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## MATHEMATICAL MODELING OF THE ION EXCHANGE PROCESSES OF SODIUM CLINOPTILOLITE WITH HEAVY METAL IONS FROM RESIDUAL WATERS

*The ion-exchange capacity of volcanic tuff in the Na<sup>+</sup> form (70% clinoptilolite content), used for removing heavy metals in residual waters, was investigated under different conditions (temperature, time and exchange solution concentration). These parameters are necessary and sufficient for the mathematical modeling of the ion-exchange process. The corresponding mathematical models show common characteristics due to the good arrangement of the experimental points on the response surfaces and correlation coefficients close to unity. Differences appear with respect to the shape of the response surface and model equations.*

*Key words: ion exchange, natural clinoptilolite, mathematical models.*

Residual industrial waters often contain significant amounts of heavy metal ions which could be harmful to both people and the environment. Heavy metals, such as Cr<sup>3+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> have a low atomic density and are usually associated with toxic materials [1].

Among the procedures applied for removing heavy metals, ion-exchange on natural zeolites is the most advantageous from the economical point of view as made evident in previous studies [2–8]. This method has shown remarkable performances when used for removing undesirable ions from residual waters, the ion-exchange capacity being influenced by both the chemical and structural properties of zeolites (composition, porosity, pre-treatment, etc) and exchange process parameters (ion concentration, temperature, time, etc).

Using the Table Curve 3D program, a dependence between the exchange process parameters (temperature, time, concentration of the exchange ions) can be established. The Table Curve 3D program consists of an efficient surface approximator able to find the best equations representing the arrangement of the experimental data within tridimensional space. These equations represent a mathematical models of the process under study. In order to give an ideal approximation, this program uses 36000 procedures based on different equations [9]. The same program was previously used [10,11] to describe the behavior of native volcanic tuff in ion-exchange processes with solutions containing heavy metal ions found in residual waters.

Taking into consideration the above mentioned facts, we aimed to develop a mathematical model describing the behaviour of Na<sup>+</sup> modified clinoptilolite in ion-exchange processes with heavy metal ions such as Cr<sup>3+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>.

### EXPERIMENTAL PART

Volcanic tuff with 70% clinoptilolite content (Source: Mirsid – Romania) was considered for the present study [12]. This material was first washed with distilled water, dried and screened. A clinoptilolite tuff of 0.25–0.50 mm grain size was obtained and then mixed with a 1M NaCl solution (1:10 volume ratio) for 24 hours to obtain Na<sup>+</sup> modified clinoptilolite. Further, the sodium clinoptilolite was subjected to an ion-exchange process with 0.1N salt solutions containing Cr<sup>3+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> ions (1:10 volume ratio) at various temperatures (40, 60, 80°C) for several hours (3–4 hours). Samples were then prepared at different time intervals (10 minutes).

The Na<sup>+</sup> cations of the exchange solution were analysed by flame photometry, the Cr<sup>3+</sup> cations by the permanganometric dose in neutral medium [13], and Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> were determined by complexometric titration [14].

### RESULTS AND DISCUSSION

In the first stage of the study, the behavior of Na<sup>+</sup> modified clinoptilolite was followed in the ion-exchange process with Cr<sup>3+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> ions. The variation of the exchange capacity in time of the above mentioned ions is depicted in Figure 1.

It can be noticed that the exchange of the metal ions proceeds very fast, the retained amounts being significant. The exchange capacities are different, depending on the metal type and decrease in the following order: Cr<sup>3+</sup> ≈ Fe<sup>3+</sup> > Ni<sup>2+</sup> > Cd<sup>2+</sup> > Pb<sup>2+</sup>.

As can also be seen in Figure 1, the exchange process attains equilibrium after almost two hours of contact between sodium clinoptilolite and solutions of different ions. Consequently, the exchange capacity can be estimated for every ion under the given conditions [15]. The exchange capacities of the Na<sup>+</sup>-modified clinoptilolite with the ions under study are plotted in Figure 2.

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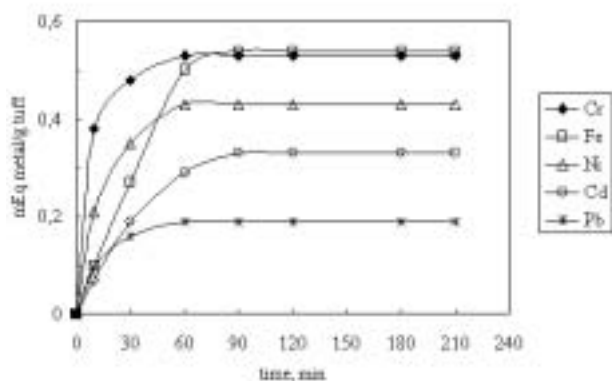


Figure 1. Kinetics of the ion exchange of  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ , and  $Pb^{2+}$  ions on sodium clinoptilolite

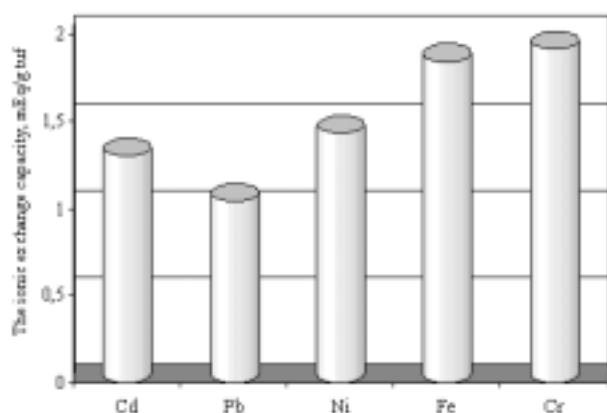


Figure 2. Ion exchange capacities of the Na form of clinoptilolite, for all the investigated ions

A correlation of these results with the data from Table 1 [16] clearly shows a dependence between the exchange capacity and the ion radius. Thus, at smaller ionic radius, higher exchange rates and higher ion-exchange capacity values were observed.

Most probably, this behaviour is mainly caused by ionic diffusion through the solid pores since ions of large radius have little or even no access to certain internal regions of the clinoptilolite structure. The native clinoptilolite contains a two dimensional system of intersectable channels of 8 and 10 tetrahedra. The effective diameters of the access windows to the channels and cavities are of the size  $4.4 \times 3 \text{ \AA}$  and  $7.9 \times 3.5 \text{ \AA}$ , respectively [17].

In order to develop a mathematical model of the ion-exchange process, the experimental data were processed using the Table Curve 3D program. The best mathematical models were chosen by taking into account the following criteria [9]:

1. shape of the response surface;
2. the best positioning of the experimental points on the graph;
3. the simplicity of the mathematical equation characteristics;
4. a correlation coefficient ( $r^2$ ) close to unity.

Table 1. Ionic radius of the metal cations

Cations	$Fe^{3+}$	$Cr^{3+}$	$Ni^{2+}$	$Cd^{2+}$	$Pb^{2+}$
Ionic radius	0.64	0.69	0.74	0.97	1.20

Table 2. The original equation numbers of the mathematical models for the ion-exchange process with all the investigated cations

Exchange ions	$Cr^{3+}$	$Fe^{3+}$	$Ni^{2+}$	$Cd^{2+}$	$Pb^{2+}$
Equation Number	384	381	374	375	386

Table 3. The corresponding equations of the mathematical models describing the exchange processes with  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$  and  $Pb^{2+}$  ions

Ions	Mathematical equations	( $r^2$ )
$Cr^{3+}$	$C = (5.058 + 0.018\tau + 0.011\tau^2 + 5.194\tau^3 + 0.050T + 4.350T^2) / (1 + 0.002\tau + 3.482\tau^2 + 1.119\tau^3 + 0.010T)$	0.9938
$Fe^{3+}$	$C = [4.348 + 0.154\ln\tau + 0.019(\ln\tau)^2 + 6.724(\ln\tau)^3 + \ln T] / [(1 + 0.029\ln\tau + 0.004(\ln\tau)^2 + 0.278\ln T + 0.014(\ln T)^2)]$	0.9872
$Ni^{2+}$	$C = 2.231 + 0.064\tau + 0.165T + 0.002\tau^2 + 0.001T^2 + 0.002\tau \cdot T + 1.350\tau^3 + 2.405T^3 + 1.501\tau T^2 + 3.185\tau^2 T$	1
$Cd^{2+}$	$C = (0.766 + 0.008\tau + 1.216\tau^2 + 0.497T + 0.010T^2 + 5.625T^3) / (1 + 0.0009\tau + 0.012T)$	0.9774
$Pb^{2+}$	$C = (20.723 + 0.006\tau + 5.226\tau^2 + 1.139\tau^3 + 0.239T) / (1 + 0.0004\tau + 2.295\tau^2 + 4.237\tau^3 + 0.0115T)$	0.9945

The following notations were chosen in the equations and plots:

$z$  – concentration (C) [mg ion/ml solution];  $x$  – time ( $\tau$ ) [min];  $y$  – temperature (T) [ $^{\circ}C$ ]. The original number of the equations provided by the Table Curve 3D program for every exchange process with the ions under study is given in Table 2.

Taking into account the above mentioned criteria, the number of equations first found for every exchange process (Table 2) is considerably decreased to a low number. The most representative equations and the correlation coefficients are given in Table 3.

The representations of the mathematical model equations in Table Curve 3D are presented in Figure 3.

These models show common characteristics such as very good positioning of the experimental points on the response surfaces and a correlation coefficient close to unity. Some differences are noticed with respect to the response surface and model equation.

## CONCLUSIONS

The mathematical modelling method, performed with the Table Curve 3D program, was employed in order to describe the behavior of the  $Na^+$  modified clinoptilolite in ion-exchange processes with solutions

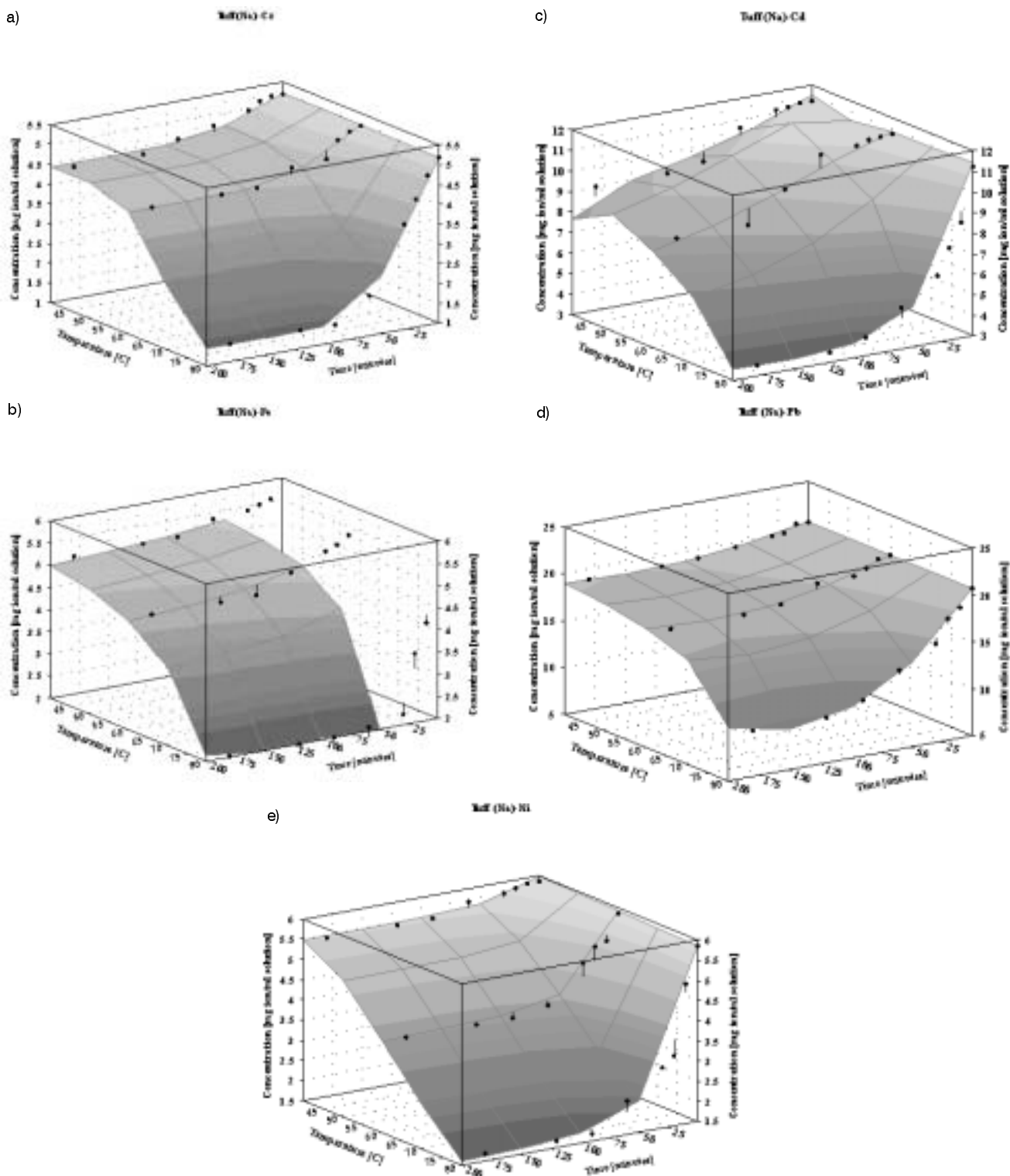


Figure 3. Mathematical models characteristic of ion exchange with the investigated ions: a) Tuff(Na)-Cr; b) Tuff(Na)-Fe; c) Tuff(Na)-Ni; d) Tuff(Na)-Cd; e) Tuff(Na)-Pb

containing  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$  and  $Pb^{2+}$  ions. The resulting models showed common characteristics such as very good arrangement of the experimental points on the response surfaces and similar correlation coefficients close to unity. Although they exhibit

similarities, these models differed between them with regard to the response surface shape and model equation.

This procedure proved to be one of the most rapid and exact possibilities used to describe the influence of

the ion-exchange capacity of sodium clinoptilolite under different conditions (process time, temperature and solution concentration).

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#### IZVOD

#### MATEMATIČKI MODEL PROCESA JONSKE IZMENE NATRIJUM KLINOPTILOLITA SA TEŠKIM METALIMA IZ OTPADNIH VODA

(Naučni rad)

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Ispitivan je kapacitet jonske izmene vulkanske lave iz Rumunije obrađene sa jonima Na<sup>+</sup> (udeo od 70% klinoptilolita) za uklanjanje teških metala iz otpadnih voda (Fe<sup>3+</sup>, Cr<sup>3+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>) u zavisnosti od operativnih uslova (temperatura, vremena i koncentracije rastvora koji je korišćen u cilju za jonsku izmenu). Navedeni operativni parametri su neophodni i dovoljni za definisanje matematičkog modela procesa jonske izmene. Izvedene jednačine modela jonske izmene imaju slične karakteristike za različite jone teških metala što je posledica dobrog slaganja eksperimentalnih podataka. Koeficijent korelacije predloženih jednačina za definisanje jonske izmene i eksperimentalno utvrđenih vrednosti je vrlo blizak jedinici.

Ključne reči: jonska izmena, prirodni klinoptilolit, matematički modeli.