PRELIMINARY EXAMINATIONS OF METAL UPTAKE ON IRON-COATED ZEOLITE

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INTRODUCTION

Natural zeolites are very good sorbents and ion exchangers of heavy metal ions from aqueous solutions. In order to increase their sorption properties, scientists explore different methods of surface modifications. Usually, modifications change the type and quantity of the surface charge and therefore natural zeolites even become good adsorbents for nonpolar organic molecules. Some modifications entail the formation of a new porous solid phase on the inner and outer surface of the zeolitic particle. One of the methods that change the sorption properties of natural zeolite clinoptilolite is the treatment in aqueous solutions containing Fe (III) at higher pH values. Table 1 indicates different methods with Fe (III) salts in aqueous media.

Table 1. Comparison of different methods of natural zeolite modification.

Preparation method	Metal removal	Reference
Zeolite pretreated with $FeCl_3$ and NaOH at 80^oC, heated at 500^oC, washed and dried.	Cu(II)	R. Han, L. Zou et al., 2009. [1]
Zeolite pretreated with $FeCl_3$ and NaOH in a rotary evaporator at 150^oC (mixture-sludge), washed and dried.	As(III), As(V)	C.S. Jeon, K. Beak et al., 2009. [2]
Zeolite pretreated with $Fe(NO_3)_3$ and KOH at 70^oC, washed and dried.	Mn(II)	A. Dimirkou, M.K. Doula, 2008. [3]
Zeolite pretreated with $FeCl_3$ and NaOH at 25^oC, washed and dried.	As(III), As(V)	M.H. Stanić, B. Kalajdžić, et al., 2008. [4]

This paper examines the pretreatment of natural zeolite in aqueous solutions containing $Fe(NO_3)_3 \times 9H_2O$ and NaOH at 25^oC.

EXPERIMENTAL

Zeolite sample

The natural zeolite (NZ) originating from the Vranjska Banja deposit (Serbia) has been used in preparation of iron-coated zeolite (ICZ). The sample was crushed up and sieved to two particle size fractions: < 0.04 mm and 0.6-0.8 mm. Each sample was rinsed in doubly distilled water in order to remove possible impurities. After drying at 60^oC, the samples were stored in the desiccator. The pretreatment of both natural zeolite samples was performed by shaking 20.0 g of natural zeolite samples with 100 ml freshly prepared 0.1 mol/l $Fe(NO_3)_3$ x9H_2O in an acetate buffer at pH = 3.6, for 2 h at room temperature. The sample was filtered and 90 ml of 1 mol/l NaOH solution was added to the solid phase. The suspension was shaken for an hour and filtered. Thereafter, the zeolite was shaken at 50^oC for one hour with 50 ml 4% $NaNO_3$ solution. After filtering, the zeolite was washed with doubly distilled water (until the negative test for NO_3^- ions) and shaken with 50 ml of 50% ethanol for an hour at 50°C. The samples were filtered and after drying for 24 hours at 40°C, kept in a desiccator [4].

Batch adsorption studies

Brief batch experiments were performed by equilibration of 0.5 g of natural (NZ) and iron-coated zeolites (ICZ) with 25 ml of aqueous solution of Zn, Cu and Pb, in closed glass vessels at room temperature. The solutions of Zn, Cu and Pb were prepared by dissolving $Zn(NO_3)_2x6H_2O$, $Cu(NO_3)_2x3H_2O$ and $Pb(NO_3)_2$ in doubly distilled water; their concentrations were determined complexometrically using highly selective indicators [5].

The preliminary examinations of zinc uptake were carried out by shaking of 1g of natural (NZ) and iron-coated zeolites (ICZ) with 100 ml of aqueous solutions containing various initial zinc concentrations. Experiments were performed at room temperature, using the batch technique for 24 hours. After equilibration, the suspensions were filtered and concentrations of zinc ions were determined by ion chromatography.

RESULTS AND DISCUSSION

Figure 1 shows the results of the brief examination of Zn, Cu and Pb uptake on natural and iron-coated zeolite. The amount removed on iron-coated zeolite was significantly higher than that of metal ions removed on natural zeolite.

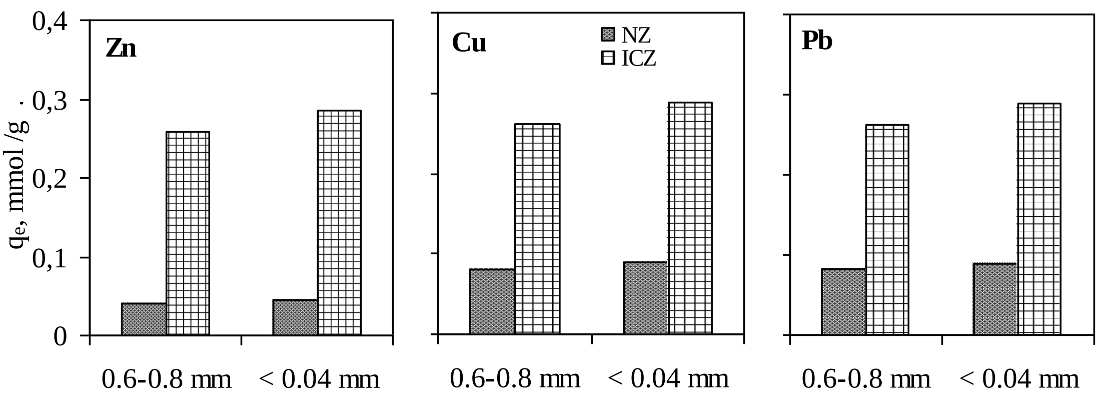

Figure 1. Results of brief examinations of Zn, Cu and Pb removal on natural (NZ) and iron-coated zeolite (ICZ) for both sample particle sizes.

The results presented in Figure 1 had indicated a successful pretreatment method of natural zeolite in Fe(III) solutions, but also the need for the following examinations to be more precise. Therefore, the examinations were continued with preliminary examinations of removal of zinc ions on NZ and ICZ. The results of these experiments are shown in Figure 2. For both zeolite samples and particle sizes, the removal of zinc increased with the increase of the initial concentration. The quantities of zinc ions removed are about four times higher for ICZ compared to NZ. The experimental results for zinc removal have been fitted to linearized Langmuir and Freundlich empirical isotherms and are shown in Figures 3 and 4. From linear dependences the correlation coefficients have been calculated, which indicate fitting of experimental results to each isotherm equation. The Langmuir isotherm equation was used to calculate the capacity of zeolite for zinc ions. It is in agreement with the experimentally observed capacity in Figure 1.

All parameters calculated from isotherms are presented in Table 2. A slight increase in removal capacity was observed for zeolite samples of the lower particle size. This can be attributed to the increase in the specific surface area.

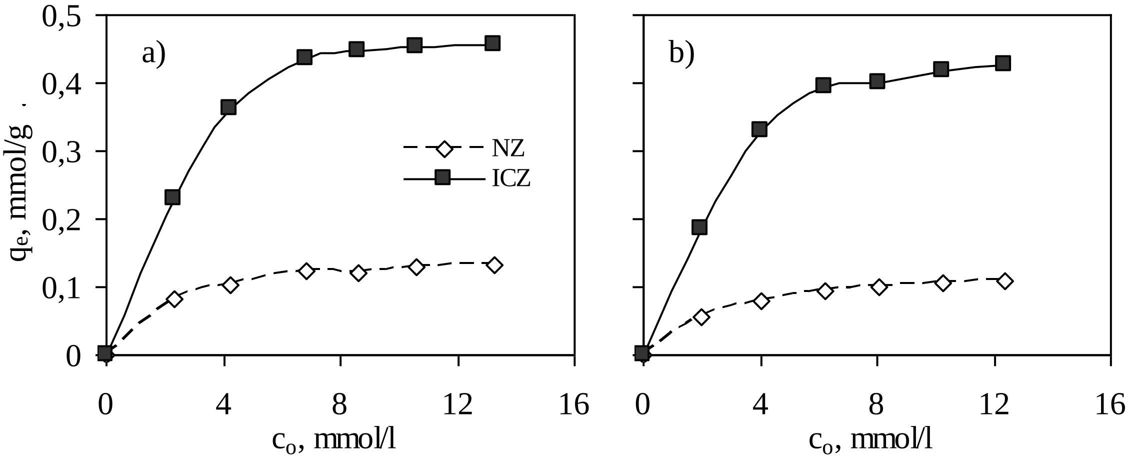

Figure 2. Quantity of zinc uptake on natural (NZ) and iron-coated zeolite (ICZ) for each particle size sample: a) <0.04 mm; b) 0.6-0.8 mm.

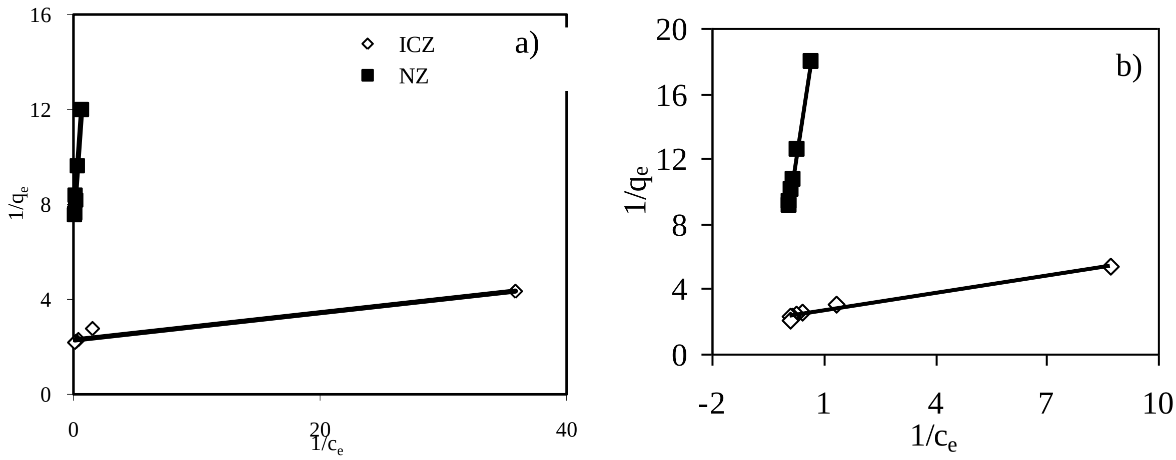

Figure 3. Langmuir isotherm on natural and iron-coated zeolite for each particle size sample: a) <0.04 mm; b) 0.6-0.8 mm.

Table 2. Calculated parameters of Langmuir and Freundlich isotherms.

Sample	Particle size, mm	Langmuir isotherm parameters			Freundlich isotherm parameters		
		K_L l/mmol	q_o, mmol/g	R^2	K_F (mmol/g)(l/mmol)$^{1/n}$	n	R^2
NZ	**0.6-0.8**	**0.070**	**0.127**	**0.999**	**0.052**	**3.040**	**0.974**
	<0.04	**0.132**	**0.142**	**0.981**	**0.078**	**4.466**	**0.956**
ICZ	**0.6-0.8**	**2.902**	**0.418**	**0.993**	**0.309**	**5.244**	**0.923**
	<0.04	**17.301**	**0.438**	**0.950**	**0.369**	**8.065**	**0.978**

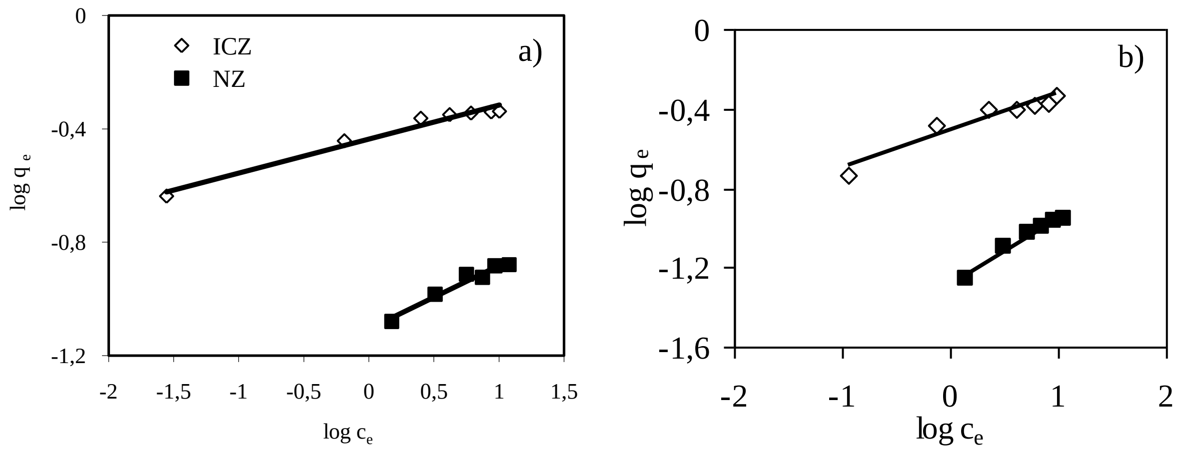

Figure 4. Freundlich isotherm on natural and iron-coated zeolite for each particle size sample: a) <0.04 mm; b) 0.6-0.8 mm.

CONCLUSIONS

The results show that both isotherms are applicable to removal of Zn, where Langmuir isotherm showing a slightly better fit to the experimental results. The capacity of ICZ for zinc ions is about 3-4 times higher compared to NZ. This confirms the validity of this pretreatment method, and directs further investigation to finding out the mechanism of coating of natural zeolite and the mechanism of binding of metal ions to ICZ. For this purpose it is necessary to perform a chemical analysis of all used samples, the XRD analysis, SEM-EDX analysis and BET sorption isotherms.

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