

The effect of concentration and pH on selectivity of ion exchange in system natural zeolite – Na⁺/Zn²⁺ aqueous solutions

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The removal of zinc ions from synthetic binary solutions on natural zeolite clinoptilolite has been studied. The investigations were conducted to study the effect of concentration and pH value on the selectivity of natural zeolitic tuff (>80% clinoptilolite) for zinc ions. The results for different concentrations of binary solutions have yielded ion exchange isotherms that show sigmoid shape for all examined concentrations. This indicates a substantial unselectivity for zinc ions that decreases by the decrease of total concentration. The selectivity is significantly improved if solutions originate from acetate than from sulphate salts, and by increasing of pH in the solution from 4 to 5 or 6. This could be explained by changes of hydration energy of divalent zinc ion.

1. INTRODUCTION

Natural zeolites are one of the most important inorganic cation exchangers that exhibit relative high ion exchange capacity, selectivity and compatibility with the natural environment. Among them, clinoptilolite has a high affinity for heavy metals and a possibility of their recovery, particularly from solutions with low concentrations, is of interest in the area of prevention of environmental pollution. Ion exchange using zeolites is an alternative to the usual wastewater processing. The selectivity of ion exchange is the preference that the zeolite-clinoptilolite exhibits for one cation compared to another, and a useful parameter in predicting the zeolite behaviour in practical application [1]. Among other factors, the selectivity depends on the total concentration in the aqueous phase, cation valence, size and shape. In natural zeolite clinoptilolite, the Si/Al ratio ranges from 4 to 5.2 so it exhibits a preference for monovalent cations with lower charge density (Cs⁺, NH₄⁺), or divalent cations with lower hydration energies (Pb²⁺) [1,2]. The selectivity for cations with higher hydration energy such as Zn²⁺ could be increased with decreasing of charge and hydration radius. For zinc ions they are in dependence on the pH value in the solution during the ion exchange process. An evaluation of selectivity may be obtained by studying the profile of the ion exchange isotherm that shows the relation between equivalent cation fractions in zeolite (X_z) and the solution (X_s) [2]:

$$X_{z(Me)} = (C_{z(Me)}) / (C_{z(Me)} + C_{z(A)}) \quad (1)$$

$$X_{s(Me)} = (C_{s(Me)}) / (C_{s(Me)} + C_{s(A)}), \quad (2)$$

where

c_s – concentration in the solution, mol L⁻¹

c_z – concentration in the zeolite, mol L⁻¹

Me – metal ion,

A – exchangeable ion.

This isotherm is easily obtainable from the equilibrium data and gives exact selectivity estimation.

2. EXPERIMENTAL

Experiments have been performed on samples of clinoptilolite tuff from the mineral deposit Vranjska Banja (Serbia and Montenegro). Characterisation by the qualitative X-ray analysis has indicated the major mineralogical component to be clinoptilolite (>80%), with quartz as main impurity, and a low content of clay minerals. A natural zeolitic sample has been milled and dry sieved, producing three fractions: <0.04 mm, 0.04-0.10 mm, and 0.10-0.40 mm. Each fraction has been separately preconditioned in a thermostated shaker with the NaCl solution at 37°C for five days, and dried at 60°C. These samples, transformed into a homoionic Na-form, have been analysed, and the empirical formula has been calculated from results of the chemical analysis, based on twenty-four oxygens per unit cell:

(Na_{1.548} K_{0.088}) (Ca_{0.144} Mg_{0.106}) (Al_{1.976} Fe_{0.193}) (Si_{19.838}) O₂₄ × 6.18 H₂O. The Si/Al ratio equals 4.979 and corresponds to the ratio of idealised sodium-clinoptilolite [3].

The theoretical exchange capacity (*TEC*) of homoionic Na-clinoptilolite has been calculated from the empirical formula according to equation [2,4]:

$$TEC = [(n(Al^{3+} + Fe^{3+})) - (n(K^+) + n/2(Ca^{2+} + Mg^{2+}))] \times 0.5/M \quad (3)$$

where

n – number of moles

M – the molar weight of the Na-clinoptilolite, mol g⁻¹.

The *TEC* calculated by equation (3) equals 1.71 × 10⁻³ equivalents per gram of Na-clinoptilolite, (eqg⁻¹).

Ion exchange experiments were performed by equilibrating a weighted amount of the sample, grain size 0.04-0.10 mm with a series of binary solutions of Na₂SO₄ and ZnSO₄ salts. The mass/volume ratio was in range 0.0015-0.014. The experiments were conducted at 23±1°C in a thermostated shaker for three days. From our previous experiments we have established that equilibrium was achieved up to 24 hours [5]. The zinc and sodium cations were at different equivalent concentration ratios in the solution, but at constant total normality equal to 0.0005, 0.005 and 0.05 equivalents per litre of solution [2,4,5,7]. Examinations of ion exchange at different initial pH values were also carried out under the same experimental conditions by equilibrating a weighed amount of the sample with a series of binary solutions of NaAc and ZnAc, at a constant total normality equal to 0.005 equivalents per litre of solution. The mass/volume ratio was in range 0.00075-0.0045. The initial pH values of 4, 5 and 6 were adjusted by a few drops of acetic acid and kept constant during three days of the experiments. The concentration of zinc remaining in the liquid phase after equilibration was measured by complexometric titration with the highly selective indicator 3,3-dimethylnaphthidine, or spectrophotometrically by the *Zincon* method [8]. Equivalent fraction of Zn²⁺ on the zeolitic phase $X_{z(Zn)}$ and equivalent fraction of Zn²⁺ on the liquid phase $X_{s(Zn)}$ are

dimensionless and were calculated for each experimental series from the experimental data on initial and final concentrations in the liquid phase, theoretical exchange capacity and the volume of solution/weight of zeolite ratio [4]:

$$X_{z(\text{Zn})} = ((c_o - c_e) \times V) / (m \times \text{TEC}) \quad (4)$$

$$X_{s(\text{Zn})} = (2 \times c_e) / \text{TN} \quad (5)$$

where

c_o – initial concentration of zinc in the binary solution, mmol L^{-1}

c_e – equilibrium concentration of zinc in the binary solution, mmol L^{-1}

V – volume of the binary solution, L

m – mass of the zeolite, g

TN – total normality of the binary solution, eq L^{-1} .

3. RESULTS AND DISCUSSION

The isotherm data for the $\text{Na}^+/\text{Zn}^{2+}$ system of different concentration ratios have been calculated from the equilibrium experimental results using equations (4) and (5), and plotted for total normality of 0.05 eqL^{-1} and 0.005 eqL^{-1} (Fig. 1.). The data for 0.0005 eqL^{-1} have not been plotted because all Zn^{2+} ions have been exchanged for all initial concentration ratios.

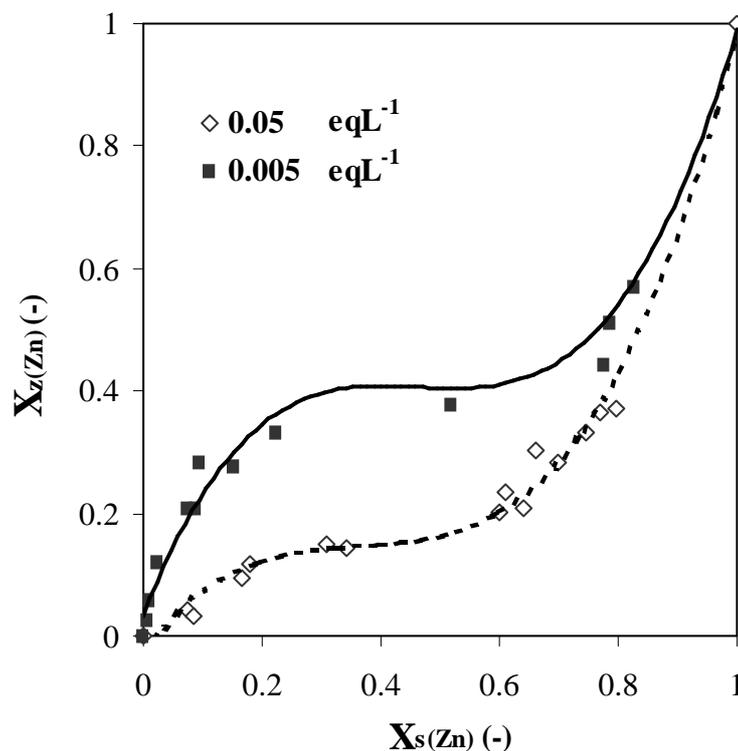


Fig. 1. Effect of the total normality of the binary solution $\text{Na}_2\text{SO}_4/\text{ZnSO}_4$ on selectivity for zinc ions.

The shape of plotted curves indicates a strong dependence of the isotherm profile and ion exchange selectivity on total concentrations of binary solutions [4,7,9,10]. The selectivity of Na-clinoptilolite sample for zinc ions increases with the decrease of the total cation

concentration. The characteristic sigmoid shape of isotherm curves is typical for the $\text{Na}^+/\text{Zn}^{2+}$ system, which involves ion exchange between a monovalent and a divalent cation. This shape of curves is characterised as a substantial unselectivity of Na-clinoptilolite towards divalent Zn^{2+} ion that occurs at high hydration energies [1,2].

A significant difference of ion exchange selectivity is observed in the $\text{NaAc}/\text{ZnAc}_2$ system compared to the $\text{Na}_2\text{SO}_4/\text{ZnSO}_4$ system. The equilibrium isotherms of these two systems were compared in order to understand the effect of the anion and pH of the binary solution on the selectivity. Figure 2 shows the ion exchange isotherms of zinc ions for acetate and sulphate binary solutions for the same total normality of 0.005 eqL^{-1} .

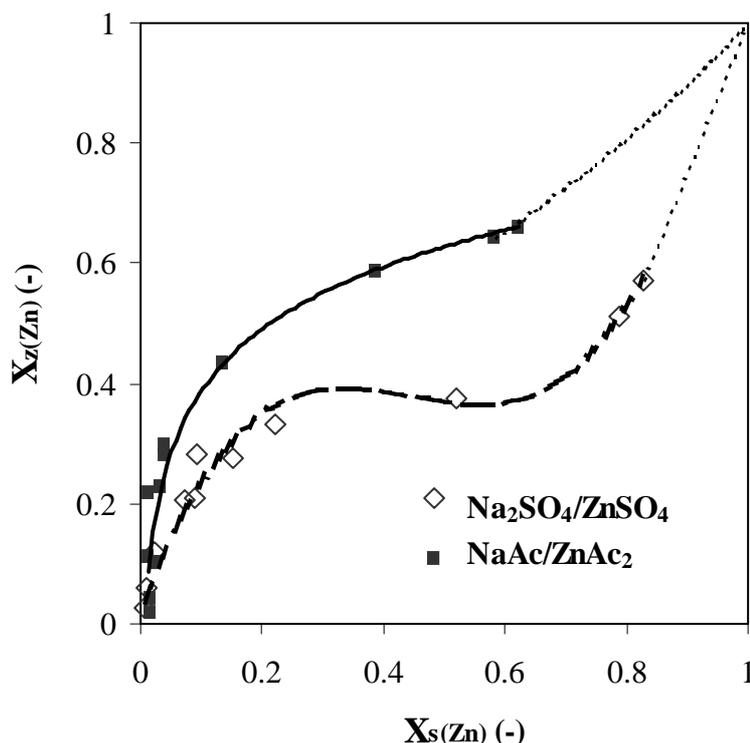


Fig.2. Comparison of selectivity for zinc ions from binary solutions of different anions at the same total normality of 0.005 eqL^{-1} , without adjustment of the pH value.

The equilibrium pH values in the $\text{Na}_2\text{SO}_4/\text{ZnSO}_4$ system ranged from 5.06 to 5.87, and in $\text{NaAc}/\text{ZnAc}_2$ one from 6.02 to 6.60. The selectivity in acetate binary solutions is higher than in sulphate binary solutions that could be attributed to higher pH values due the hydrolysis of acetate ion as a weak acid anion:



Examinations of selectivity for zinc ions in acetate binary solutions of different pH have confirmed that a slightly increased pH value is responsible for the increased selectivity. Namely, the selectivity in the binary solutions of total normality of 0.005 eqL^{-1} increases with increasing pH value of the solution from pH=4 to pH=5 and pH=6. These isotherms are shown on Fig. 3. The slightly increased concentration of OH^- ions induces forming of zinc-hydroxyl species, particularly ZnOH^+ according to the reaction [11-13]:



Zinc ion is coordinated with six water molecules and has a high hydration energy that decreases its mobility within zeolite structure.

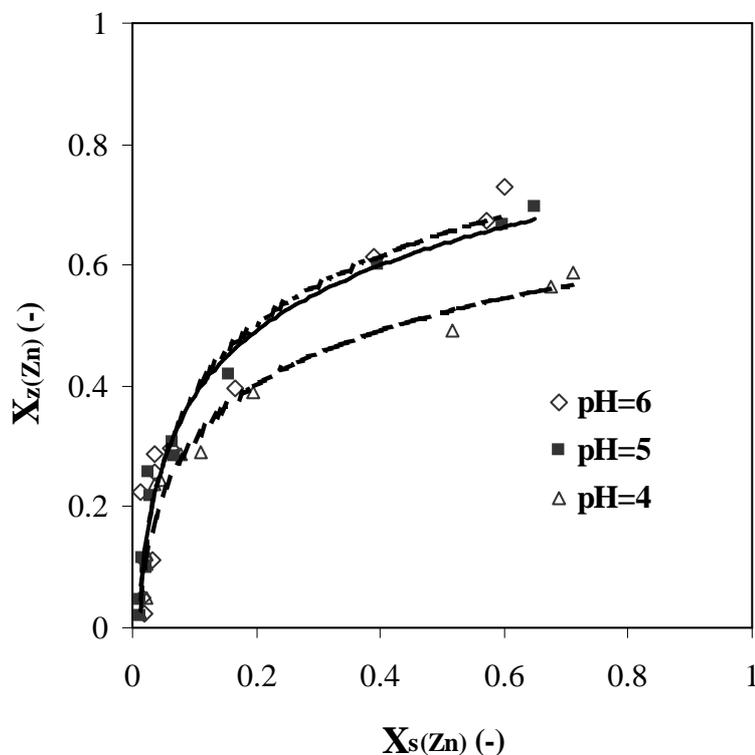


Fig. 3. The ion exchange isotherms for zinc ions in NaAc/ZnAc₂ solution at total normality 0.005 eqL⁻¹ and different pH values.

The low concentration of the formed zinc-hydroxyl species could change ion exchange reaction from a mono-divalent to mono-monovalent. Siliceous zeolite such as natural zeolite-clinoptilolite prefers monovalent cations with a low charge density, so it becomes more selective for zinc. At increased pH value, the impact of competition exchangeable H⁺ ion is negligible that increases the number of exchangeable sites in the clinoptilolite structure.

4. CONCLUSIONS

The natural zeolite-clinoptilolite shows a substantial unselectivity for zinc ions from the binary Na₂SO₄/ZnSO₄ system. The selectivity is higher at lower total concentration of ionic species e.g. at lower total normality. At total solution normality of 0.005 eqL⁻¹ the clinoptilolite is more selective for zinc ions in NaAc/ZnAc₂ than in Na₂SO₄/ZnSO₄ solution systems. That is attributed to the impact of pH of the solution on ion exchange of zinc ion on clinoptilolite. At pH near 6, zinc ion exists also as monovalent zinc-hydroxyl species, which could change the type of the ion exchange reaction to mono-monovalent. This reaction type makes clinoptilolite more selective for zinc ions that could become the critical parameter for the practical use of clinoptilolite in heavy metal removal processes.

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