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Water pollution

KINETICS AND THERMODYNAMICS OF COPPER, CADMIUM AND LEAD REMOVAL BY NATURAL AND MODIFIED ZEOLITE

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Abstract. Some kinetic and thermodynamic parameters have been found for the process of removal of cadmium (Cd^{2+}), copper (Cu^{2+}), and lead (Pb^{2+}) ions from their water solutions by natural and modified (with NaCl) Bulgarian zeolite. The overall rate constant, the equilibrium constant and the apparent activation energy have been determined for the uptake process. Standard free energy, standard enthalpy and standard entropy of the adsorption process have been calculated. Influence of zeolite modification on kinetics and thermodynamics of the process of heavy metal ions removal is pointed out. Results obtained throw more light on Cd^{2+}, Cu^{2+} and Pb^{2+} uptake by zeolite and can be used for intensifying the work on finding more environmentally friendly technologies for wastewater purification from heavy metal ions.

Keywords: heavy metal ions, zeolites, wastewater.

AIMS AND BACKGROUNDS

Zeolites represent a perspective material for removing ions of heavy metals from wastewater because of their relatively low price coupled with the fact that their exchangeable ions are relatively harmless Na^+, Ca^{2+} and K^+. In addition, zeolite loaded with heavy metal ions can be easily regenerated. Mainly zeolites removal ability and selectivity have been studied. Also, influence of processs parameters and zeolites modification on the effectiveness of pollutants uptake has been investigated. The thermodynamic analysis of results obtained from zeolites use in wastewater treatment has been restricted to data processing and fitting to Freundlich and Langmuir adsorption isotherms, with few exceptions[1-3]. Kinetics of pollutants uptake has been studied mainly in terms of finding the dependence "uptake, %/ time of contact" or breakthrough curves by frontal dynamic methods[1]. Some attempts to find the reaction order and other kinetic parameters have been made mainly for clays[4,5]. In order to implement successfully the zeolites technology on a practical basis more fundamental knowledge is needed on thermodynamics and kinetics of pollutants uptake by zeolite. The goal of work presented was to determine some thermodynamic and kinetic parameters describing the uptake of heavy metal ions by natural zeolite and to investigate the influence of zeolites modification on kinetics and thermodynamics of the process of heavy metal ions removal.

EXPERIMENTAL

Bulgarian natural zeolite with the following chemical composition, in mass % was used: SiO_2 – 68.70, Fe_2O_3 – 2.28, TiO – 0.15, Al_2O_3 – 11.83, CaO – 2.66, MgO – 0.76, MnO – 0.04, Na_2O – 1.60, K_2O – 4.01, P_2O_3 – 0.14, SO_3 – 0.225, ignition loss – 7.62, totally – 100.02. Clinoptilolite was the predominating material. Zeolite was modified by placing in a contact with 2 mol dm^{-3} NaCl (with and without heating), at a ratio of solution volume to mass of zeolite = $1 dm^3$:100 g. Solutions containing heavy metal ions (Me^{2+}) were prepared by dissolving corresponding quantities of metal nitrates – p.a. in distilled water. Solutions were analyzed by means of ICP – AES analysis. Zeolites composition was determined by means of a classical silicate analysis. Solutions pH value was measured with the aid of Metrohm E 588 pH-mV-meter. Experiments were conducted batchwise; 1 g of zeolite contacting with solutions was stirred by means of a LR 40–Medingen/Dresden paddle stirrer. Temperature was kept constant with the aid of a universal ultra-thermostat UTU-2/77 (Poland). Cation exchange capacity (CEC) of zeolite was determined by means of modified Kjeldahl method, as described in Ref. 1.

Experimental conditions found in our previous works[6,7] were the following: solutions concentrations – 50 mg dm^{-3} Me^{2+}; solutions pH value of 5; zeolite particles size – 0.09–0.325 mm; solution to zeolite ratio – 100:1.

Uptake efficiency was calculated using the equation:

$$\text{uptake, \%} = [(C_o - C_{eq}) / C_o] \times 100 \qquad (1)$$

where C_o is the initial concentration of pollutant, mg dm^{-3}, C_{eq} is the equilibrium concentration of pollutant, mg dm^{-3}.

Data obtained were processed with the aid of EXCEL'97 computer program. Each experimental result was obtained by averaging the data from two parallel experiments.

Data obtained were fitted to kinetic equations (used by other authors for similar natural systems[4,5,8]) for the first order reversible, first and second order irreversible reactions and kinetic equation describing adsorption of heavy metal ions uptake by zeolite. Data fitting to equations was tested in the usual way[9], i.e. processing the data in a suitable manner and checking whether they obey the straight line found after corresponding mathematical transformations. Kinetic equation found describes the uptake process at room temperature.

The apparent energy of activation of the process was determined in the usual way, using the Arrhenius equation and the fact that concentration of reagents practically does not depend on the temperature[9]. Energy of activation was found from the plot of ln v versus $1/T$, where v is the average rate of metal ion uptake by zeolite at temperature T. Uptake data found at room temperature were processed for fitting to the Freundlich and Langmuir isotherm. To calculate values of the thermodynamic parameters describing the heavy metal ions uptake by zeolite the following equations were used:

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$$\Delta G^{o} = -RT\ln K \quad (2)$$

$$\Delta H^{o} = [RT_1T_2 / (T_2 - T_1)] \ln (K_2/K_1) \quad (3)$$

$$\Delta S^{o} = (\Delta H^{o} - \Delta G^{o}) / T \quad (4)$$

where R is the gas constant, K, K_1 and K_2 – the equilibrium constants at temperature T, T_1 and T_2, respectively. The equilibrium constant was calculated from:

$$K = C_{eq,s} / C_{eq,l} \quad (5)$$

where $C_{eq,s}$ and $C_{eq,l}$ are the equilibrium concentrations of Cu^{2+} in solution and on the sorbent correspondingly.

RESULTS AND DISCUSSION

Treatment with NaCl causes increase in Na^+ and decrease in Ca^{2+} relative amounts in zeolite, leading to increase of the ratios Na^+/K^+ and Mg^{2+}/Ca^{2+}. CEC of zeolite treated with NaCl was 155.841 meq/100 g versus 132.729 meq/100g of natural zeolite.

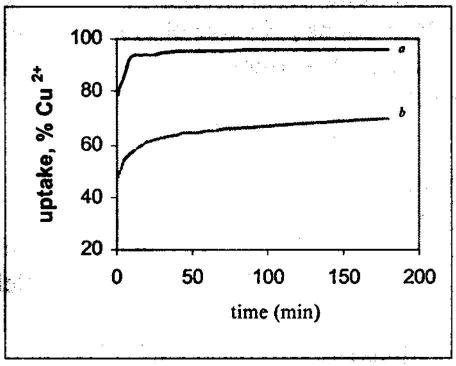

Fig. 1. Uptake of Cu^{2+} by:
a – natural zeolite, *b* – modified zeolite

Kinetics of Me^{2+} uptake by natural and modified zeolite is presented in Figs 1–3. Kinetic equations best describing the uptake process, corresponding coefficients of correlation (r), overall rate constants (k) and values found for the apparent energy of activation are presented in Table 1. Faster Me^{2+} uptake by zeolite modified with NaCl in the beginning (of the contact) that leads to an increase in Me^{2+} removal probably is due to the raised relative concentration of more easily ex-

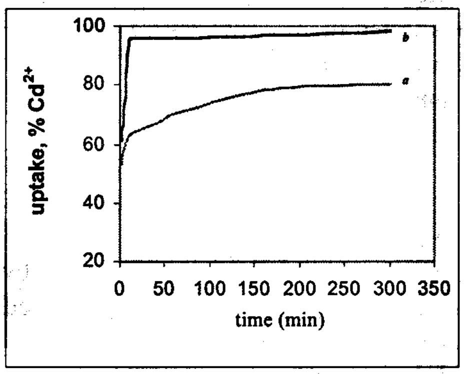

Fig. 2. Uptake of Cd^{2+} by:
a – natural zeolite, *b* – modified zeolite

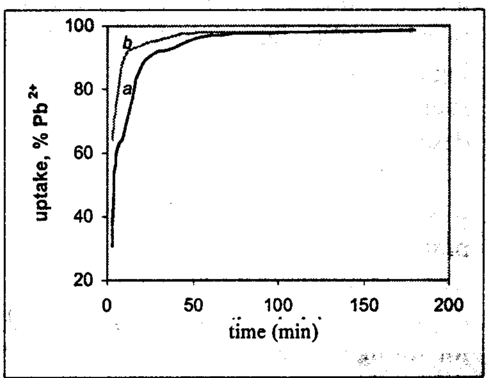

Fig. 3. Uptake of Pb^{2+} by:
a – natural zeolite, *b* – modified

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changeable Na^+ and increased CEC as a result of the modification. Decreased value of E_a for Cu^{2+} and Cd^{2+} uptake also shows that zeolite modification with NaCl facilitates the uptake process. Values obtained for the apparent energy of activation imply that the process can be easily carried out with a satisfactory rate.

Thermodynamic data found for the heavy metal ions uptake by natural and modified zeolite are presented in Table 2.

Table 1. Some parameters describing kinetics of heavy metal ions uptake by natural and modified with NaCl zeolite

Zeolite	Metal ions: Cd^{2+}	Cu^{2+}	Pb^{2+}
Natural	2nd order r=0.948 k=0.417×10^{-3} dm^{3}mol^{-1}s^{-1} E_a=18.374 kJ mol^{-1}	2nd order r=0.905 k=0.875×10^{-3} dm^{3}mol^{-1}s^{-1} E_a=18.390 kJ mol^{-1}	2nd order r=0.976 k=16.430×10^{-3} dm^{3}mol^{-1}s^{-1} E_a=5.128 kJ mol^{-1}
Modified	2nd order r=0.925 k=5.002×10^{-3} dm^{3}mol^{-1}s^{-1} E_a=15.151 kJ mol^{-1}	2nd order r=0.890 k=14.10×10^{-3} dm^{3}mol^{-1}s^{-1} E_a=10.768 kJ mol^{-1}	2nd order r=0.928 k=17.503×10^{-3} dm^{3}mol^{-1}s^{-1} E_a=12.793 kJ mol^{-1}

Table 2. Thermodynamic data on heavy metal ions uptake by natural and modified with NaCl zeolite

Metal ions	T (K)	$K_{equil.}$	ΔG (J mol^{-1})	ΔH (J mol^{-1})	ΔS (J mol^{-1} K^{-1})
Cd^{2+}, natural	300	3.89	-3390.99	2076.80	18.22
	310	4.00	-3573.25	24529.50	90.65
	320	5.08	-4298.48		
Cd^{2+}, modified	300	25.33	-8061.91	-32049.36	-79.96
	310	16.74	-7262.43	-13144.02	-18.97
	320	14.72	-7110.64		
Cu^{2+}, natural	298	3.00	-2732.91	11807.47	48.63
	305	3.50	-3176.97	22264.60	83.41
	315	4.62	-4011.14		
Cu^{2+}, modified	298	19.63	-7376.50	11499.49	63.13
	305	21.50	-7780.65	8037.82	51.86
	315	23.78	-8299.29		
Pb^{2+}, natural	300	14.25	-6626.34	-12191.84	-18.55
	310	12.17	-6440.82	-7415.74	-3.14
	320	11.42	-6418.81		
Pb^{2+}, modified	300	12.93	-6384.76	14831.37	70.72
	310	15.66	-7091.96	7838.00	48.16
	320	16.75	-7429.09		

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Negative values found for ΔG are indicative for the spontaneous nature of the uptake process both for natural and modified zeolite. More negative values of ΔG as well as the increased values of the equilibrium constant obtained for modified zeolite in the case of Cd^{2+} and Cu^{2+} can be related with the increased uptake of Cd^{2+} and Cu^{2+} by modified zeolite. Bigger increase in Cu^{2+} uptake compared to increase of Cd^{2+} uptake by modified zeolite may be related with the bigger decrease of ΔG and bigger increase of K_{equil} for the process of Cu^{2+} uptake by modified zeolite. Values found for ΔG, K_{equil} and E_a for the three Me^{2+} are in a good agreement with the uptake observed for these ions by natural and modified zeolite at temperature of 298-300 K and with the findings of other authors.

CONCLUSIONS

Thermodynamic parameters obtained for the uptake of Cd^{2+}, Cu^{2+} and Pb^{2+} by natural and modified with NaCl zeolite show that the uptake process is spontaneous. Modification with NaCl decreases ΔG and increases K_{equil} which leads to increased possibility for Cd^{2+} and Cu^{2+} uptake. Modification with NaCl does not improve considerably the uptake of Pb^{2+} at room temperature, which corresponds to change found in values of ΔG and K_{equil} and to increased value of E_a as a result of modification. Values obtained for the overall rate constants and E_a show that the uptake process is fast and easily to be conducted.

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