PREDICTING THE COPPER ADSORPTION CAPACITY ON DIFFERENT ZEOLITES

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Abstract

In this paper the ability of three natural zeolites from different localities (Vranjska banja-VB, Igroš-I and Baia Mare-BM deposits) to remove copper has been investigated. These three zeolites were subjected to the elementary analysis as well as XRDP and DTA/TG analysis due to complete characterization. Cation exchange capacity of VB, I and BM zeolites were 150.1, 169.2, and 176.5 meq/100g. The maximum adsorption capacity for the copper adsorption on VB, I and BM- zeolites were 7.75, 8.51, and 11.18 mg/g. Based on the obtained results the mathematical expression that describes correlation between the CEC and copper adsorption capacity has been developed. This linear dependance has been tested with the vast variety of experimental results. According to this expression it is possible to predict the copper adsorption capacity for different zeolites based only on their CEC value.

Key words: zeolite; adsorption capacity; copper; mathematical expression.

1. Introduction

Many investigations have been undertaken with the aim of removing heavy metals from the waste streams before their releasing into the environment, mostly because of their toxicity. Heavy metals released into the environment present not only the environmental ballast but also the loss of the valuable nonrenewable raw material. This is especially relevant in a case of the copper mine industry which produce large amount of waste streams that contain high concentration of copper. Additionally, last few years copper leaching has gain more attention [1] in Serbia because of the increasing amount of the oxide copper particles present at the deposits that has been exploited, for the last few years, in RTB Bor. This results also in the higher copper concentration in the waste streams. Due to the high copper price on the market and high demand for it, it is of great importance to reduce losses of this metal. One of the ways is to provide the removing mechanism that offers the possibility to valorize this metal. Recently, many investigations in this filed pointed out the zeolite as low cost adsorbent that can efficiently remove the copper [2-6]. Thanks to the ion exchange behavior of the zeolite it is,

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also, possible to regenerate it and in that way obtain the starting material ready for use [7]. The byproduct of the regeneration process is the highly concentrated copper solution that can be further treated in order to valorize the recovered copper. Additionally, the zeolites are abundant material which produces no secondary pollution.

The primary building units of the aluminosilicates are the TO_4 tetrahedra, where T is Si or Al. The tetrahedra are linked in such a way that zeolites contain many channels and cavities [8]. Each tetrahedral Al ion in the zeolite framework yields a net negative charge. The negatively charged surface is balanced by mono and divalent exchangeable cations such as Na, Ca, K, and Mg which give zeolites a large cation exchange capacity (CEC) [9]. The key characteristic of zeolite is their CEC that varies in different deposits depending on the level of Si^{4+} substitution with Al^{3+} in a zeolite crystalline framework. The quality of the zeolite i.e. the CEC value can vary within the same deposit, too. Therefore, whenever this data deviate from the designed one for the wastewater treatment, the losses in copper can occur. The aim of the investigations which part of the results is presented in this paper was to determine the mathematical expression that can predict the zeolite adsorption capacity for copper knowing only the CEC of that zeolite.

2. Experimental

2.1. Sample preparation

Raw zeolites (clinoptilolite) from the Zlatokop deposit Vranjska banja (VB), Brus deposit Igroš (I), both in Serbia, and Baia Mare (BM) deposit in Romania were used as the starting materials. After crushing and grinding, the samples were sieved to the fractions below 0.043 mm.

2.2. Samples characterization

After melting the sample, chemical composition of starting zeolitic tuffs was determined by atomic absorption spectrophotometry (AAS) using the "Perkin Elmer PinAAcle 900T".

The XRD method was used to determine the phase composition. The XRD patterns were obtained on a Philips PW 1710 automated diffractometer. All the XRD measurements were performed at room temperature in a stationary sample holder.

Thermal analyses were conducted on the samples that were kept in a relative atmospheric humidity of 100 % for 24 h. The thermogravimetric/differential thermal (TG/DT) analysis was carried out in an air atmosphere in a temperature range of 20–1000 ^0C. Heating rate was 10 ^0C/min using a Netzsch STA-409 EP analyser.

The CEC value of the zeolite was determined using a standard procedure that is applicable to both calcareous and noncalcareous soils (EPA Method No. 9081, September 1986.). The concentration of the exchanged cations has been measured also using the "Perkin Elmer PinAAcle 900T".

2.3. Sorption experiments

The examination of copper uptake was carried out by shaking 1 g of VB, I and BM with 50 ml of aqueous solution of $CuSO_4·5H_2O$ containing various initial copper concentrations (1-14 mmol dm^{-3}).

Experiments were performed at room temperature using the batch technique for 24 h. After equilibration the suspensions were centrifuged at 10000 rpm for 10 minutes and in supernatants the concentration of remaining copper was determined by atomic absorption spectrophotometry.

3. Results and Discussion

3.1. XRDP

According to the semi quantitative X-ray powder diffraction (XRPD) analysis, the clinoptilolite (Cli) content in all three naturally occurring samples is around 75 % among crystalline phase. The accessory minerals are quartz (Q), feldspar (F), mica (M), smectite (Sm), and carbonate (C), as impurities, but their effect on physicochemical behavior are limited (Figure 1).
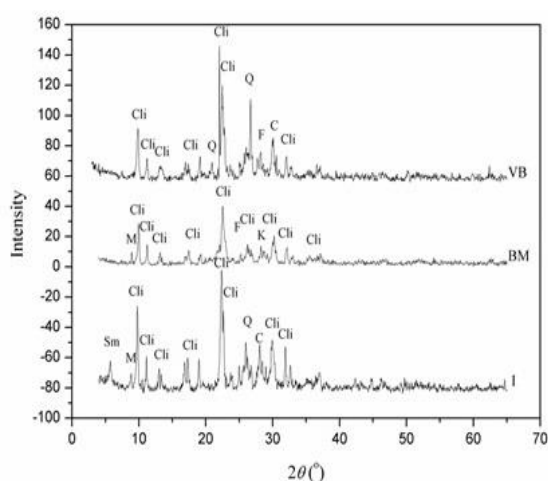

Figure 1. XPRD patterns for samples VB, BM, and I

3.2. Chemical composition

According to the chemical analysis of the starting samples (Table 1) it is obvious that they all have very similar composition. The Si/Al ratio is 4.74, 4.47, and 4.58 respectively for BM, VB and I zeolites. The highest Si/Al ratio indicates the highest negative net charge and the presence of the exchanged cations. From the chemical composition results we can also assume that Ca^{2+} ion is the dominant ion in exchangeable position while the sodium, magnesium and potassium are present at a lower amount in exchangeable position.

3.3. Cation exchange capacity

The assumptions, based on the previous chemical composition results were confirmed by measuring the total cation exchange capacity (CEC). Namely, the highest value of the Si/Al ration was calculated for the BM sample and lowest one for the VB sample. The obtained values of the CEC were in the same order like Al/Si ratio 176.5, 169.2, and 150.1 meq/100g for BM, I and VB zeolite, respectively. Additionally, Figure 2 clearly indicates that the calcium ion is the dominant one in the exchangeable position.
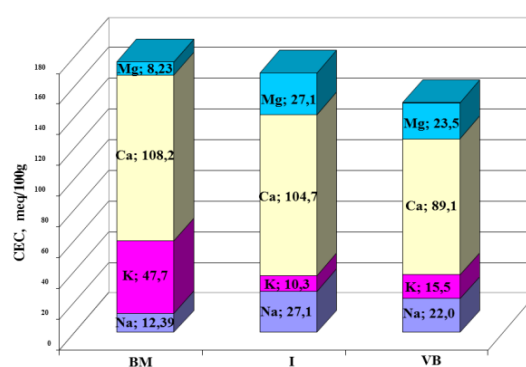

Figure 2. CEC values for natural occurring zeolites

3.4. Thermal analysis

The open framework structures of zeolites, containing variable amounts of extra framework cations and water molecules, are responsive to changes in temperature [10]. By analysing the DTA diagrams (Figure 3) of the clinoptilolites it is possible to notice that there are no significant differences in behaviour. As previously reported [11], the first endothermic peaks on DTA curves of analysed clinoptilolite referred to the process of dehydration occurring in two mildly separated steps. This corresponds to the classification of water into two groups according to its bond strength with cations.

From the channels the first to leave is the weakly bonded water whose content varies with the type of cation and the degree of occupancy of particular cationic sites [12]. This is expressed by sharp endothermic peaks around the 120ºC, and less noticeable peak around 210ºC. This thermal dehydration process is followed by the weight loss on the TG diagrams in the temperature ranged till 250ºC (Figure 3, Table 2), while after this point, weight loss decrease. The water molecules strongly bonded with cations gradually leave at a higher temperature.
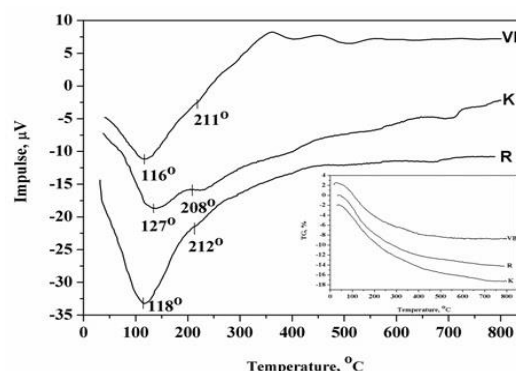

Figure 3. DTA and TG curves for the natural occurring zeolites

Table 1. Chemical composition of the zeolites

Locality	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	TiO₂	Na₂O	K₂O	I.L.*
	%
BM	63.60	11.81	1.74	7.35	0.69	0.17	0.40	4.40	9.81
VB	66.57	13.13	2.30	3.85	0.56	/	1.27	1.17	11.05
I	65.89	12.86	2.06	4.90	0.95	0.17	0.97	1.14	11.26

*I.L. – Ignition loss

Table 2. Weight loss of natural zeolites for the different temperature range

Locality	TG, %				
	0-200 ºC	200-400 ºC	400-600 ºC	600-800 ºC	Σ (0-800 ºC)
R	7.9	4.4	1.29	0.69	14.37
VB	6.75	3.62	0.85	0.09	11.26
K	7.51	4.93	1.97	0.97	15.35

3.5. Copper adsorption experiments

Copper adsorption by BM, I and VB zeolites was examined by using extent range of Cu initial concentration. The experimental data from the equilibrium studies were analyzed using Langmuir and Freundlich sorption isotherms (Figure 4). According to the Langmuir model, the sorption capacity, qm, which is a measure of the maximum sorption capacity corresponding to complete monolayer coverage, showed that the amount of copper removed by VB, I and BM zeolites were 7.75, 8.51, and 11.18 mg/g, respectively. The highest value of the sorption capacity for

the BM zeolite is expected according to the CEC data.

Zeolite has a three-dimensional crystal structure. The size of the ion, that needs to be adsorbed, and dimension of the zeolite channels determine whether the cation will fit into certain frameworks. The entry channels of the zeolite are small for the easy diffusion of Cu^{2+} ions so mostly surface cations are replaceable. One of the important parameters for the zeolites is, also, the external cation exchange capacity (ECEC). ECEC is the sum of the exchange cations on the external surface of the zeolite and has a theoretical value of 10% CEC [13].

When the results of the maximum sorption capacity presented in mg/g are calculated into the meq/100g and compared to the CEC and ECEC it can be noted that they are much smaller than CEC value but approximately 2 times higher than the ECEC. This indicate that copper adsorbs on surface of the zeolite but also, diffuse slightly in the zeolite structure.
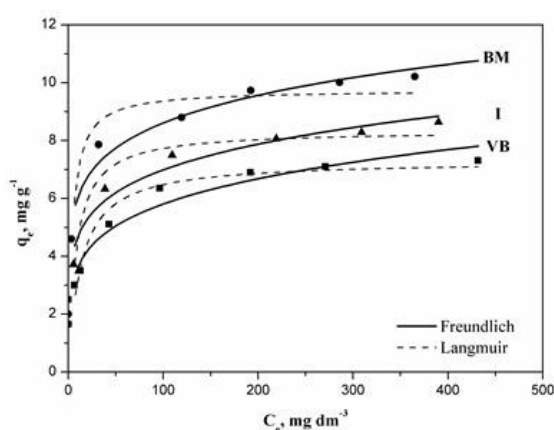

Figure 4. Langmuir and Freundlich sorption isotherms for copper uptake by three natural occurring zeolites

The observations from the obtained results were that the adsorption capacity decrease with the reduction in a CEC value. In order to determine if there are some connections between these two parameters the results of the CEC vs. maximum adsorption capacity were plotted. The obtained dependence was linear. Since the three data are not enough to claim something, the results were compared and confirmed with the results from the different scientific papers that were investigating the similar topics. Three more different salts from Sardinia, Italy (S) [14], Australia (A) [15], and Greece (G) [16] were taken into consideration. The obtained linear dependence is presented at Figure 5. This diagram shows that the collected results from other papers gives a perfect match with our experimental results and, therefore, confirm this hypothesis.
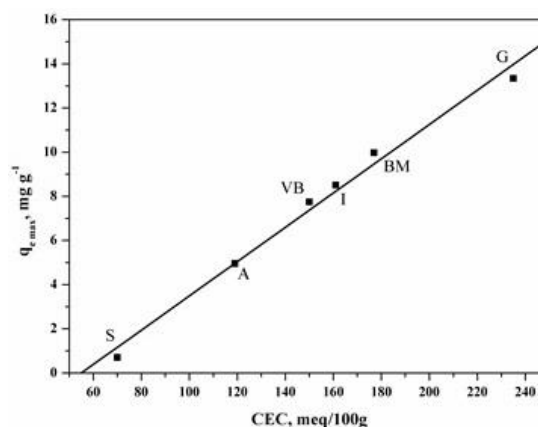

Figure 5. Linear dependence between the CEC value and the maximum adsorption capacity for Cu^{2+} removal

The defined mathematical expression that describes the dependence between these two parameters, with the 0.994 level of correlation is:

$$CEC = -0.06715 + 0.00122 \, q_{e,max} \qquad (1)$$

The obtained results are of great importance since they provide us the possibility to replace the zeolite from one deposit or manufacture with another one. If this dependence is determine, than there is no need for the great amount of investigations in order to define the maximum adsorption capacity but it is enough to define only CEC capacity for that zeolite. Of course, these results are obtained under the same examined conditions, by the mean of the zeolite type (clinoptilolite) and the particle size (- 63 µm). We assume that this dependence varies with the changes in the particle size of the zeolite and this will be the subject of the further investigations.

4. Conclusion

In this paper three different zeolites from the local (Vranjska banja and Igroš, Kopanik) and neighbour (Baia Mare, Romania) locality

were investigated. All three samples were completely characterized and there was no big differences in their structure. The difference in the Si/Al ratio caused the BM zeolite to have the highest CEC (176.5 meq/100g) and therefore to be the most efficient copper adsorbent with the maximum sorption capacity of 11.18 mg/g. Results of these investigations indicate that zeolite (clinoptilolite) can efficiently adsorb the copper from solutions. Copper adsorption efficiency decrease with the reduction of the CEC value. Maximum adsorption capacity for copper is linearly dependent on CEC value and this dependence for the clinoptilolite with the -63 μm particle size is:

$$CEC = -0.06715 + 0.00122 \, q_{e,max}$$

The obtained results are scientifically confirmed and supported with the other results available in the scientific literature.

5. Acknowledgements

6. References

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