# Studying the Eficiency of Retaining Ammonium on Modified Natural Zeolites Using MATLAB® Software Programs

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The efficiency of retaining ammonium on modified natural zeolites was investigated using a natural zeolite, the experimental program assuming the preparation of two types of ion exchangers that have been tested in the ammonium retaining process in comparison with the natural volcanic tuff by means of passage of  $NH_4Cl$ solutions of 10 mmol/L concentration, respectively 5 mmol/L concentration. The graphical representations of the adsorption isotherms, as an indicator of the analyzed efficiency, performed using MATLAB<sup>®</sup> software programs, concluded that a modification of the natural tuff considerably improves the performances of the adsorbent material in the ammonium retaining process.

Keywords: zeolites, ammonium retaining efficiency, adsorption isotherms

Ammonium pollution is mainly caused by the industrial technologies of manufacturing chemical fertilizers, oil and carbon processing. This is the reason why the ammonium overloaded waste waters exist in the downstream of chemical fertilizers and petrochemical plants, refineries, and coke chemical factories from the iron and steel platforms.

The international goals regarding ammonium-based sewage take into account the following aspects:

- pollution reduction by diminishing the ammonium content from waste waters;

- recovered ammonium recycling and usage in manufacturing flows.

The technical solutions that allow ammonium efficient removal from waste waters assume either its retention by adsorption on a solid adsorbent, followed by adsorption and recovery, or its chemical conversion into nonpolutted compounds (such as molecular nitrogen) [1 - 5].

The adsorbents are usually ion-exchanging resins, with the following disadvantages:

- low recovery cycles number;

- relative high price of the resin;

- high material expenses related to the regeneration of the ion exchanger.

The paper presents the testing procedure in the ammonium retaining process of an inorganic ion exchanger, volcanic tuff type that has the advantage of high ion exchange ability, as well as of lower investment and acquisition expenses, due to a reduced volume of the reaction zone.

The inorganic ion exchanger used for retaining the ammonium from ammonium waste waters is a natural zeolite, modified, from the Mâr<sup>o</sup>id area, having over 60% clinoptilolite content. The use of this ion exchanger is mainly justified by its huge selectivity in comparison with the ammonium ion  $Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^+$ .

Among the cations with a higher ability of being retained in comparison with the ammonium ion, only  $K^+$  may be found in waste waters, this being the reason why clinoptilolite is selective in relation with the retaining process of the ammonium ion from these waters.

The calculus and drawing of the graphical representations of the adsorption isotherms, as an indicator of the ammonium ion retaining efficiency, has been performed using MATLAB<sup>®</sup> software programs. A high performance software package dedicated to digital calculus and graphical representations in science and engineering, MATLAB<sup>®</sup> is a standard in the academic field, recommended by applications specific to experimental data processing and by its graphical properties and resources.

## **Experimental part**

The ion exchanger used in the experimental program is a volcanic zeolitic tuff,  $M\hat{a}r^{\circ}id-S\tilde{a}laj$  area, having granules dimensions of 0,09 mm. The chemical analysis of the volcanic tuff indicated the presence of the following compounds: SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, Fe<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>, K<sub>2</sub>O, Na<sub>2</sub>O (the tuff has low sodium ions content).

The experimental program assumed the preparation of two types of ion exchangers, namely 1A and B, both being tested in the ammonium retaining process in comparison with the natural volcanic tuff, unconditionally, by means of passage of  $NH_4Cl$  solutions of 10 mmol/L, respectively 5 mmol/L concentration.

Ion exchangers preparing

The natural tuff was conditioned by means of treatment with a  $NH_4NO_3$  mixture in a  $HNO_3$  environment. The obtained product was filtrated, washed, mixed, extruded and dried at 105°C, then burnt at 500°C. The next step consisted in activating the ion exchanger by the passage of an HCl 2M solution. The main characteristics of the two modified ion exchangers are presented in table 1.

Ions exchanger name	Activating conditions	Usage form		
1A	HCl 2M sol.	Dust form		
В	HCl 2M sol.	Extrudate form		

Table 1						
THE CHARACTERISTICS OF THE						
MODIFIED ION EXCHANGERS						

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Beside the two modified exchangers whose characteristics have been presented in table 1, one was also used for comparison the 0,09 mm natural tuff, unconditioned, but activated by a HCl 2M solution.

# Testing the ionic exchange capability

In order to test the ammonium ion retaining capability by these ion exchangers, there have been prepared two NH<sub>4</sub>Cl solutions, having 10 mmol/L, respectively 5 mmol/L concentrations. Determining the ammonium ions concentration of the solutions has been performed accordingly to STAS 6328-85, applied for determining the ammonium from drinkable water. This method uses the ammonium ion graduation by spectrophotometric means of the assembly formed by the ammonium ion with the

Nessler reactive. The spectrophotometric assay values have been performed using an UV-VIS Jasco V-550 spectrophotometer.

## **Results and discussions**

# Determination of the retaining capability of the ammonium ion on the analyzed ion exchangers

The study of the retaining efficiency of the ammonium ion on these ion exchangers has been performed by the passage of a NH<sub>4</sub>Cl solution through columns containing ion exchangers, in each case the material mass being 9g. Thus, one has determined the ammonium ion concentration, for the affluent, as well as for the effluent (tables 2-4), with the meaning:  $V_{effluent}$  -natural tuff, 1A tuff,

Table 2 VALUES OF THE EFFLUENT AMMONIUM ION CONCENTRATION FOR DIFFERENT NATURAL TUFF COLUMN ELUATED VOLUMES AFTER THE PASSAGE OF 10 MMOL/L NH, CI SOLUTION (T=25°C)

No.	V <sub>effluent</sub> , cm <sup>3</sup>	c, mmol/l	No.	V <sub>effluent</sub> , cm <sup>3</sup>	c, mmol/l
1	0	0	5	400	4,722
2	100	0,25	6	500	5,333
3	200	2,333	7	600	8,736
4	300	3,528			

#### Table 3

VALUES OF THE EFFLUENT AMMONIUM ION CONCENTRATION FOR DIFFERENT 1A TUFF COLUMN ELUATED VOLUMES AFTER THE PASSAGE OF 5 MMOL/L NH, CI SOLUTION (T=25°C)

No.	V <sub>effluent</sub> , cm <sup>3</sup>	c, mmol/l	No.	V <sub>effluent</sub> , cm <sup>3</sup>	c, mmol/l
1	0	0	9	800	3,425
2	100	0	10	900	3,489
3	200	0,644	11	1000	3,793
4	300	1,100	12	1100	4,056
5	400	1,400	13	1200	4,267
6	500	2,346	14	1300	4,694
7	600	3,056	15	1400	4,886
8	700	3,385	16	1500	5,000

## Table 4

VALUES OF THE EFFLUENT AMMONIUM ION CONCENTRATION FOR DIFFERENT B TUFF COLUMN ELUATED VOLUMES AFTER THE PASSAGE OF 5 MMOL/L NH<sub>4</sub>Cl SOLUTION (T=25°C)

No.	V <sub>effluent</sub> , cm <sup>3</sup>	c, mmol/l	No.	V <sub>effluent</sub> , cm <sup>3</sup>	c, mmol/l
1	0	0	10	900	3,370
2	100	0,016	11	1000	3,378
3	200	0,344	12	1100	3,565
4	300	0,678	13	1200	3,612
5	400	1,389	14	1300	3,722
6	500	2,167	15	1400	3,815
7	600	2,417	16	1500	3,968
8	700	3,361	17	1600	4,083
9,	800	3,364			

respective B tuff column eluated volumes, c-effluent ammonium ion concentration.

For each of the three experimental sets there has been elaborated a MATLAB® function (Computing program\_1.m; Computing program\_2.m; Computing program\_3.m), with the following structure: - initial data;

- calculus;

- display of the results;

- graphical representations.

Consequently, the following presentation for the Computing program\_1.m function is valid for the other two functions.

## Computing program\_1.m

**Initial data** –defining the achievement conditions (  $c_{ipit}, Q_{sch}, m$ ) and the experimental data ( $V_{effluent} = V_i, c_i$ ) % Initial data: %-

cinit=10; *Qsch*=0.65; m=9;V(1)=0;

Vtotal(1)=V(1); n=7; %Vtotal(1)=0; for i=2:n V(i)=100; Vtotal(i)=Vtotal(i-1)+V(i); end V Vtotal pause cefl=[0 0.25 2.333 3.528 4.722 5.333 8.736]; % mmol/l

**Calculus** –application of the calculus relations for each experimental reading

% Calculus

% for i=1:n% For each determination: % Vl=V/1000; % Volume, in litres qinit(i)=cinit\*Vl(i); % mmol q(i)=cefl(i)\*Vl(i); % mmol x(i)=qinit(i)-q(i); % mmol/g  $x_m(i)=sum(x)/m;$  % mmol/g lncefl(i)=log(cefl(i));  $lnx_m(i)=log(x_m(i));$  xefl(i)=cefl(i)/cinit;  $xR(i)=x_m(i)/Qsch;$ % end

Display of the results

% Display of the results: %\_\_\_\_\_

**Graphical representations-** one graphically represents the following

 $ln\left(\frac{\mathbf{x}}{\mathbf{m}}\right)_{i} = f(ln c_{efl i})$ 

 $x_{R\,i} = f(x_{efl\,i})$ 

Computing program\_1.m

Results Crt.no V[1] cefl qinit In cefl ln x/m xefl xR q х x/m  $0.00 \quad 0.000 \quad 0.00 \quad 0.0000 \quad 0.0000 \quad 0.0000$ -Inf -Inf 0.0000 0.0000 1. 2. 0.10 0.250 1.00 0.0250 0.9750 0.1083 -1.386 -2.2230.0250 0.1667 3. 0.10 2.333 1.00 0.2333 0.7667 0.1935 0.847 -1.642 0.2333 0.2977 4. 0.10 3.528 1.00 0.3528 0.6472 0.2654 1.261 -1.326 0.3528 0.4084 5.  $0.10 \ \ 4.722 \ \ 1.00 \ \ 0.4722 \ \ 0.5278 \ \ 0.3241 \ \ 1.552$ -1.127 0.4722 0.4986 6. 0.10 5.333 1.00 0.5333 0.4667 0.3759 1.674 -0.978 0.5333 0.5784 7. 0.10 8.736 1.00 0.8736 0.1264 0.3900 2.167 -0.942 0.8736 0.6000

having the meaning:

- \* represents the points obtained by calculus;
- the continuous line is the final graphical representations.
- % Graphical representations:

fprintf( '\nIn order to display the graphical representations press any key ...'); pause figure set(gcf,'NumberTitle','Off','Name','Graphical representations', 'Position', [174 102 654 573]); subplot(2,1,1)*plot(lncefl(2:n),lnx\_m(2:n),'\*');* hold on coef=polyfit(lncefl(2:n),lnx\_m(2:n),1); z = coef(1) \* lncefl(2:n) + coef(2);plot(lncefl(2:n),z,'red'); axis tight title((ln(x/m)=f(ln cefl)), FontSize, 12);xlabel('ln(cefl)'); ylabel((n(x/m)));*subplot*(2,1,2) plot(xefl,xR, '\*'); hold on coef2=polyfit(xefl,xR,2); *i*=*xefl*(1):0.01:*xefl*(*n*); i2=i.\*i; *zz*=*coef2*(1)\**i*2+*coef2*(2)\**i*+*coef2*(3); plot(i,zz,'red'); axis tight title('xR=f(xefl)', 'FontSize',12); xlabel('xefl'); ylabel('xR');%-

Consequently, the paper presents the obtained results and the respective graphical representations of the adsorption isotherms (figs. 1-3), on the basis of which may be enunciated significant conclusions about the efficiency of the ammonium ion retaining process. The significance of the variables in figures (1-3) is the following:

$$\mathbf{x}_{efli} = \frac{C_{NH_4^+ in}}{C_{NH_4^+ out}} = \frac{c_{efli}}{c_{init}}$$
(1)

 $= \frac{\frac{amount of retained NH_{4}^{+}}{m_{adsorbent}}}{\frac{m_{adsorbent}}{m_{adsorbent}}} = \frac{\left(\frac{x}{m}\right)_{i}}{Q_{sch}}$ (2)





Computing program\_2.m

Results	:									
Crt.no.	<b>V</b> [l]	cefl	qinit	q	х	x/m	ln_cefl	ln_x/m	xefl	xR
1.	0.00	0.000	0.00	0.0000	0.0000	0.0000	-Inf	-Inf	0.0000	0.0000
2.	0.10	0.000	0.50	0.0000	0.5000	0.0556	-Inf	-2.890	0.0000	0.0855
3.	0.10	0.644	0.50	0.0644	0.4356	0.1040	-0.440	-2.264	0.1288	0.1599
4.	0.10	1.100	0.50	0.1100	0.3900	0.1473	0.095	-1.915	0.2200	0.2266
5.	0.10	1.400	0.50	0.1400	0.3600	0.1873	0.336	-1.675	0.2800	0.2881
6.	0.10	2.346	0.50	0.2346	0.2654	0.2168	0.853	-1.529	0.4692	0.3335
7.	0.10	3.056	0.50	0.3056	0.1944	0.2384	1.117	-1.434	0.6112	0.3667
8.	0.10	3.385	0.50	0.3385	0.1615	0.2563	1.219	-1.361	0.6770	0.3943
9.	0.10	3.425	0.50	0.3425	0.1575	0.2738	1.231	-1.295	0.6850	0.4213
10.	0.10	3.489	0.50	0.3489	0.1511	0.2906	1.250	-1.236	0.6978	0.4471
11.	0.10	3.793	0.50	0.3793	0.1207	0.3040	1.333	-1.191	0.7586	0.4677
12.	0.10	4.056	0.50	0.4056	0.0944	0.3145	1.400	-1.157	0.8112	0.4839
13.	0.10	4.267	0.50	0.4267	0.0733	0.3227	1.451	-1.131	0.8534	0.4964
14.	0.10	4.694	0.50	0.4694	0.0306	0.3261	1.546	-1.121	0.9388	0.5016
15.	0.10	4.886	0.50	0.4886	0.0114	0.3273	1.586	-1.117	0.9772	0.5036
16.	0.10	5.000	0.50	0.5000	0.0000	0.3273	1.609	-1.117	1.0000	0.5036



Fig. 2. Adsorption isotherms corresponding to 1A tuff column

### Computing program\_3.m

Results

Crt.no	<b>V[l]</b>	cefl	qinit	q	x	x/m	ln_cefl	ln_x/m	xefl	xR
1.	0.00	0.000	0.00	0.0000	0.0000	0.0000	-Inf	-Inf	0.0000	0.0000
2.	0.10	0.016	0.50	0.0016	0.4984	0.0554	-4.135	-2.894	0.0032	0.0852
3.	0.10	0.344	0.50	0.0344	0.4656	0.1071	-1.067	-2.234	0.0688	0.1648
4.	0.10	0.678	0.50	0.0678	0.4322	0.1551	-0.389	-1.863	0.1356	0.2387
5.	0.10	1.389	0.50	0.1389	0.3611	0.1953	0.329	-1.633	0.2778	0.3004
6.	0.10	2.167	0.50	0.2167	0.2833	0.2267	0.773	-1.484	0.4334	0.3488
7.	0.10	2.417	0.50	0.2417	0.2583	0.2554	0.883	-1.365	0.4834	0.3930
8.	0.10	3.361	0.50	0.3361	0.1639	0.2736	1.212	-1.296	0.6722	0.4210
9.	0.10	3.364	0.50	0.3364	0.1636	0.2918	1.213	-1.232	0.6728	0.4490
10.	0.10	3.370	0.50	0.3370	0.1630	0.3099	1.215	-1.171	0.6740	0.4768
11.	0.10	3.378	0.50	0.3378	0.1622	0.3280	1.217	-1.115	0.6756	0.5045
12.	0.10	3.565	0.50	0.3565	0.1435	0.3439	1.271	-1.067	0.7130	0.5291
13.	0.10	3.612	0.50	0.3612	0.1388	0.3593	1.284	-1.024	0.7224	0.5528
14.	0.10	3.722	0.50	0.3722	0.1278	0.3735	1.314	-0.985	0.7444	0.5746
15.	0.10	3.815	0.50	0.3815	0.1185	0.3867	1.339	-0.950	0.7630	0.5949
16.	0.10	3.968	0.50	0.3968	0.1032	0.3982	1.378	<b>-0.92</b> 1	0.7936	0.6125
17.	0.10	4.083	0.50	0.4083	0.0917	0.4083	1.407	-0.896	0.8166	0.6282



The adsorption isotherm of the ammonium ion on 1A tuff (fig. 2) is convex and has the biggest convexity that indicates the fact that, in this case, the ammonium retaining process from waste waters is the best of all the three studied adsorbent materials. Moreover, the retaining efficiency on this material is maintained on the whole time interval.

The adsorption isotherm of the logarithm of the retained substance amount, referred to the adsorbent mass (mmol/ g), depending on the equilibrium concentration ln (mmol/ l), shows that the experimental data may be satisfactory correlated by the Freundlich equation

$$\frac{x}{m} = k \cdot \left(c_{effluent}\right)^{1/n} \tag{3}$$

which by linearization turns into

$$ln(x/m) = lnk + (1/n)ln C_{effluent}$$
(4)

Fig. 3. Adsorption isotherms corresponding to B tuff column

## Conclusions

Considering the shape of the adsorption isotherms presented above, it may be concluded that a modification of the natural tuff considerably improves the performances of the adsorbent material in the ammonium retaining process. The 1A ion exchanger has the best efficiency, that it is maintained on the entire range.

As for the behaviour of these ion exchangers after the recovery, it can be assumed that a better efficiency with respect to the retaining process of the ammonium ion is obtained after the recovery. The recovery may be accomplished with NaCl solutions or a NaCl and NaOH mixture, considering the fact that the tuff, brought to a Na form, has a good ammonium retaining from aqueous solutions.

The behaviour of the adsorbent materials after recovery will be studied in a second part of this paper, the aim of this first part being that of testing the adsorbent properties of the materials in a fresh state, as well as founding a method that allows the interpretation, by means of calculus and graphical representations, in a time as short as possible, of the huge amount of experimental data.

It may be therefore, concluded, that computing and drawing of the adsorption isotherms using MATLAB<sup>®</sup> allows the enunciation of important conclusions referring to the ammonium retaining efficiency, considering the short term

processing of a huge amount of experimental data based upon a, nevertheless, quite workmanlike calculus.

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