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Influence of Alginate Encapsulation on Point of Zero Charge (pH_{pzc}) and Thermodynamic Properties of the Natural and Fe(III) - Modified Zeolite

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Abstract

In this paper influence of alginate encapsulation on point of zero charge (pH_{pzc}) and thermodynamic properties of the natural and Fe(III)- modified zeolite were investigated. The pH_{pzc} was determined by using 0.1000 g of the samples and 50 cm³ of the solution containing KNO₃ in concentrations of 0.0001–0.01 mol/dm³ for initial pH (pH_i) in range between 2 and 12. The obtained pH_{pzc} were 6.2 for natural (NZA) and 6.5 for modified zeolite encapsulated with alginate (FeA). Influence of the temperature on the adsorption of lead was investigated for different initial lead ions concentrations (180–3200 mgPb²⁺/dm³) and temperatures of 30, 40 and 60°C. For both adsorbents, adsorption of lead ions increased with increasing its initial concentration as well as with increasing of the temperature. Also, the best fits of the experimental data were obtained by Freundlich isotherm. The temperature had positive influence adsorption and removal of lead ions increased with increasing its initial concentration as well as with increasing of the temperature. The thermodynamic parameters (the standard free energy of adsorption, standard enthalpy and standard entropy) were also determined. The results showed that lead ions removal from aqueous solutions is much favourable for FeA then NZA.

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1. Introduction

Toxic metals are discharged to the environment mainly as industrial wastes and represent a serious problem to human health, living resources and ecological systems. Due to their toxicity and tendency to accumulate in living organisms, the treatment methods for heavy metals removal are essential [1]. Among numerous methods for water purification, sorption technologies such as adsorption and ion exchange have gained the most attention because of low cost and easy operation [2]. In recent years, a lot of studies have been obtained with aim of the selection and/or production of low-cost adsorbents with good adsorption capacities for heavy metals. These materials in unmodified forms could be used as an alternative to the most used, but expensive adsorbents for wastewater treatment such as activated carbon [3-5], but also, in order to improve their adsorption properties and applicability, various modifications may be performed [6-10].

In our previous studies [11, 12] natural zeolite with particle size $<0.043\text{mm}$ (NZ) was modified with Fe(III) ions in order to improve its adsorption properties for lead ions. Results showed a significant increase of the adsorption capacity after modification (from 66 mg/g for natural to 133 mg/g for Fe(III)-modified zeolite). However, even Fe(III)-modified zeolite (FeZ) demonstrated good adsorption properties for lead, the main limitation for practical applications is its inappropriate physical i.e. powder form. Thus, its additional modifications are needed. For that reason, in another study [13] encapsulation of the FeZ with Na-alginate was performed. Results showed that after immobilization with polymer molecule, the micro-sized particles were fixed by alginate in spherical beads with size 2-3mm. The obtained composite beads remain shape and stability and consequently kept the water solution transparent. From that point applied modification could solve problems with water turbidity or facilitate filtration and separation solids from liquid. At the same time, modification had no negative effect on adsorption capacities of the starting materials, and after encapsulation maximum adsorbed amount of lead changed from 66 to 102 mg/g for the natural zeolite and from 134 to 136 mg/g for the Fe(III)-modified zeolite.

On efficiency of heavy metals removal different factors may influence such as: temperature, heavy metals or adsorbent concentrations, pH, etc. The pH is a very important parameter because pH influences chemical speciation of the metals in solutions and also on the ionization of chemically active sites on the adsorbent surface [14]. In our previous papers [13, 15] it was investigated the effect of solution pH on the lead adsorption on natural and Fe(III)-modified zeolite before and after encapsulation with alginate for initial pH from 2.5 up to ~ 5.5 . It was concluded that in all investigated pH range lead was predominantly in cationic, Pb^{2+} form and the best removals were obtained for initial pH higher than ~ 4 . In other studies [11, 16] surface properties of the natural and Fe(III)-modified zeolite were followed by determination of the point of zero charge (pH_{pzc}). Results showed that after modification, pH_{pzc} increased from 6.8 to 7.5 so that it was between pH_{pzc} of the NZ and clear goethite ($\text{pH}_{\text{pzc}}=9.4$) [17].

The aim of this paper is a further and extended investigation of the abilities of natural and Fe(III)-modified zeolite-alginate beads to remove lead ions from aqueous solutions. The influence of temperature on adsorption of lead by both encapsulated samples were studied. Characterization of the samples was performed by determination of the point of zero charge.

2. Experimental

All chemicals used in this study were of high purity and supplied by Sigma Aldrich Germany.

The natural zeolite-clinoptilolite from Zlatokop deposit (VranjskaBanja, Serbia) with a particle size $<0.043\text{ mm}$ had been used as a starting material in this study. The Fe(III)-modified zeolite was obtained combining the method for the goethite preparation and that for the preparation of Fe-coated zeolite [18, 19], and detailed procedure is given elsewhere [11].

The procedure for obtaining natural zeolite-alginate (NZA) and Fe(III)-modified zeolite-alginate (FeA) composite was based on a method used by Viraraghavan and Yuan [20]. A 2 % polymer solution was prepared by dissolving certain amount of sodium alginate in distilled water. After a homogenous polymer solvent mixture were prepared the natural or Fe(III)-modified zeolite was blended with sodium alginate solution. Spherical beads were

prepared by dropping the mixed solution into CaCl_2 solution. Beads 3-5 mm in diameter were formed by drop-wise extrusion through a pipette tip. The beads were hardened by placing them in 2 % solution of CaCl_2 for 24 h. The remaining beads were washed and then dried gradually at room temperature to constant weight. Finally natural zeolite-alginate beads (NZA) and Fe(III)-modified zeolite beads (FeA) were obtained with final diameter of 2-3 mm (Fig. 1) and then used for the adsorption experiments. Detailed procedure is given elsewhere [13].

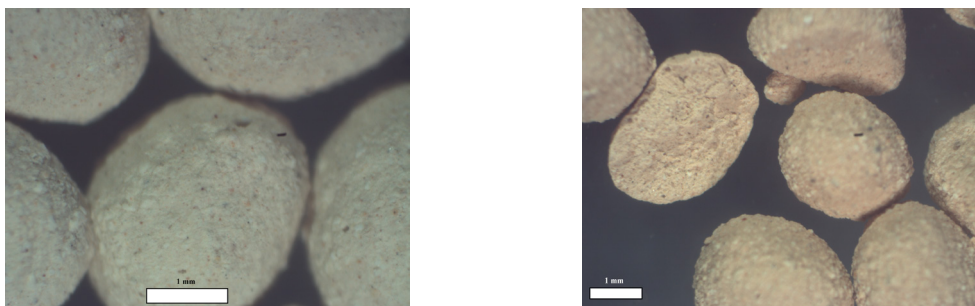


Fig. 1. Spherical beads of the natural zeolite-alginate (left) and Fe(III)-modified zeolite-alginate (right)

The point of zero charge, pH_{pzc} , of NZA and FeA was determined using the method described by Milonjić et al. [21]. Potassium nitrate, in concentrations of 0.0001–0.01 mol/dm³ was used as a background electrolyte. The initial pH values (pH_i) of each solution were adjusted in range between 2 and 12 by small additions of 0.1 mol/dm³ of HNO_3 or 0.1 mol/dm³ of KOH and measured on pH/ion meter, “Metrohm 781”. In each initial solution (50 cm³), 0.1000 g of sample was added and the bottles were shaken at 350 rpm for 24 h at room temperature, centrifuged at 10000 rpm for 10 min and the pH of each supernatant was measured (pH_f). The pH_{pzc} of the samples was determined as the plateau of the curve $\text{pH}_f = f(\text{pH}_i)$.

Influence of the temperature on the adsorption of lead was investigated for different initial lead ions concentrations by mixing 0.5000 g of the NZA or FeA with 50 cm³ of aqueous solutions, containing various initial concentrations of $\text{Pb}(\text{NO}_3)_2$ (180–3200 mgPb²⁺/dm³) at 350 rpm for a period of 24 h. Experiments were performed at three different temperatures: 30, 40 and 60°C. Initial pH in all experiments was adjusted to 4.2. After 24 h, suspensions were centrifuged and the concentrations of Pb^{2+} were determined on atomic absorption spectrophotometer (AAS) “Analytic Jena Spekol 300”. In all adsorption experiments, final pH was also measured.

3. Results

3.1. Determination of the point of zero charge (pH_{pzc})

In presented paper, pH-metric measurements were performed in order to consider if alginate at the surface of natural or Fe(III)-modified zeolite changed adsorbent surface charge by determination of the point of zero charge. For that reason, the evolution of pH of the NZA and FeA as a function of initial pH and ionic strength was studied and results are shown at Fig. 2. Obtained results were compared with previously determined values for NZ and FeZ [11, 22]. According to the literature [23], the point of zero charge (pH_{pzc}) is defined as pH of the solution at which charge of the positive surface sites is equal to that of the negative ones, i.e. the adsorbent surface charge has zero value. The surface charge is negative at $\text{pH} > \text{pH}_{\text{pzc}}$ and positive at $\text{pH} < \text{pH}_{\text{pzc}}$.

As can be seen from Fig. 2, the curves of equilibrium pH (pH_f) vs. initial pH (pH_i) show the same shape for both adsorbents and all three concentrations of the electrolyte. At first, increasing of the initial pH up to 4.6 for NZA and FeA causes increasing of the pH_f . After that, for the $\text{pH}_i < 9.0$ changing of the initial pH had no influence on the pH_f and curves reached plateaus. Further increasing of the pH_i caused increasing of the pH_f . The plateaus of each curve represent the range of the initial pH where samples showed buffer properties. That means that for initial pH from 4.6 to 9.0 for both adsorbents addition of the H^+ or OH^- has no influence on the equilibrium pHs and they are equal to point of zero charge. The obtained values of the pH_{pzc} were 6.2 for NZA and 6.5 for FeA. Finally, it can be concluded that surface of the adsorbents takes a positive charge for initial pH up to 4.6, for initial pH between 4.6 and 9.0 surfaces charge were zero, while for initial pH higher than 9 surface of the NZA as well as FeA takes a

negatively charge. The same values for the pH_{pzc} obtained for different concentrations of the KNO_3 means that pH_{pzc} is independent of the ionic strength and no specific adsorption of K^+ or NO_3^- occurred [23].

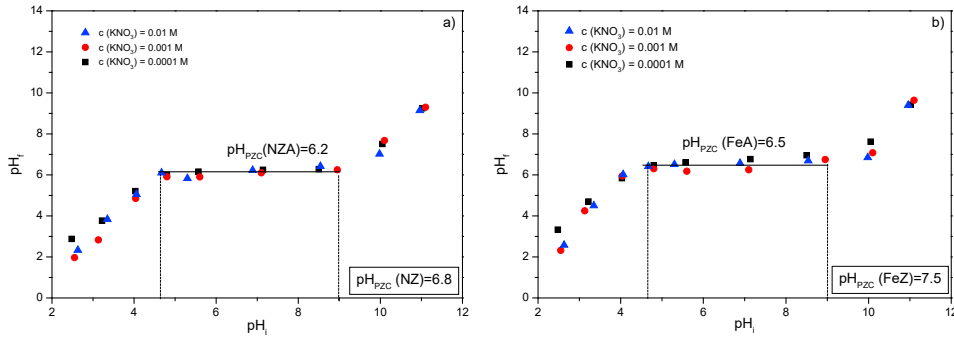


Fig. 2. Determination of the point of zero charge (pH_{pzc}). a) NZA, b) FeA.

In comparison with pH_{pzc} of the starting materials (6.8 for NZ and 7.5 for FeZ) [11, 22] it can be seen that encapsulation of the samples causes decreasing of the point of zero charge so that it was equal (NZA) or almost the same (FeA) with pH_{pzc} of the clear alginate beads ($\text{pH}_{\text{pzc}}=6.2$) [24]. That indicated that after encapsulation, surface of the starting zeolite samples is probably mainly covered by alginate molecules. After encapsulation, the buffering capacity of the NZ decreased, while for FeZ increased. From Fig. 2 it can be seen that NZA and FeA have the same width of the plateaus (the same buffer capacity) what is additional indication that surface of the NZ as well as FeZ is mainly covered by the alginate molecules.

3.2. Thermodynamic experiments

In our previous study [13] it was shown that both samples, NZA and FeA, are very stable in water as well as in lead ions solutions. Results obtained from adsorption experiments demonstrated significantly higher adsorption capacity of FeA for lead (136 mg/g) than NZA (102 mg/g). After fitting of the results with Langmuir and Freundlich adsorption model, better fitting was obtained with Freundlich isotherm. By comparison of the adsorbed amount of lead with total amount of exchanged cations (Ca^{2+} , Na^+ , Mg^{2+} , K^+) released from both adsorbents, it was clearly showed that ion exchange is the only mechanism included in removal of lead ions by NZA and FeA.

For better understanding of the adsorption process, additional experiments were performed and lead ions adsorption on NZA and FeA at three different temperatures for different initial concentrations was tested. Experiments were performed in order to determine influence of temperature on adsorption capacities of the adsorbents as well as to determine thermodynamic parameters (the standard free energy of adsorption (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°)). During these experiments final pHs were also measured and increasing of pH up to maximum ~ 6.2 for all suspensions was observed confirming that lead was predominantly and mainly in cationic- Pb^{2+} form [25]. The results of thermodynamic experiments are shown in Fig. 3.

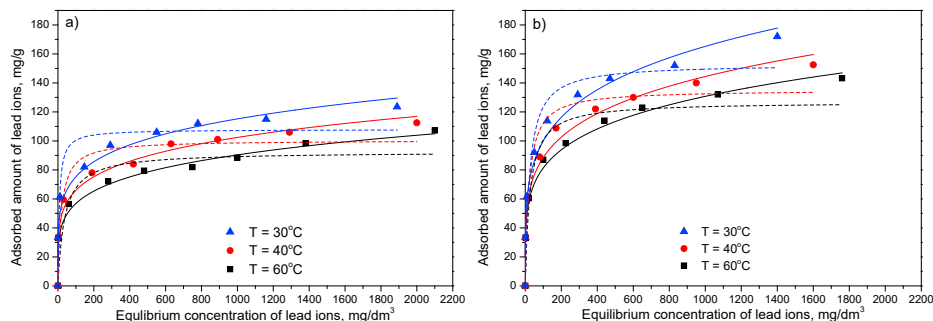


Fig. 3. Lead ions adsorption isotherms for the NZA (a) and FeA (b) obtained for three different temperatures. Solid lines (Freundlich model) and dashed lines (Langmuir model).

As it can be seen from Fig. 3, for both adsorbents, adsorption of lead ions increased with increasing its initial concentration as well as with increasing of the temperature. However, although both samples were prepared by using the same method and contain the same amount of alginate, a significantly higher adsorption capacity was obtained for FeA. The maximum adsorbed amounts of lead ions obtained for the highest initial concentration were: 107, 113 and 132 mg/g for NZA and 143, 152 and 172 mg/g for FeA at temperatures 30, 40 and 60°C respectively. The experimental results were fitted to Langmuir (Fig. 4 dashed lines) and Freundlich (Fig. 4 solid lines) models given in equations 1 (Langmuir) and 2 (Freundlich model) [26]:

$$q_e = \frac{bq_{\max}C_e}{1+bC_e} \quad (1)$$

$$q_e = K_F C_e^n \quad (2)$$

where q_{\max} is maximal adsorption capacity (mg/g); b is Langmuir constant related to heat of the adsorption (dm^3/mg); C_e is equilibrium concentration of lead ions (mg/dm^3) and q_e (mg/g) is adsorbed amount of lead ions when equilibrium amount is C_e , K_F (dm^3/mg) and n are Freundlich constants related to the adsorption capacity and factor of heterogeneity of surface, respectively. The characteristic parameters are given in Table 1.

Table 1. Characteristic parameters of the Freundlich and Langmuir isotherms.

	Freundlich model								
	30°C			40°C			60°C		
	K_F [dm^3/mg]	n	R^2	K_F [dm^3/mg]	n	R^2	K_F [m^3/mg]	n	R_2
NZA	22.50	0.20	0.9656	27.36	0.19	0.9561	32.18	0.18	0.9480
FeA	31.47	0.21	0.9562	33.27	0.22	0.9662	36.60	0.23	0.9684
	Langmuir model								
	30°C			40°C			60°C		
	q_{\max} [mg/g]	b [dm^3/mg]	R^2	q_{\max} [mg/g]	b [dm^3/mg]	R^2	q_{\max} [mg/g]	b [dm^3/mg]	R^2
NZA	93	0.027	0.8522	100	0.052	0.8751	108	0.133	0.8982
FeA	127	0.038	0.9342	135	0.049	0.9156	153	0.041	0.9173

From Table 1 it can be seen that the values of correlation coefficients of Freundlich model were higher, for both adsorbents and all temperatures, than the correlation coefficients of the Langmuir equation. That means that Freundlich isotherm better fitted the experimental data and even changes in temperature increased adsorption capacities of NZA and FeA, it had no influence on adsorption mechanism. For all temperatures, values of the Freundlich parameter, n , obtained in this study were less than one for both adsorbents, confirming that adsorption intensity was favourable over the entire range of temperature and concentration studied [27].

For better explaining of the adsorption process, results obtained during these investigations were also used for determination of the thermodynamic parameters. The ΔG° , ΔH° and ΔS° were calculated from following equations:

$$\Delta G^\circ = -RT \ln K \quad (3)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

where R is the gas constant (8.314 J/(K mol)) and K is the equilibrium constant at the temperature T , calculated as the ratio of the equilibrium lead ion adsorbed amount and equilibrium concentration in solution. The values of ΔH° and ΔS° were calculated from the slope and the intercept of linear regression of $\ln K$ vs. $1/T$ (results are not showed).

The obtained thermodynamic parameters are presented in Table 2. From Table 2 it is observed that for the initial lead ions concentrations up to 1900 for NZA, and 2350 mg/dm^3 for FeA, ΔG° was negative at all temperatures, indicating that adsorption process is spontaneous in nature. For initial lead ion concentrations higher than 1900 for NZA and 2350 mg/dm^3 for FeA, ΔG° was positive suggesting that at these concentrations adsorption process becomes non-spontaneous. For FeA, ΔG° is lower and more negative in the wider concentration range than for the

NZA, suggesting the higher number of active sites available for spontaneous adsorption of lead ions. Also, for every concentration, ΔG° becomes more negative with increasing temperature demonstrating that the adsorption capability of Pb^{2+} becomes greater at a higher temperature [28]. In comparison with results obtained for NZ and FeZ [12] it is clear that ΔG° obtained for NZA and FeA was lower, meaning that modification with alginate had a positive influence on the spontaneity of the adsorption process and increased adsorption capability for lead ions of the NZ as well as FeZ. Lower values of the ΔG° obtained for NZA and FeA can be explained by the changed adsorption mechanism for NZA and FeA, and removal of lead ions from water solutions only by ion exchange which is more energetically favourable than chemisorption which is beside ion exchange also included for NZ and FeZ.

Table 2. Thermodynamic parameters for lead ions adsorption on NZA and FeA.

	C_i (mg/dm ³)	T (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/(K mol))	R ²
NZA	335	30	-12.02	40.4	153.1	0.912
		40	-14.05			
		60	-15.81			
	625	30	-5.55	20.0	108.1	0.999
		40	-7.78			
		60	-10.91			
	970	30	-2.23	19.2	72.1	0.928
		40	-3.67			
		60	-4.76			
	1260	30	-1.21	17.4	60.4	0.924
		40	-1.80			
		60	-3.32			
	1610	30	-0.35	12.3	41.4	0.954
		40	-1.15			
		60	-1.80			
	1900	30	0.27	11.1	36.3	0.997
		40	-0.31			
		60	-1.00			
	2350	30	0.89	8.2	24.7	0.999
		40	0.52			
		60	0.03			
3125	30	1.76	2.5	15.6	0.954	
	40	7.31				
	60	7.78				
FeA	335	30	-12.44	17.5	100.4	0.972
		40	-14.74			
		60	-15.95			
	625	30	-8.42	17.7	88.1	0.995
		40	-10.15			
		60	-11.52			
	970	30	-5.35	17.8	77.4	0.961
		40	-6.27			
		60	-8.06			
	1260	30	-3.79	16.5	68.1	0.999
		40	-4.81			
		60	-6.17			
	1610	30	-2.43	12.6	50.2	0.940
		40	-2.97			
		60	-4.18			
	1900	30	-1.61	11.0	41.9	0.906
		40	-2.00			
		60	-3.07			
	2350	30	-0.45	9.9	34.7	0.999
		40	-0.99			
		60	-1.66			
3125	30	0.64	10.8	34.2	0.999	
	40	0.13				
	60	-0.55				

The enthalpy of the adsorption ΔH° is a measure of the energy barrier that must be overcome by reacting molecules during adsorption process. The values for ΔH° were all positive for both adsorbents, suggesting that the adsorption of lead ions onto NZA and FeA is endothermic in nature. Changing the temperature from 25 to 60°C ΔH° decreased from 40.4 to 2.5 kJ/mol for NZA, while for FeA, from 17.5 to 10.8 kJ/mol, confirming that increasing of the temperature favour the adsorption of heavy metal ions onto both adsorbents [28]. The possible explanation of endothermicity of heats of adsorption is that the metal ions are well solvated and in order for the metal ions to be adsorbed, they have to lose part of their hydration sheath. This dehydration process of the ions requires energy and this energy of dehydration supersedes the exothermicity of the ions getting attach to the surface and consequently, adsorption process is endothermic [29].

The entropy measures is the width of the saddle point of the potential energy surface over which reactant molecules must pass as activated complexes and its value can be an indication whether adsorption process occurs by associative ($\Delta S^\circ < -10 \text{ J/(K mol)}$) or dissociative mechanism ($\Delta S^\circ > -10 \text{ J/(K mol)}$) [30, 31]. Entropy values obtained in this study were higher than -10 J/(K mol) confirming dissociative mechanism for both, NZA and FeA. According to the literature, positive values of ΔS° could mean some structural changes in the adsorbents during the adsorption process [32]. The endothermic behaviour of the adsorption process is supported by the fact that the values of ΔS° were positive, indicating that the system entropy increased after adsorption process. Adsorption of Pb^{2+} ions on the surface of the NZA and FeA leads to the separation of hydrated water molecules before they attach to the surface of the adsorbents leading to an increase of the system disorder and thus increase its entropy [33]. Also, since ion exchange is the only mechanism included in removal of lead ions from water solutions, exchanged cations from surface of the NZA or FeA also had an influence and changed disorganization in solution.

4. Conclusion

In presented paper, the obtained values of the pH_{pzc} were 6.2 for NZA and 6.5 for FeA. The surface of the adsorbents takes a positive charge for initial pH up to 4.6, for initial pH between 4.6 and 9.0 surfaces charge were zero, while for initial pH higher than 9 surface of the NZA as well as FeA takes a negatively charge. Also, the pH_{pzc} was the same for all KNO_3 concentrations what means that there were not specific adsorption of K^+ or NO_3^- . Lower values of the pH_{pzc} for both samples (NZA and FeA) in comparison with starting materials (6.8 for NZ and 7.5 for FeZ) which is equal (NZA) or almost the same (FeA) with pH_{pzc} of the clear alginate beads ($\text{pH}_{\text{pzc}}=6.2$) indicated that after encapsulation, surface of the starting zeolite samples were mainly covered by alginate molecules.

Results of thermodynamic experiments showed that adsorption of lead ions increased with increasing its initial concentration as well as with increasing of the temperature. The maximum adsorbed amounts of lead ions obtained for the highest initial concentration were: 107, 113 and 132 mg/g for NZA and 143, 152 and 172 mg/g for FeA at temperatures 30, 40 and 60°C respectively. The best fits of the experimental results were obtained with Freundlich model. Results of determination of the thermodynamic parameters indicated that adsorption process is spontaneous in nature and also, increasing of the temperature favour the adsorption of heavy metal ions onto both adsorbents. Based on the values of the standard entropies which were higher than -10 J/(K mol) it may be concluded that in removal of lead ions dissociative mechanism is also included for both, NZA and FeA.

Acknowledgements

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