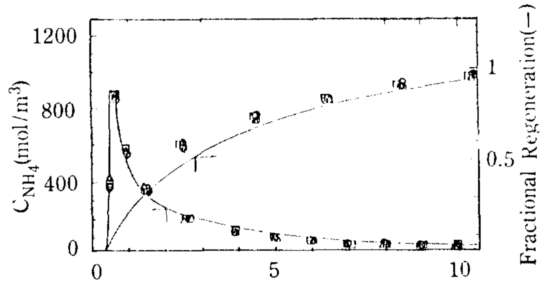

Fig. 2. Experimental and calculated results of ammonium elution concentration and fractional regeneration change in regeneration of spent clinoptilolite in case of new regenerant use.

Key	Recyclic time	Key	Recyclic time
○	1st run	△	2nd run
□	3rd run	●	4th run

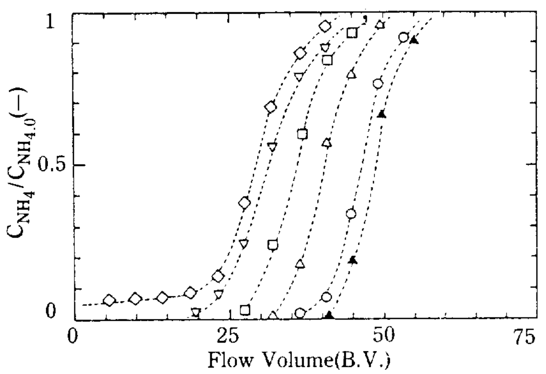

Fig. 3. Experimental results of cyclic adsorption breakthrough curves of ammonium in case of 100% reuse of regenerant.

Key	Recyclic time	Key	Recyclic time
▲	Start run	○	After 1st regeneration run
△	After 2nd regeneration run	□	After 3rd regeneration run
▽	After 4th regeneration run	◇	After 5th regeneration run

nection with the feasibility of recovery of ammonium in high concentration in two cases. The first cases is 100% and the other is 80% recyclic use.

1) 100% recyclic use

Fig. 3 and 4 show the experimental results of cyclic adsorption-desorption of ammonium when all of the regenerant solution was reused. Fig. 3 illustrates the change of the breakthrough curve of ammonium with repeat times and Fig. 4 shows the change of the elution curve of ammonium with bed volume of regenerant, concentration of ammonium and fractional regeneration of the bed. The wave of elution curve in Fig. 4 results from experimental method. That is, all 10 bed volume eluted from column was fractionated into every 2 bed volumes and each 2 bed volume is introduced into column step by step to regenerate the spent clinoptilolite in the next regeneration run.

The results of model calculation in accordance with the experimental conditions are also shown in the figure with solid lines to verify the validity of suggested model in case of cokes wastewater. Fractional regeneration was calculated from the integration of the elution curve. The predicted lines of ammonium elution and fractional regeneration in Fig. 4 agree with the observed values as a whole.

As the number of recyclic use increased, the ammonium concentration in the eluted regenerant solution increased and the ability of regeneration decreased. Finally effective adsorption capacity was reached to zero as shown in Fig. 3. The other side, the concentration of ammonium in the regenerant was increased upto $1.3 \times 10^3 mol/m^3$ at peak as shown in Fig. 4.

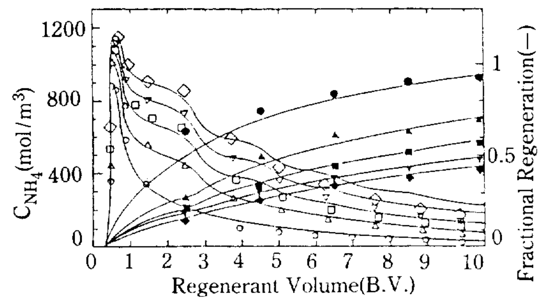

Fig. 4. Experimental and calculated results of ammonium elution curve and fractional regeneration.

Key	Recyclic time	Key	Recyclic time
○ ●	1st regeneration	△ ▲	2nd regeneration
□ ■	3rd regeneration	▽ ▼	4th regeneration
◇ ◆	5th regeneration	—	calculated line

2) 80% recyclic use

The regeneration process with 100% recyclic use of the regenerant is hardly accepted as the stable and steady operating process because of the unstable fractional regeneration in every run. Therefore, in order to operate under steady state it is required to reuse the regenerant less than 100%.

The first 20% of the all regenerant eluted from column in regeneration operation, that is two bed volumes in this experiment, which contains high concentration of ammonium ion as shown in Fig. 6 was replaced by the fresh regenerant of the same volume and concentration.

Typical calculation results of ammonium elution curve and fractional regeneration by the suggested model are plotted in Fig. 5. This figure show the steady state of the regeneration process has been reached from 6th run. And the fractional regeneration was calculated as 70% at that time. In case of no recyclic

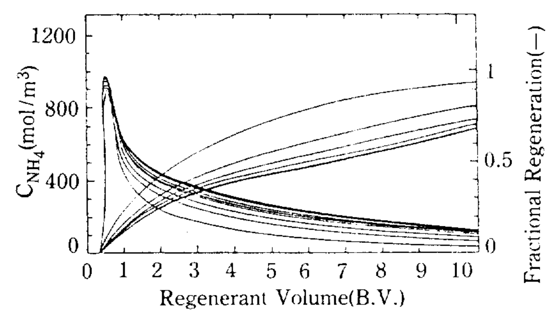

Fig. 5. Caculation results of elution concentration of ammonium and fractional regeneration in regeneration of spent clinoptilolite in case of 80% regenerant reuse.

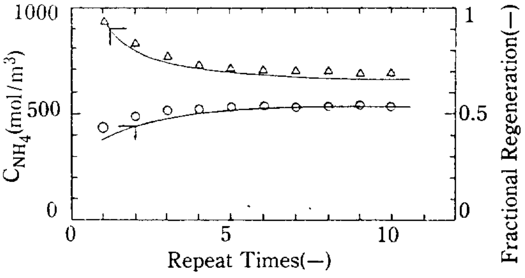

Fig. 6. Experimental and calculated results of average elution concentration of the ammonium of first two bed volumes and fractional regeneration in case of 80% regenerant reuse
(△ Average elution concentration of ammonium, ○ fractional regeneration, -Calculated line)

use of regenerant 5 bed volumes of regenerant solution was needed to obtain 70% fractional regeneration (calculated from Fig. 2). Therefore, 60% of regenerant solution was saved by the simple calculation in case of 80% recyclic use.

Otherwise, if we consider the recovery of ammonium from the wasted regenerant in high concentration of ammonium, the more concentrated solution is desired. In case of 80% recyclic use of regenerant, the average ammonium concentration of the first 2 bed volumes and fractional regeneration of the bed were plotted in Fig. 6 with repeat time. To verify the validity of the model developed here, the results of model calculation in accordance with the experimental conditions are also shown in this figure by solid lines.

The predicted lines of the average ammonium concentration of the 2 bed volumes and fractional regeneration in Fig. 6 agree with observed values as a whole. This fact suggests that the model developed here is valid for the search of the optimum conditions of chemical treatment.

CONCLUSIONS

The removal test of ammonium ion from cokes wastewater by Korean natural clinoptilolite was performed by experiments and mathematical method.

The conclusions of this work are summarized as follows;

1. The natural clinoptilolite used in this experiment can be used without any degradation of exchange capacity in recyclic use.
2. The recyclic use of regenerant is desirable for the effective regeneration process and the recovery of ammonium from the wasted regenerant.
3. The model developed here can be applicable for the seek of the optimum conditions of chemical regeneration process and the recovery of ammonium.

ACKNOWLEDGEMENT

This work was supported by Grand-in Aid for scientific research 1986 from the Ministry of Education, Korea.

NOMENCLATURE

av : external surface area of particles per unit packed volume [m^2/m^3]
C_{Na} : sodium ion concentration [mol/m^3]
$C_{Na,s}$: sodium ion concentration at particle surface [mol/m^3]
C_T : total cation concentration [mol/m^3]
D_s : solid-phase diffusion coefficient of sodium ion [m^2/s]
E_z : dispersion coefficient in L-direction in the bed [m^2/s]
K_c : selectivity coefficient of sodium ion [-]
k_f : liquid-to-particle mass transfer coefficient [m/s]
L : length of bed [m]
q_{Na} : particle phase sodium ion concentration [mol/kg]
r,R : particle radius [m]
t : time [s]
u : superficial fluid velocity [m/s]
z : position in bed [m]

Greek Letters

ρ_s : particle density [kg/m^3]
ε : void fraction

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