INVESTIGATION OF THE ADSORPTION CAPACITY OF THE ZEOLITE STONE FROM ZALAU

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abstract: Paper presents the investigation of the ammonia adsorption capacity on activated zeolite, using synthetic solutions of 5 mmol/L and 10 mmol/L of ammonia. The correlation between the mass of activated zeolite, the concentration of ammonium ions and the column flow rate has been studied. The paper also presents the dynamic regime adsorption isotherms at 25°C, for the zeolite initially conditioned and then regenerated by treatment with 1N solution of NaCl.

1. Introduction

Removal of the ammonium ion represents a major interest to maintain the ecological equilibrium of the environment, frequently polluted by both major industry and small agriculture and industry entrepreneurs.

Because of the relatively high cost of the ion exchange resins, other materials with similar properties but cheaper have been searched for. Thus, the zeolite stone contains clinoptilolyte, which shows a great selectivity for ammonium ion [1,2]. The literature mentions some interest for utilisation of the adsorption capacity of granulated zeolites [3], as well as for the removal of the metallic ion pollutants from water, on a chemically modified zeolite [4,5].

In order to assure a good ion exchange capacity, the zelite suffers granulation by the help of bindings, which induce higher mechanic strength and increase the porosity. Clay bindings like haloysite, bentonite, montmorilonite, caolinite, sodium silicate, etc. are used to granulate the zeolite, and the coagulation medium is concentrated solution of calcium chloride [3,6].

The ion exchange capacity of the conditioned zeolite [2] has been determined using solutions of ammonium ion of various concentrations driven over the zeolite surface packed into fixed length columns. Then the columns have been regenerated with solutions of HCl and NaCl, rechecking the adsorption capacity of the zeolite.

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2. Experimental

In order to determine the ion exchange capacity of the activated zeolite, a standard solution of 1000 mg NH_4^+/L has been prepared, and working solution of 5 mmol/L, and 10 mmol/L respectively, have been prepared from it.

The flow rate has been set to 5 cm^3/min. Several portions of 100 cm^3 volume of effluent have been sampled and the concentration of the ammonium ion has been determined according to STAS 6328-85.

The adsorption isotherms for the samples of raw zeolite and 1 M HCl and nitric acid/ammonium nitrate conditioned zeolite have been drawn; the relation between the quantity of the adsorbed ammonium per unit of mass of zeolite and the concentration of the ammonium in the effluent phase satisfies the Freundlich's equation:

$$\frac{x}{m} = k \cdot \left(c_{\text{effluent}}\right)^{\frac{1}{n}}$$

where $\frac{x}{m}$ is the quantity of the adsorbed ammonium per unit of mass of zeolite, in mmol/g, c_{effluent} is the concentration of the ammonium in the effluent phase, and k and n are characteristic constants for the adsorbent – solution system, at a given temperature.

The linearization of the Freundlich's equation results in:

$$\ln\left(\frac{x}{m}\right) = \ln k + \frac{1}{n}\ln\left(c_{\text{effluent}}\right)$$

The 0.09 mm sample of conditioned zeolite has been labelled B; the adsorption isotherms are drawn as a function of concentration of the ammonium ion in the effluent phase.

3. Results and Discussion

Table 1 presents the values of the ammonium ion concentration in the effluent phase, for various volumes of effluent sampled in dynamic regime from the zeolite B packed column, that has been pre-treated with 1M solution of HCl and washed with distilled water, and then 10 mmol/L NH_4Cl solution was allowed to cross the column.

Fig. 1 shows the variation of the ammonium ion content of the effluent as a function of the total solution volume of the 10 mmol/L NH_4^+ concentration that crosses the zeolite column.

Table 1

No.	V_{effluent}, cm^3	c, mmol/L	No.	V_{efluent}, cm^3	c, mmol/L
1	0	0	7	600	2.389
2	100	0.067	8	700	6.000
3	200	0.111	9	800	6.833
4	300	0.139	10	900	6.944
5	400	0.178	11	1000	7.222
6	500	0.350			

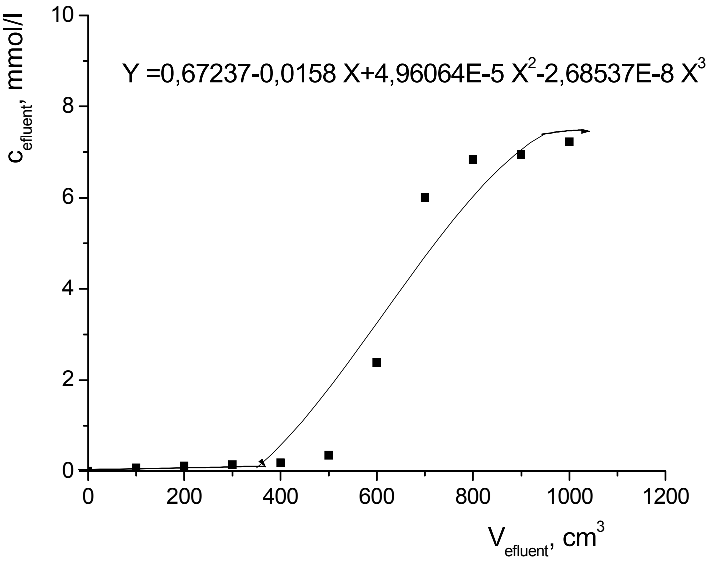

Fig. 1. *The variation of the ammonium ion concentration in effluent, function of the effluent volume, in dynamic regime, for zeolite B treated in column with 1M HCl solution, at 25°C.*

From Fig. 1 one can observe that ammonium ion is retained almost integrally until the exchange capacity decreases to approximately half of initial value. In dynamic regime, the ion exchange capacity is 1.7 mmol/g of adsorbent.

Data of the adsorption equilibrium for B treated in column with 1M HCl solution, washed, and 10 mmol/L NH_4Cl solution crossed over the column, at 25°C are presented in Table 2.

Table 2

No.	$c_{ech.}$, mmol/L	x/m, mmol/g	ln$c_{ech.}$	ln(x/m)
1	0.111	0.2175	–2.198	–0.834
2	2.389	0.4341	0.871	0.218
3	6.001	0.650	1.792	0.286
4	6.883	0.8519	1.929	0.335
5	6.945	1.0764	1.938	0.383
6	7.221	1.2431	1.977	0.426

Fig. 2 shows the adsorption isotherm of the ammonium ion on conditioned zeolite B, as resulted from Table 2.

The adsorption isotherm for a 5 mmol/L solution of NH_4Cl (t = 25 °C) has been drawn, and the values of the ammonium ion concentration in effluent, for various volumes of effluent sampled from the column with zeolite B, in dynamic regime, are presented in Table 3.

Variation of the ammonium ion content in effluent, as a function of the volume of the solution crossed over the zeolite B in column, is shown in Fig. 3.

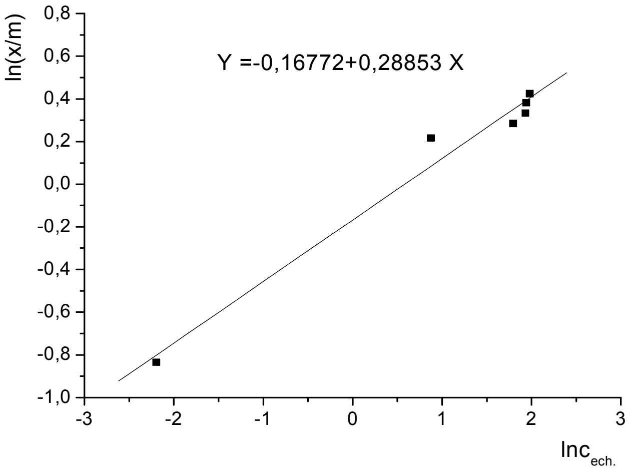

Fig. 2. *Adsorption isotherm of the zeolite B, in dynamic regime, treated in column with 1M HCl solution, at 25°C.*

Table 3

No.	$V_{effluent}$, cm³	*c*, mmol/L	No.	$V_{efluent}$, cm³	c, mmol/L
1	0	0	7	600	2.417
2	100	0.016	8	700	3.361
3	200	0.344	9	1000	3.378
4	300	0.678	10	1300	3.722
5	400	1.389	11	1600	4.083
6	500	2.167			

The variation of the ammonium ions adsorbed on the unit of mass of zeolite B, in dynamic regime, washed and then a 5 mmol/L solution of NH_4Cl crossed over (t = 25 °C), respects the linearity within the concentration range of 0.4÷4.5 mmol/L.

The processing of data shown in Table 3 is presented in Table 4, and the corresponding adsorption equilibrium data are presented in Fig. 3.

Table 4. Adsorption equilibrium data for zeolite B, in dynamic regime, washed and a 5 mmol/L solution of NH_4Cl crossed over (t = 25 °C).

No.	$c_{ech.}$, mmol/l	x/m, mmol/g	ln$c_{ech.}$	ln(x/m)	$x_{sol.}$	x_R
1	0.344	0.161	–1.067	–1.826	0.069	0.248
2	0.678	0.233	–0.388	–1.457	0.136	0.358
3	1.389	0.294	0.329	–1.224	0.078	0.452
4	2.167	0.342	0.773	–1.073	0.433	0.526
5	2.417	0.386	0.883	–0.952	0.483	0.594
6	3.378	0.441	1.217	–0.819	0.676	0.678
7	3.722	0.567	1.314	–0.567	0.744	0.872
8	4.083	0.618	1.407	–0.481	0.817	0.951

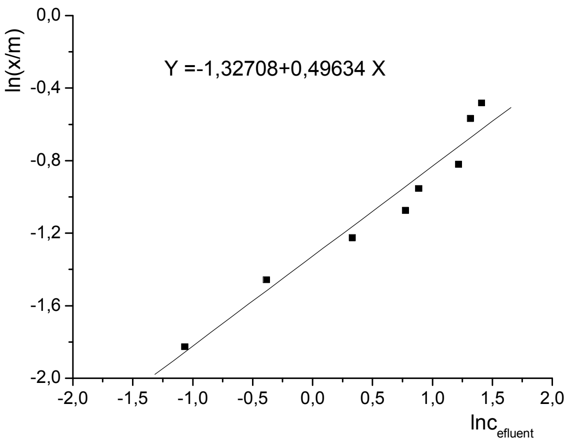

Fig. 3. *The adsorption isotherm in dynamic regime for the zeolite B initial, washed and 5 mmol/L solution of NH_4Cl crossed over (t = 25 °C).*

The adsorbent properties of zeolite B, in dynamic regime, after regeneration with 2M solution of NaCl have been studied also, using a 5 mmol/L solution of NH_4Cl (t = 25°C).

The corresponding experimental data are presented in Tables 5 and 6.

Table 5. The Values of the ammonium ion concentration in effluent, for various volumes of effluent sampled from the zeolite B column, in dynamic regime, after regeneration with 2M solution of NaCl, washed and a 5 mmol/L solution of NH_4Cl crossed over (t = 25°C).

No.	$V_{efluent}$, cm^3	c, mmol/l	No.	$V_{efluent}$, cm^3	c, mmol/l
1	0	0	6	500	1.889
2	100	0.078	7	600	2.456
3	200	0.356	8	700	2.922
4	300	1.178	9	800	3.861
5	400	1.233	10	900	4.806

Table 6. Adsorption equilibrium data for zeolite B, in dynamic regime, after regeneration with 2M solution of NaCl, washed and a 5 mmol/L solution of NH_4Cl crossed over (t = 25°C).

No.	$c_{ech.}$, mmol/l	x/m, mmol/g	ln$c_{ech.}$	ln(x/m)	$x_{sol.}$	x_R
1	0.356	0.162	–1.033	–1.820	0.071	0.324
2	1.178	0.226	0.164	–1.487	0.236	0.452
3	1.233	0.290	0.209	–1.238	0.247	0.580
4	1.889	0.342	0.636	–1.073	0.378	0.684
5	2.456	0.385	0.899	–0.955	0.491	0.770
6	2.922	0.420	1.072	–0.868	0.584	0.840
7	3.861	0.437	1.351	–0.828	0.772	0.874
8	4.806	0.443	1.570	–0.814	0.961	0. 886

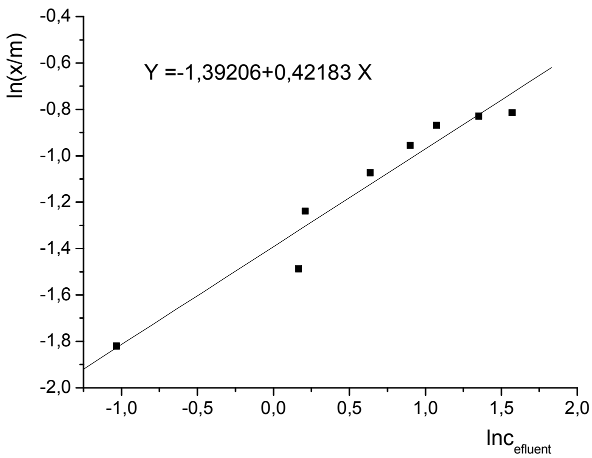

Fig. 4. *Adsoption isotherm of zeolite B, in dynamic regime, after regeneration with 2M solution of NaCl, washed and a 5 mmol/L solution of NH_4Cl crossed over (*t = *25°C).*

Conclusions

Studies on the activated zeolite, in view to establish the optimal concentration range which for the zeolite exhibits maximum adsorption capacity and the dynamic adsorption-desorption regime is set, have been done with synthetic solutions of NH_4Cl of 10 mmol/L and 5 mmol/L concentrations, respectively, at room temperature.

The adsorption isotherm in dynamic regime of the activated zeolite show is linear over a sufficiently wide range, proving that the adsorption capacity of zeolite is high, so that it is suitable for depollution of waste waters, which usually do not have a content level higher than 1 ppm.

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