Sorption-selective properties of natural and synthetic zeolite with respect to heavy metals in the liquid medium

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The sorption-selectivity properties of natural zeolite clinoptilolite and synthetic zeolites – erionyte, NaA, NaX, NaY concerning the heavy metals – lead, copper, cadmium and mercury are studied depending on concentration, pH solution, and temperature.

The bulks of absorption properties have been estimated for zeolites in their relation to heavy metals: for high-silica-containing – Hg> Pb> Cu> Cd; for low-silica-containing – Pb> Hg> Cu> Cd. It is clear that the studied sorbents have high sorption ability for heavy metals at low metal ion concentrations and at low pH values. Thus, the studied sorbents could be suggested for water-purification by elimination of heavy metals from water.

1. INTRODUCTION

One of the main problems of modern water chemistry is the search for potable and technical water sorption from toxic metals. One of the expedient ways of solving of this problem is the use of sorbents, namely, natural ones (clay minerals, zeolites, carbon containing ones and so on) that have low cost and whose supplies are practically unlimited in Ukraine.

Synthetic zeolites that due to their high homogeneity and purity higher than those of natural ones meet the demands of technologies, possess high quality and are comparatively inexpensive sorbents used recently. Also, their volume capacity is much higher than that of natural ones [1, 2]. Preliminary research has shown [3-8] that natural and certain synthetic zeolites possess high sorption-selective properties as far as caesium-137 and strontium-90 radionuclides are

concerned. There exists much less data about zeolites sorption properties concerning ions of metals, that is why the purpose of this research was to study comparatively the sorption-selective properties of natural zeolite – clinoptilolite obtained from the Sokirnitsa deposit and the synthetic zeolites: erionite, NaA, NaX, NaY in relation to toxic metal ions, i.e. – lead, copper, cadmium and mercury in accordance with concentration of solution, pH, and temperature.

2. EXPERIMENTAL

Materials and reagents. Natural zeolite-clinoptilolite obtained from Sokirnitsa the deposit and the synthetic zeolites: erionite, NaA, NaX, NaY of the grain sizes 0.3–0.5 mm were used. Synthetic zeolites were synthesized and discussed by the Scientific-Research and Project Institute of General Chemistry, Kharkov. Model solutions of the concentrations 0.005 mol/l, 0.01 mol/l and 0.02 mol/l were prepared with $Cd(NO_3)_2 \cdot 4H_2O$; $Hg(NO_3)_2 \cdot H_2O$; $Pb(NO_3)_3$; $CuCl_2 \cdot 2H_2O$ salts.

Adsorption study. Sorption ability of clinoptilolite and synthetic zeolites, i.e. erionite, NaA, NaX, NaY as to Pb, Cu, Cd, Hg heavy metals has been studied by the method of limited volume (static sorption) at pH=2 and pH=5 and the temperatures of 293.15 and 308.15 K. Under such conditions weighted sorbents (0.05 g) were stirred vigorously with a magnet stirrer with 20 cm^3 of metal salt solutions until the thermodynamic equilibrium was achieved. The liquid to solid phase ratio was L:S = 200).

Solution acidity control was made by a pH-meter and the addition of HNO_3 or NaOH solution. Heavy metals concentration was determined. Copper and mercury concentration in the solution was determined by the atomic absorption spectroscopy method.

Measurement of copper analytical signal was performed in the acetylene-air flame at the wavelength of λ=324.7 nm, the monochromator slot was 0.1 nm, the lamp current – 2 mA. The maximum relative copper determination by atom-absorption spectroscopy was 0.9 per cent.

Mercury concentration in the solutions studied was determined by the method of flameless atomisation aided by the mercury PR-115 unit. The measurement of mercury analytical signal was made at λ=253.7 nm wavelength, the monochromator slot width of 0.1 nm, the current – 5 mA.

Lead and cadmium concentration was determined by means of radionuclide X-ray fluorescent analysis, radionuclide X-ray fluorescent spectrometer with a silicon-lithium detector, isotopic excitation being used.

Ion exchange kinetics of zeolites was studied in order to determine time necessary for thermodynamic equilibrium. Kinetic curves were obtained by the method of consistent determination of metal concentration in the time interval

from 0 to τ_∞, where τ_∞ is the time of equilibrium achieved between solution and zeolite and measurement of metal concentration in solution. The analysis of kinetic curves of metal ions exchange on zeolite obtained experimentally showed that the equilibrium between liquid and solid phases was achieved for 2–6 hours and depends on zeolite selectivity, temperature and physico-chemical characteristics of ions.

The data obtained showed that the ion exchange process consists of two stages: fast and slow ones. Contributon of each stage depends on peculiarities of zeolite structure and physico-chemical characteristics of exchanging ions. Kinetic curves analysis shows the rate of ions exchange in metals studied on zeolites to change in the range of: NaA > NaX > NaY > erionite > clinoptilolite.

3. RESULTS AND DISCUSSION

Quantitative characteristics of sorbents interaction with heavy metals was determined according to the partition coefficients (Kp, cm^3/g).

$$K_p = \frac{(C_0 - C_{eq})V}{C_{eq}m}$$

where C_0 and C eq – the initial and equilibria concentration of solutions respectively; V – the total volume of solution; m – the mass of sorbent.

The partition coefficient values (K_p, cm^3/g) of heavy metals on zeolites (see Tables 1, 2, 3) allow us to compare zeolites sorption selective properties and reveal peculiarities of their interaction with Pb^{2+}, Hg^{2+}, Cd^{2+}, Cu^{2+} metal ions.

Zeolites sorption ability depends on a great number of factors, such as zeolite structure, solution concentration, pH, temperature, nature and physico-chemical properties of ions, hydration energy, charge, ionic radius. Thus two characteristic regularities are observed in the present physico-chemical conditions. First, the shorter the radius of bivalent cation and correspondingly larger its hydration ability, ion potential and the relation of the charge to the coordination number, the smaller is its capacity. Second, the sum of exchanged cations that was determined according to the physico-chemical analysis data is lower than the maximum volume capacity of these zeolites.

The data on the bicharged cation exchange on zeolites on concentration are relatively insufficient [3, 8, 9], general regularities being manly the same as for the charged ions: zeolite exchange capacity depends essentially on the concentration of solution and it increases with its decrease. The decrease of the absorbed ions number with the solution concentration increase shows that the ion

exchange reactions on zeolites studied obey the law of acting mass. Besides, the results obtained show that in real conditions it is impossible to achieve such high stages of sorption that are usually obtained in distilled water.

Tab. 1. Partition coefficients (K_p, cm^3/g) of heavy metals on zeolites for various solution concentrations C; L:S =1:200, fraction – 0.25–0.4 mm; T=293.15 K, pH=2.

C, mol/dm^3	Zeolite	Cu	Pb	Hg	Cd
		K_p			
0.005	Clinoptilolite	104	127	145	97
	Erionite	10211	1640	1121	5105
	NaY	1601	2940	2673	672
	NaX	3025	5351	5906	1910
	NaA	9230	13921	13230	8450
0.01	Clinoptilolite	8.1	23	34.5	7.6
	Erionite	74.5	132	482	32.5
	NaY	140	234	522	105
	NaX	367	1640	822	294
	NaA	2780	7810	3240	928
0.02	Clinoptilolite	2.5	10.2	16.4	3.7
	Erionite	15.5	52.4	142	7.3
	NaY	74.8	84.6	97	51.5
	NaX	122	132	251	76.1
	NaA	151	251	520	97.2

In the case of the metals studied the change of zeolites selectivity depends mainly on electronic configuration (Table 2) and not always agrees with the order of ions size decrease and hydration energy increase.

Tab. 2. Ionic radius, electronic configuration and thermodynamic characteristics of ions Pb^{2+}, Hg^{2+}, Cd^{2+}, Cu^{2+}.

Ion	Electronic configuration	Ionic radius, nm	$-\Delta H^0_g$, kJ/mole	$-\Delta S^0_g$, J/(mole·K)	$-\Delta G^0_g$, kJ/mole·
Pb^{2+}	$6p^2$	0.132	1514	125	1477
Hg^{2+}	$5d^{10} 6s^2$	0.110	1853	171	1803
Cd^{2+}	$4d^{10} 5s^2$	0.103	1836	201	1778
Cu^{2+}	$3d^{10} 4s^1$	0.080	2129	247	2054

Zeolites sorption characteristics of heavy metals depends essentially on acidity of the solution (Table 3).

Tab. 3. Partition coefficients (K_p, cm^3/g) of heavy metals on zeolites at various temperatures L:S=1:200, fraction-0.25–0.4 mm, T=293,15 K, pH=2, C=0.01 mole/dm^3.

Zeolite	Cu		Pb		Hg		Cd	
	293.15	328.15	293.15	328.15	293.15	328.15	293.15	328.15
	K_p							
Clinoptilolite	8.1	11.2	23	127	34.5	235	7.6	31.5
Erionite	74.5	84	132	153	482	769	32	68.2
NaY	140	290	234	480	522	959	105	110
NaX	367	527	1640	1860	822	1526	294	352
NaA	2780	5098	7810	9240	3240	4945	928	1530

The data of heavy metals K_p values on zeolite in relation to pH (Table 4) of the solution show heavy metals ion sorption in the range of pH studied to increase with the increasing pH. Such a dependence of sorption upon pH of the solution shows zeolites to be slightly acidic ion exchangers; and heavy metals sorption on zeolites proceeds according to the ion exchange mechanism.

The data obtained about heavy metals sorption on zeolites show that considerable discrepancies are observed in zeolite behavior in the ion exchange. The analysis of literary data [9, 10] showed selectivity and thermodynamic constants of zeolites to depend largely upon the relationship of SiO_2/Al_2O_3 in the zeolite composition.

Thus when cations are exchanged on high silica zeolites (clinoptilolite, erionite and zeolite Y) the most important factor is the interaction of exchanged ions with the lattice, and in the case of low silica zeolites whose frame contains the great number of aluminium atoms the exchange process is determined by the change of hydration degree of big cavities.

The comparison of the data obtained (Tables 1, 3, 4) allowed to suggest the range of zeolites selectivity as far as heavy metals cations: NaA>NaX >NaY> erionite> clinoptilolite are concerned. This range correlated well with the SiO_2/Al_2O_3 relation values according to which low silica zeolites have substantially higher sorption-selective ability than the silica ones.

On the basis of the data obtained (Table 1) we may suggest the following ranges of zeolites sorption applicability for heavy metals cations:
- for high silica ones – Hg> Pb> Cu> Cd;
- for low silica ones – Pb> Hg> Cu> Cd.

Generalizing the results obtained the following conclusion can be drawn: the sorbents studied possess high absorbing ability for heavy metals at their low

equilibrium concentrations in solutions and low pH values; and may be used for water sorption from these metals.

Tab. 4. Influence of pH on the partition coefficients (K_p, cm^3/g) on zeolites (p:т=1:200), fraction – 0.25–0.4 mm; T=293,15 K, pH=2, C=0.005 mole/dm^3 (K-suspension).

Zeolite	Cu		Pb		Hg		Cd	
	pH=2	pH=5	pH=2	pH=5	pH=2	pH=5	pH=2	pH=5
	K_p							
Clinoptilolite	104	31	127	317	145	K	97	102
Erionite	1021	3190	1640	7953	2120	K	510	1504
NaY	1601	6210	2940	12540	3900	K	672	2074
NaX	3025	8320	5351	17191	5670	K	1910	6080
NaA	9230	12820	13921	47365	12900	K	8450	11840

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