LEAD REMOVAL FROM WATER SOLUTIONS BY NATURAL AND FE(III)-MODIFIED ZEOLITE ENCAPSULATED WITH ALGINATE

Milan Kragović, Aleksandra Daković, Marija Marković, Anđela Petković,
Živko Sekulić, Mirjana Stojanović
Institute for technology of nuclear and other mineral raw materials, Franše d'Eparea 86, Belgrade, Serbia
E-mail: m.kragovic@itnms.ac.rs

ABSTRACT

In presented paper removal of lead ions from water solutions by the natural and Fe(III)-modified zeolite encapsulated with alginate was investigated. Experiments were performed for the initial lead concentrations in the range from 330 to 3100 mgPb(II)/dm^3 and for three temperatures: 25, 40 and 60°C. Results showed increase of adsorbed amount of lead with increasing temperature and the initial lead concentrations. Much better removal of lead was obtained with Fe(III)-modified zeolite encapsulated with alginate. The maximal removed amounts of lead obtained for highest initial concentration were: 103, 113 and 124 mg/g for NZA and 137, 153 and 173 mg/g for FeA at 30, 40 and 60°C, respectively. Obtained results were fitted with Freundlich and Langmuir model, and for all temperatures the best fits were obtained with Freundlich model (R^2>0.97).

Keywords: natural zeolite, Fe(III)-modified zeolite, alginate, encapsulation, lead, temperature.

INTRODUCTION

It is well known that heavy metals are very toxic, mobile in water solutions and have high tendency to accumulate in living organisms causing various diseases and disorders. For that reason, the treatment methods for their removal from contaminated waters are essential for environmental protection and human health[1]. For that purpose, adsorption and ion exchange have gained attention compared to all the other techniques used for heavy metal removal, primarily because of their low cost and easy operation. These two techniques are especially interesting in combination with the natural (organic or inorganic) materials such as alginate, chitosan, zeolites, clays, biomaterials, etc. These materials are classified as adsorbents with a potential to be widely used for purification of waters contaminated with heavy metals because they are available in large quantities, often biodegradable, relatively cheap, usually recyclable and show high adsorption ability towards a great number of heavy metals [2,3]. However, in order to improve their adsorption properties and applicability, various modifications have been performed[4], or very often, new adsorbents with improved properties were prepared by mixing or combining few adsorbents such as for example: natural zeolite-bentonite[5], alginate-kaolinite[6], etc.

In our previous studies[7,8] improved adsorption capacity for Pb(II) was obtained after modification of the natural zeolite with particle size <0.043mm with Fe(III) ions under strongly basic conditions (pH~10). Results showed a significant increase of the adsorption capacity after modification (from 66mg/g for the natural to 133mg/g for Fe(III)-modified zeolite). However, even Fe(III)-modified zeolite demonstrated good adsorption properties for lead, the main limitation for column experiments and practical application is its inappropriate physical i.e.

powder form. Thus, its additional modification is needed. Since, it is well known that alginate has a good adsorption capacity for heavy metals and especially for lead[9], in our another study[10] encapsulation of the natural and Fe(III)-modified zeolite with Na-alginate was performed. Results showed that after immobilization with alginate, the micro-sized particles of starting zeolites samples were fixed in spherical beads with average size of 2-3mm. Prepared 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 increased from 66 to 102 mg/g for the natural zeolite, while for Fe(III)-modified zeolite was practically unchanged (134 mg/g before and 136 mg/g after encapsulation).

The aim of this paper is an extended investigation of the abilities of the natural and Fe(III)-modified zeolite-alginate beads to remove lead from aqueous solutions. The influence of temperature on adsorption of lead by samples encapsulated with alginate was studied.

EXPERIMENTAL

The natural zeolite (NZ) clinoptilolite from Zlatokop deposit, Serbia with a particle size <0.043 mm was used as a starting material. The mineralogical composition of the natural zeolite was primarily clinoptilolite with small amounts of quartz and feldspar (X-ray powder diffraction analysis)[10]. The Fe(III)-modified zeolite (FeZ) was obtained according to procedure given elsewhere[7]. The natural and Fe(III)-modified zeolite-alginate composites were prepared using a method described by Mahamadi and Zambara[11]. Briefly, a 2g of Na-alginate was dissolved in 100cm^3 of distilled water and agitated for 24h at 300rpm. Then, 10g of the NZ or FeZ was blended with 100cm^3 of 2% Na-alginate solution for 2h. Spherical beads were prepared by dropping the mixed solution into 0.1mol/dm^3 $CaCl_2$ solution. The beads were hardened by placing them in 2% solution of $CaCl_2$ for 24h. The remaining beads were 5 times washed with water (for every time agitated at 100rpm for 30min). Finally, the beads were dried at room temperature to the constant weight.

The influence of temperature on adsorption of lead was investigated for four different initial lead ions concentrations (330, 1600 2100 and 3100 mgPb(II)/dm^3) by mixing 0.5g of the encapsulated samples with 50 cm^3 of aqueous solutions containing various initial concentrations of $Pb(NO_3)_2$ at 350 rpm for 24 h. Experiments were performed at three different temperatures: 30, 40 and 60^{o}C. The initial pH in all experiments was adjusted to 4.2. After 24 h, suspensions were centrifuged and the initial and non-adsorbed amounts of Pb(II) were determined on atomic absorption spectrophotometer (AAS) “Analytic Jena Spekol 300”.

RESULTS AND DISCUSSION

The results of removal of lead by natural zeolite-alginate (NZA) and Fe(III)-modified zeolite-alginate (FeA) samples at different temperatures are shown in Figure 1. As can be seen, for both adsorbents, adsorption of lead increased with increasing its initial concentration as well as with increasing of temperature. However, although both samples were prepared by using the same method and contain the same amount of alginate, significantly higher adsorption capacities were obtained for FeA. The maximum adsorbed amounts of lead calculated for the highest initial concentration (3100 mg/dm^3) were: 103, 113 and 124 mg/g for NZA and 137, 153 and 173 mg/g for FeA at 30, 40 and 60°C respectively. Differences in adsorption capacities at the same temperatures obtained for NZA and FeA indicate that active centers in NZ for NZA or FeZ for FeA are still available for lead adsorption. On the other side, higher adsorption capacities of the NZA and FeA in comparing with starting zeolites samples (NZ and FeZ)[11] suggests that alginate also contribute to lead adsorption by these composites.

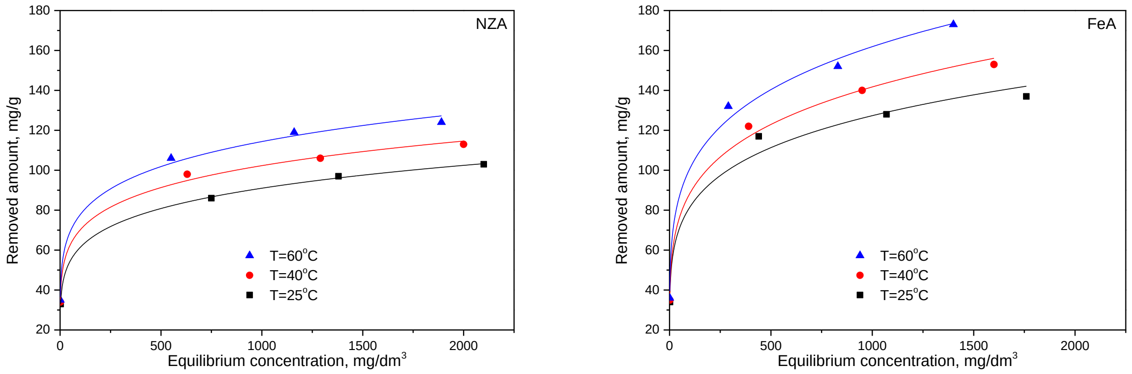

Figure 1. Lead ions adsorption onto the NZA and FeA, obtained at three different temperatures.

In order to better understand mechanism of lead removal results were fitted to the two most common adsorption models (Langmuir (eq. 1) and Freundlich (eq. 2)):

$$q_e = \frac{bq_{\max}C_e}{1+bC_e} \tag{1}$$

$$q_e = K_F C_e^n \tag{2}$$

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

Table 1. Parameters of the Freundlich and Langmuir isotherms for NZA and FeA.

		Freundlich isotherm			Langmuir isotherm		
T, °C		K_F (dm^3/mg)	n	R^2	$q_{\max}$ (mg/g)	b (dm^3/mg)	R^2
25	NZA	27.94	0.17	0,9994	95.76	0.20	0.8306
	FeA	33.34	0.19	0.9731	128.41	0.16	0.8611
40	NZA	32.97	0.16	0.9945	106.00	0.31	0.8594
	FeA	34.31	0.21	0.9917	156.61	0.01	0.8079
60	NZA	35.98	0.17	0.9935	116.68	0.39	0.8517
	FeA	39.05	0.22	0.9906	178.12	0.01	0.8280

From Table 1 it can be seen that the values of correlation coefficients of Freundlich model which predicted adsorption on heterogeneous surfaces were higher, for both adsorbents and all temperatures, than the correlation coefficients of the Langmuir model characteristic for adsorption on homogeneous surfaces. That means that Freundlich isotherm better fits the experimental data and even changes in temperature increased adsorption capacities of NZA and FeA, it had no influence on adsorption mechanism. Better fitting of the obtained results with Freundlich model additionally suggests that adsorption of lead on NZA and FeA occurred on both, alginate and starting zeolites (NZ in NZA and FeZ in FeA).

CONCLUSIONS

Presented results showed that removal of lead ions from water solutions by NZA and FeZA increased with increasing its initial concentration and temperature. Significantly higher adsorption capacity was obtained for FeA. Obtained differences in adsorption capacities indicated that active centers in NZ or FeZ in composite samples are still available–for lead adsorption, while higher adsorption capacities in comparing with starting zeolites samples suggests that alginate also contribute to lead adsorption by these composites.

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