

## Removal of Mn(II), Fe(III) and Cr(III) from aqueous solutions using Bulgarian clinoptilolite

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The main purpose of the present work was to study the adsorption of Mn(II), Fe(III) and Cr(III) from aqueous solutions onto natural and pretreated Bulgarian clinoptilolite from Beli plast deposit. Batch adsorption studies were carried out to evaluate the effect of contact time, temperature, solution pH and initial concentration of investigated ions. The equilibrium adsorption data were fitted to linear Langmuir, Freundlich and Dubinin-Radushkevich models and maximum adsorption capacities were calculated. The adsorption of the investigated ions followed pseudo-second-order reaction kinetics, as well as a Freundlich isotherm. The results clearly showed that the treatment with NaCl improved the adsorption capacity of natural clinoptilolite. It was found that the removal of all investigated ions from a multicomponent aqueous solution was significantly affected by the presence of competing ions.

**Key words:** clinoptilolite; adsorption equilibrium; kinetics; metal ions

### 1. INTRODUCTION

There is heavy metal contamination in the aqueous waste streams of many industries, such as metal plating facilities, mining operations, and tanneries. Especially Mn(II), Fe(III) and Cr(III) are common pollutants found in many industrial wastewaters. The presence of heavy metals in the environment can be detrimental to a variety of living species. Therefore their elimination from waters and wastewaters is important to protect public health [1]. Heavy metals are non-biodegradable and tend to accumulate in organisms, causing numerous diseases and disorders. Numerous processes exist for the removal of dissolved metals, including ion exchange, chemical precipitation, coagulation, phytoextraction, ultrafiltration, reverse osmosis, electrodialysis and adsorption. Among various treatment methods, ion exchange seems to be the most attractive one when effective low-cost ion exchangers are used. Generally, ion exchange and adsorption are preferred for heavy metal ions removal due to easy handling [2,3]. Zeolites, which represent the largest group of microporous materials, are crystalline inorganic polymers based on a three-dimensional arrangement of SiO<sub>2</sub> and AlO<sub>4</sub> tetrahedra connected through their oxygen atoms to form large negatively-charged lattices with Brønsted and Lewis acid sites. The use of zeolitic materials for

the environmental protection is stimulated by their good physico-chemical properties, e.g. selective adsorption, non-toxic nature, availability and low cost. Pretreatment of natural zeolites by acids, bases, surfactants, etc. is an important method to improve their ion-exchange capacity [4-6]. A great deal of research on natural zeolites has been focused on the most commonly occurring types, especially clinoptilolite and mordenite. Many researchers have investigated various aspects of heavy metal removal from wastewater and synthetic aqueous solutions by clinoptilolite and other zeolites [2,3,6-10]. As is seen from the literature review, zeolites can be used for the removal of some metal ions from wastewaters. The ion-exchange process is influenced by several factors, such as concentration and nature of cations and anions, temperature, pH level, crystal structure and composition of the zeolites. The composition, purity and mineralogical characteristics of clinoptilolite may vary widely from one deposit to another and even within the same deposit. For this reason clinoptilolite samples from different regions show different behavior in ion-exchange processes [3,8,10].

The aim of this study was to investigate the efficiency of clinoptilolite from a Bulgarian deposit in the removal of Mn(II), Fe(III) and Cr(III) from aqueous solutions and to estimate the optimal operation parameters of the process. Such studies

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are important for the future practical use of this natural material in wastewater treatment.

## 2. EXPERIMENTAL

A sample of clinoptilolite was taken from the Beli plast deposit in the Eastern Rhodopes Mountain, Bulgaria. The clinoptilolite was crushed and classified to a size range 0.2-1.0 mm. Then it was washed several times with distilled water, filtered, dried in an oven at 378 K for 24 h and stored in closed containers for further tests. The clinoptilolite sample was characterized by X-ray diffraction and chemical analysis. The chemical composition of the samples was determined by conventional analytical methods for silicate materials [11]. Characterization of the texture parameters of clinoptilolite was carried out by low-temperature adsorption of nitrogen at 77 K using a conventional volumetric apparatus. The clinoptilolite sample was outgassed at 473 K for 6 h under vacuum ( $10^{-3}$  Torr) before  $N_2$  adsorption.

Natural clinoptilolite (CL) was treated with 2 mol/L NaCl solution (clinoptilolite/solution ratio of 100 g/L) at 363 K over a period of 7 h in a thermostat. After a cool-down period, the sample was filtered, washed several times with distilled water and dried at 378 K for 6 h. In this way Na-modified clinoptilolite (CL\_Na) was obtained.

The adsorption properties of CL and CL\_Na with respect to Mn(II), Fe(III) and Cr(III) ions were determined by the batch method. Experiments were carried out using stoppered 50-mL Erlenmeyer flasks containing 0.25 g clinoptilolite sample and 25 mL of an aqueous solution of the metal ion(s) under study. The mixture was shaken at 295 K on an automatic shaker. On reaching equilibrium, the adsorbent was removed by filtration through a Millipore filter (0.2  $\mu$ m). The initial and equilibrium concentrations of the metal ions were determined by flame AAS on a Pye Unicam SP 192 flame atomic absorption spectrometer (UK). The kinetics of adsorption was studied by placing 0.25 g adsorbent in 25 mL of a 50 mg/L aqueous solution of a metal ion at pH 4.0 at 295 K. The contact time varied between 1 and 300 min. The effect of acidity on the removal efficiency of the adsorbents was investigated over the pH range 2.0–5.0 employing an initial concentration of 5 mg/L for all investigated ions at 295 K. Thus, to determine the effect of the initial metal ion concentration on the adsorption capacity of CL and CL\_Na, initial concentrations in the range 5–150 mg/L at pH 4.0 were chosen.

The removal efficiency (%) and the amount of metal ions adsorbed by clinoptilolite samples at

equilibrium ( $Q_e$ , mg/g) were calculated using the expressions:

$$\text{Removal efficiency (\%)} = (C_0 - C_e) * 100 / C_0 \quad (1)$$

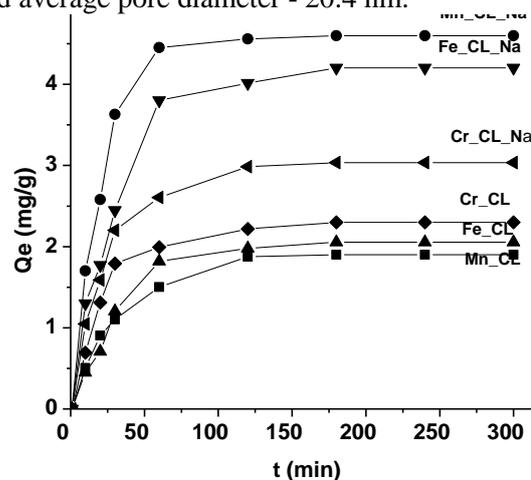
$$Q_e = (C_0 - C_e) * V / m \quad (2)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of the investigated ions (mg/L), respectively.  $V$  is the solution volume (L) and  $m$  is the adsorbent weight (g).

Analytical grade reagents were used in all experiments. The working solutions containing different concentrations of Mn(II), Fe(III) and Cr(III) ions were prepared by stepwise dilution of the stock solutions (Titrisol Merck, Germany). All adsorption experiments were replicated and the average results were used in data analyses.

## 3. RESULTS AND DISCUSSION

The chemical composition of natural clinoptilolite is as follows (wt %):  $SiO_2$ : 70.03;  $Al_2O_3$ : 12.91;  $Fe_2O_3$ : 1.89;  $Na_2O$ : 1.35;  $K_2O$ : 3.62;  $CaO$ : 2.36;  $MgO$ : 0.38;  $H_2O$ : 6.02, other 1.44%, as described in our previous study [5]. The Si/Al ratio of the sample as calculated from this composition is 5.4, which is within the typical range 4–5.5 given for clinoptilolite [8,10]. Based on the results of X-ray diffraction, Bulgarian clinoptilolite used in this study is composed of 83 % clinoptilolite, 5% cristobalite, 7% heulandite, 2% quartz, 2% albite and 1% microcline. The nitrogen adsorption isotherm was used for evaluation of textural parameters of natural clinoptilolite and the following values were obtained: specific surface area – 26.0  $m^2/g$ , total pore volume – 0.082  $cm^3/g$  and average pore diameter - 20.4 nm.



**Fig. 1.** Kinetics of adsorption of Mn(II), Fe(III) and Cr(III) onto CL and CL\_Na ( $C_0$  50 mg/L, stirring time 2 h, pH 4.0).

The experimental results of the kinetic study of Mn(II), Fe(III) and Cr(III) adsorption onto clinoptilolite samples are presented on Fig. 1. The amount of adsorbed metal ions onto both samples increases with the contact time and reaches a maximum value after 2 hours. Thus, we fixed two hours as the optimum contact time. Fig. 1 shows that the adsorption rate for all investigated ions after NaCl treatment of natural clinoptilolite is appreciably higher. In order to elucidate the adsorption kinetics of the investigated metal ions, three kinetic models: pseudo-first-order, pseudo-second-order and intraparticle diffusion, were applied to the experimental data. The pseudo-first-order [12] and pseudo-second-order [13] equations are expressed as shown in equations 3 and 4, respectively:

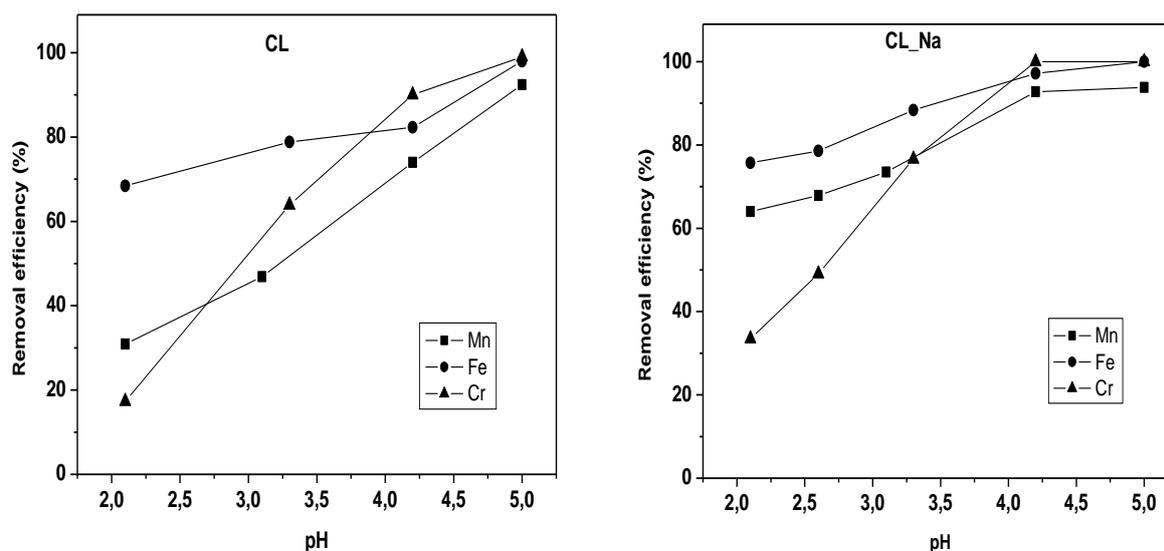
$$\log(Q_e - Q_t) = \log(Q_e) - k_1 t / 2.303 \quad (3)$$

$$(t/Q_t) = (1/k_2 Q_e) + (1/Q_e)t \quad (4)$$

where  $Q_t$  is the amount of metal ions adsorbed at various times  $t$  (mg/g); and  $k_1$  is the rate constant of pseudo-first-order adsorption (1/min);  $Q_e$  is the equilibrium adsorption capacity (mg/g);  $k_2$  is the rate constant of pseudo-second-order adsorption (g/mg min). The values of  $k_1$  can be calculated from the slope of the plots of  $\log(Q_e - Q_t)$  versus  $t$ ; the values of  $k_2$  can be calculated from the slope of the plots of  $t/Q_t$  versus  $t$ . The intercepts of these curves were used to determine the equilibrium capacity  $Q_e$ . The values obtained are presented in Table 1. The theoretical  $Q_e$  values estimated from the pseudo-first-order kinetic model differed significantly from the experimentally obtained ones and the corresponding correlation coefficients ( $R^2$ ) were found to be lower than those for the pseudo-second-order model. On the other hand, the theoretical values obtained from the pseudo-second-order kinetic model were very close to the experimental  $Q_e$  values. Thus we proved that the adsorption of all investigated ions can be described by the pseudo-second-order kinetic mechanism.

**Table 1.** Kinetic parameters for the adsorption of Mn(II), Fe(III) and Cr(III) onto CL and CL\_Na

Adsorbents	Metal ions	Pseudo-first-order constants			Pseudo-second-order constants			Intraparticle diffusion constants			$Q_{e,exp}$ (mg/g)
		$Q_e$ (mg/g)	$k_1$ (1/min)	$R^2$ (-)	$Q_e$ (mg/g)	$k_2$ (g/mg min)	$R^2$ (-)	$k_{id}$ mg/gmin <sup>1/2</sup>	C	$R^2$ (-)	
CL	Mn(II)	1.699	0.067	0.936	2.070	0.075	0.995	0.152	0.474	0.946	1.903
	Fe(III)	1.690	0.056	0.986	2.288	0.047	0.993	0.170	0.395	0.910	2.051
	Cr(III)	1.853	0.049	0.997	2.401	0.042	0.999	0.159	0.849	0.910	2.005
CL_Na	Mn(II)	2.725	0.068	0.989	4.807	0.078	0.998	0.302	1.944	0.922	4.602
	Fe(III)	3.534	0.081	0.987	4.608	0.085	0.992	0.328	1.077	0.903	4.217
	Cr(III)	2.052	0.082	0.992	3.205	0.093	0.996	0.210	1.096	0.926	3.354



**Fig. 2.** Removal efficiency (%) as a function of pH for Mn(II), Fe(III) and Cr(III) adsorption onto CL and CL\_Na ( $C_0$  5 mg/L, stirring time 2 h).

In order to assess the nature of the diffusion process reasonable for the adsorption of investigated ions onto the clinoptilolite samples, attempts were made to calculate the pore diffusion coefficients.

The intraparticle diffusion equation [14] may be written as shown in equation 5:

$$Qt = k_{id}t^{1/2} + C \quad (5)$$

where  $C$  is the intercept, and  $k_{id}$  is the intraparticle diffusion rate constant ( $\text{mg/g min}^{1/2}$ ). By using this model, the plots of  $Qt$ , versus  $t^{1/2}$  should be linear if the intraparticle diffusion is involved in the adsorption process. The values of  $k_{id}$  and  $C$  are presented in Table 1. The deviation of the straight lines from the origin indicates that intraparticle diffusion cannot be accepted as the only rate-determining step for the adsorption of the investigated ions on CL and CL\_Na, but other kinetic models may also control the rate of adsorption, all of which may be simultaneously operating. The correlation coefficients for the intraparticle diffusion model are also lower than that of the pseudo-second-order kinetic model. These results confirm that the pseudo-second-order mechanism is predominant for the adsorption of Mn(II), Fe(III) and Cr(III) onto CL and CL\_Na.

The pH of the aqueous solution is an important controlling parameter in the adsorption process. It is known that increasing the pH decreases the extent of competition between the hydroxonium ions and metal ions in the solution for surface adsorption sites, thereby resulting in increased amounts of adsorbed metals by the adsorbents. Thus, it is possible to manage metal removal from aqueous solutions by changing the pH value. The effect of pH on the metal adsorption by clinoptilolite samples is presented on Fig. 2. The removal efficiency of Mn(II), Fe(III) and Cr(III) strongly depends on the acidity of the initial solutions. Most affected by pH changes for CL and CL\_Na is the adsorption of Cr(III). pH values between 4.5 and 5 are considered as the most favourable for all systems.

The adsorption of Mn(II), Fe(III) and Cr(III) onto clinoptilolite samples as a function of temperature was studied by varying the temperature from 293 to 333 K, while keeping all other parameters constant ( $C_0$  50 mg/L, pH 4.0). The amount of adsorbed metal ions increased with increasing temperature. The increase in adsorption with temperature indicates an endothermic process. This may be attributed either to the increase in the number of active surface sites available for

adsorption on the adsorbent, or to the desolvation of the adsorbed species and the decrease in the thickness of the boundary layer surrounding the adsorbent, so that the mass transfer resistance of the adsorbate in the boundary layer decreases. The thermodynamic parameters, such as changes in the adsorption standard free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ), and entropy ( $\Delta S^0$ ) were calculated using the following equations:

$$K_d = Q_e/C_e \quad (6)$$

$$\Delta G^0 = -RT \ln K_d \quad (7)$$

$$\ln K_d = \Delta S^0/R - \Delta H^0/RT \quad (8)$$

where  $K_d$  is the equilibrium constant,  $R$  is the gas constant ( $\text{J/mol K}$ ) and  $T$  is the temperature ( $\text{K}$ ). The enthalpy change,  $\Delta H^0$ , and the entropy change,  $\Delta S^0$ , are determined from the slope and intercept of the plots of  $\ln K_d$  versus  $1/T$ , respectively. The values of  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  parameters are presented in Table 2. The negative changes in the standard free energy indicate that adsorption of the investigated metal ions on CL and CL\_Na is feasible and spontaneous. The positive values of  $\Delta H^0$  thermodynamically substantiate the assumption that the adsorption of the investigated ions on the two clinoptilolite samples is endothermic. The positive values of  $\Delta S^0$  show the existence of some structural changes at the solid–liquid interface. Also, the positive  $\Delta S^0$  favours both the complexation and stability of adsorption.

Adsorption isotherms obtained under equilibrium conditions are very important in designing adsorption systems, since such isotherms describe the distribution of adsorbed molecules between the liquid and solid phases in the equilibrium. The experimental adsorption isotherms obtained in the present study are presented on Fig. 3. According to the data shown in Fig. 3, the amounts of Mn(II), Fe(III) and Cr(III) adsorbed by CL\_Na are higher when compared to CL. The exposure of natural clinoptilolite to a NaCl solution leads to the production of a sodium-rich sample. Na-rich forms of clinoptilolite are known to have an enhanced exchange capacity, because a part of the more tightly bound K and Ca cations are also exchanged when treated with Na solutions [15,16]. There are several isotherm equations available for evaluation of experimental adsorption equilibrium data. In the present study, the experimental equilibrium data for the adsorbed metal ions onto the investigated adsorbents were analyzed using the Langmuir (9), Freundlich (10) and Dubinin–

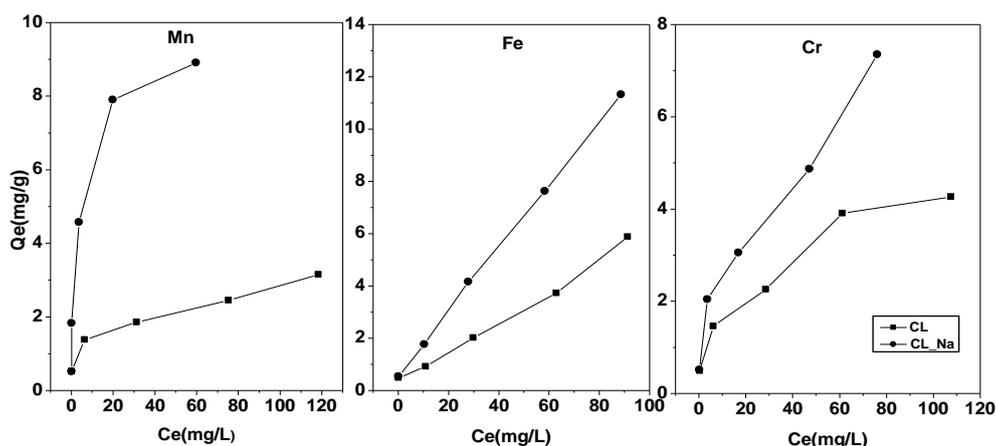


Fig. 3. Adsorption isotherms of Mn(II), Fe(III) and Cr(III) at pH 4.0 onto CL (■) and CL\_Na (●)

Table 2. Thermodynamic parameters of Mn(II), Fe(III) and Cr(III) adsorption onto clinoptilolite samples.

Adsorbents	Metal ions	$\Delta G^0$ (kJ/mol)			$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol K)
		293K	313K	333K		
CL	Mn(II)	-17.61	-18.60	-19.83	0.70	61.66
	Fe(III)	-20.85	-22.03	-23.50	0.94	73.38
	Cr(III)	-18.66	-19.99	-21.32	0.74	66.23
CL_Na	Mn(II)	-27.13	-28.64	-30.54	0.93	94.49
	Fe(III)	-22.70	-23.98	-25.57	0.94	79.61
	Cr(III)	-17.99	-18.99	-20.22	0.47	62.16

Radushkevich (11) isotherm models. The linear forms of these isotherms are as follows:

$$C_e/Q_e = 1/K_L Q_0 + C_e/Q \quad (9)$$

where  $C_e$  is the concentration of  $NH_4^+$  ions in the equilibrium solution (mg/L),  $Q_e$  is the amount of  $NH_4^+$  adsorbed (mg) by per unit mass of adsorbent (g),  $Q_0$ , the maximum adsorption capacity (mg/g);  $K_L$ , the constant of the Langmuir equation related to the enthalpy of the process.

$$\ln Q_e = \ln k_F + (1/n) \ln C_e \quad (10)$$

where  $k_F$  and  $n$  are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

$$\ln Q_e = \ln Q_0 - \beta \varepsilon^2 \quad (11)$$

where  $\beta$  is the constant of the adsorption energy ( $mol^2/J^2$ ), and  $\varepsilon$  is the Polanyi potential, described as:

$$\varepsilon = RT \ln(1+1/C_e) \quad (12)$$

where  $R$  is the gas constant (J/mol K) and  $T$  is the temperature (K). The mean adsorption energy  $E$  (KJ/mol) can be calculated from parameter  $\beta$  as follows:

$$E = 1/(-2\beta)^{1/2} \quad (13)$$

The corresponding correlation coefficients and the isotherm constants are calculated and presented in Table 3. The Freundlich model yielded a much better ( $r^2 = 0.992-0.998$ ) fit than that of the Langmuir ( $r^2 = 0.938-0.998$ ) and Dubinin–Radushkevich models ( $r^2 = 0.897-0.973$ ). The highest equilibrium adsorption capacity  $Q_0$  towards all investigated ions was obtained for the adsorbent CL\_Na. The values for the CL vary from 3.17 mg/g [for Mn(II)] to 12.44 mg/g [for Fe(III)]. For the modified adsorbent CL\_Na the values are as follows: from 7.17 mg/g (for Cr(III)) to 38.64 mg/g [Fe(III)]. Obviously, the adsorbent CL\_Na proved to be better than CL. Fe(III) is characterized by the highest adsorption capacity for both adsorbents.

The Langmuir parameters can be used to predict the affinity between adsorbate and adsorbent using the dimensionless separation factor  $R_L$ , which is defined as:

$$R_L = 1/(1 + K_L C_0) \quad (14)$$

The values of  $R_L$  for the natural and Na-modified clinoptilolites varied within the ranges 0.012 - 0.980 (for CL) and 0.066 - 0.733 (for CL\_Na). All values were within the 0–1 range,

indicating favourable adsorption for all ions investigated. In addition, the values of the separation factor demonstrated that natural and modified clinoptilolites are potential adsorbents for the removal of Mn(II), Fe(III) and Cr(III) from aqueous solutions. The Freundlich model shows a similar adsorption capacity sequence as the Langmuir isotherm according to the  $k_F$  values. In the study reported here, the values of  $n$  were all in the range from 1.17 to 4.53, indicating favourable adsorption onto the clinoptilolite samples [17].

The value of  $E$  from the D-R model is very useful in predicting the type of adsorption and gives information about chemical and physical adsorption. It is known that energy of adsorption in the range of 2–20 kJ/mol could be considered physisorption in nature [18,19]. As shown in Table 3, the values obtained in the present work are in the range 1.25 - 4.44 KJ/mol. This indicates that the type of adsorption for all investigated ions onto CL and CL\_Na is essentially physical.

It is important to assume that the mechanism of metal ions adsorption on clinoptilolite samples cannot be directly related to the Langmuir, Freundlich or Dubinin–Radushkevich models. However, from Table 3, it may be concluded that the adsorption isotherm of the investigated ions exhibits mainly Freundlich behaviour, which indicates heterogeneous surface binding. It confirms the existence of different types of possible

adsorption sites on the clinoptilolite surface with different energy if the site was on an edge or was located in a defect position.

From a practical point of view, most effluent solutions are likely to contain a range of metal ions rather than a single ionic type. Under such circumstances, it becomes essential to study not only single-component adsorption, but also the effects of present co-cations on the adsorption capacity of adsorbents [20]. For such studies, a model multi-component aqueous solution containing the three metal ions (Mn(II), Fe(III) and Cr(III)) with initial concentration 20 mg/L was prepared in order to investigate the influence of competing ions on the individual adsorption on CL and CL\_Na. The results obtained are presented in Table 4. The adsorption of the three ions investigated was significantly affected by the presence of competing ions. The amount adsorbed from multi-component solutions with concentration 20 mg/L, decreased by 33%, 21% and 35% for Mn(II), Fe(III) and Cr(III), respectively (for CL), and by 30%, 18% and 31% for Mn(II), Fe(III) and Cr(III) respectively (for CL\_Na), compared to their respective single-component solutions (see Table 4). It may be concluded that despite the similar properties of the investigated metal ions, each of them interacts only with specific adsorption sites of the adsorbents [21].

**Table 3.** Langmuir, Freundlich and Dubinin-Radushkevich parameters for the adsorption of Mn(II), Fe(III) and Cr(III) onto CL and CL\_Na.

Adsorbent	Metal ions	Langmuir			Freundlich			Dubinin-Radushkevich		
		Q <sub>0</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	k <sub>F</sub> (L/mg)	n (-)	R <sup>2</sup>	Q <sub>m</sub> (mg/g)	E (KJ/mol)	R <sup>2</sup>
CL	Mn(II)	3.171	0.057	0.977	0.866	4.534	0.992	2.12	4.44	0.897
	Fe(III)	12.439	0.569	0.978	1.118	1.176	0.997	3.97	1.25	0.900
	Cr(III)	4.673	0.004	0.974	0.943	2.73	0.994	2.74	2.00	0.898
CL_Na	Mn(II)	9.100	0.095	0.998	2.594	2.849	0.996	6.62	3.74	0.973
	Fe(III)	38.640	0.007	0.966	3.242	1.169	0.998	8.07	1.27	0.917
	Cr(III)	7.173	0.073	0.938	1.299	2.693	0.998	4.42	2.65	0.939

**Table 4.** Adsorption of Mn(II), Fe(III) and Cr(III) from single- and multi-component metal solution onto clinoptilolite samples (C<sub>0</sub> 20 mg/L, pH 4.00, stirring time 2 h).

Adsorbent	Metal ion	Adsorbed amount (mg/g)	
		single-component solution	multi-component solution
CL	Mn(II)	1.38	0.93
	Fe(III)	0.92	0.73
	Cr(III)	1.47	0.95
CL_Na	Mn(II)	1.83	1.28
	Fe(III)	1.78	1.46
	Cr(III)	2.06	1.41

#### 4. CONCLUSIONS

The adsorption of Mn(II), Fe(III) and Cr(III) onto natural and NaCl-treated Bulgarian clinoptilolite was studied. A contact time of 2 h was sufficient to attain equilibrium with both adsorbents. The experimental parameters such as solution pH, contact time, initial concentration and temperature influenced the removal of the investigated metal ions. Comparison of the equilibrium adsorption data with Langmuir, Freundlich and Dubinin–Radushkevich isotherm models showed that the Freundlich model described the process more accurately. The treatment with NaCl improved the adsorption capacity of natural clinoptilolite. The maximum adsorption capacities of CL and CL\_Na were found to be 3.17, 4.67 and 12.44 mg/g for Mn(II), Cr(III) and Fe(III), respectively (for CL) and 9.10, 7.17 and 38.64 mg/g for Mn(II), Cr(III) and Fe(III), respectively (for CL\_Na). The values of  $\Delta S^0$ ,  $\Delta H^0$  and  $\Delta G^0$  for the removal of the investigated ions by the clinoptilolite samples were calculated. The negative values of the changes in Gibbs free energy indicated that adsorption of Mn(II), Cr(III) and Fe(III) onto CL and CL\_Na was spontaneous and exothermic. The pseudo-second-order kinetic model better predicted the adsorption kinetics of the investigated ions onto clinoptilolite samples. The amounts of metal adsorbed from multi-component solutions were significantly lower than those adsorbed from single solutions.

Based on the experimental results, Bulgarian clinoptilolite from Beli plast deposit could be used as a low-cost adsorbent for the removal of Mn(II), Fe(III) and Cr(III) ions from different kinds of contaminated waters and it may be an alternative to more expensive adsorption materials.

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## ПРИЛОЖЕНИЕ НА БЪЛГАРСКИ КЛИНОПТИЛОЛИТ ЗА ИЗВЛИЧАНЕ НА Mn(II), Fe(III) И Cr(III) ОТ ВОДНИ РАЗТВОРИ

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(Резюме)

Целта на настоящата работа е изследване на адсорбцията на Mn(II), Fe(III) и Cr(III) от водни разтвори върху природен и модифициран български клиноптилолит от находището в Бели пласт. Проведени са адсорбционни изследвания в статичен режим с цел да се установи влиянието на времето на контакт, температурата, рН на изходните разтвори и началната концентрация на изследваните йони. Получени са равновестните адсорбционните изотерми и е изследвано тяхното съответствие с теоретичните модели на Лангмюир, Фройндлих и Дубинин Радушкевич. Адсорбцията на Mn(II), Fe(III) и Cr(III) се описва най-добре с модела на реакции от псевдо-втори порядък и изотермата на Фройндлих. Модификацията на природния клиноптилолит с NaCl повишава адсорбция му капацитет. Установено е, че извличането на изследваните метални йони от мулти-компонентен разтвор се влияе значително от присъствието на конкурентни йони.