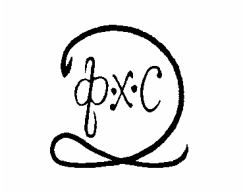

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USING OF THE NATURAL AND Fe(III)-MODIFIED ZEOLITE-ALGINATE BEADS FOR ADSORPTION OF LEAD IONS FROM WATER SOLUTIONS

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ABSTRACT

In this paper, adsorption of lead ions from water solutions by thenatural (NZA) and Fe(III)-modified zeolite-alginate (FeA) beads was investigated. Experiments were performed for different initial concentrations and results showed improving adsorption properties of the starting materials (natural (NZ) and Fe(III)-modified zeolite (FeZ)) after modification with alginate. Also, for both adsorbents, direct relation between initial concentration and adsorbed amount of lead was observed. Much higher adsorption of lead was obtained by FeA than NZA. Results also showed that presence of alginate, beside improving adsorption properties have a positive influence on physical properties of starting samples. After immobilization of the starting samples with alginate no falling apart of the beads was noticed and there was no water turbidity.

INTRODUCTION

Clinoptilolite is the most common natural zeolite in the nature. Dueto its high crystallinity, non-toxicity, highly selectiveion-exchange capacity, etc. It has found wide application and very often is used as heavy metals adsorbents. In our previous studies [1, 2] in order to improve adsorption properties of natural zeolite-clinoptilolite(NZ) for lead ions from water solutions, its surface with particle size -43μm (NZ) was modified with Fe(III) ions under strongly basic conditions. Results showed that although NZ has high adsorption capacity for lead(0.32mmol/dm^3) after its modification (FeZ) adsorption capacity increased to 0.64mmol/dm^3.However, even NZ and especially FeZ showed good adsorption properties, their powder form and micrometric particle size may cause water turbidity and problems with separation liquid from solid and that couldlimits their practical use. Using materials with higher particle size for solving these problems is not the best solution due to inverse proportionality of the adsorption capacity and particle size [2]. Thus,

immobilization and using polymer molecule such as alginate for solving these problems could be better choice.

Alginate, isa polysaccharide composed of anionic blocks of 1,4linked α-L-gluronic acid (G) and β-D-mannuronic acid (M). It is biodegradable and non-toxicbiopolymer. Also, alginate can decrease the pressure drop in the columnar operations, and the most importanthas high affinity for heavy metals, especially for Pb^{2+} ions[3, 4]. Thus, alginate has recently been used to improve properties of different materialsand increasetheir chemical, mechanical stability and applicability.

In this study, adsorption of lead from water solutions by the natural and Fe(III)-modified zeolite-alginate beads was followed. The influence of initial lead concentration on adsorption properties of materials in batch mode was investigated.

EXPERIMENTAL

The natural zeolite clinoptilolite from Zlatokop, Serbia with a particle size -43μm (NZ) was used as a starting material. The mineralogical composition of the natural zeolitic tuff was primarily clinoptilolitewith small amounts of quartz and feldspar determined by X-ray powder diffraction analysis (XRPD)(Figure 1a). The Fe(III)-modified zeolite (FeZ) was obtained according to procedure given elsewhere [1].

Natural zeolite-alginate (NZA) and Fe(III)-modified zeolite-alginate (FeA) compositeswere obtained by using a method described by Viraraghavan and Yuan [5]. Briefly, a2g of Na-alginate was dissolved in 100cm^3 of distillated 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 washed by mixing with 250$cm^3$of distillated water and agitated at 100rpm for 30min, discarding the solution and then repeating the process 5 times. Finally, the beads were dried at room temperature to the constant weight.

Adsorption of lead by NZA and FeA was investigated by mixing 0.5g of the adsorbents with 50cm^3 of aqueous solutions, containing various initial concentrations of Pb^{2+} (1.6-15mmol/dm^3) at 25^{o}C and initial pH 4.2. After 24h, suspensions were centrifuged and amounts of Pb^{2+}were determined on atomic absorption spectrophotometer “Analytic Jena Spekol 300”.

RESULTS AND DISCUSSION

Encapsulation of the NZ and FeZ with alginate, improved their mechanical properties. Thus, after modification, NZ and FeZ were transformed from

powder with particle size -43μm into 2-3 mm spherical beads form. The shape of beads remains constant in water solutions and consequently there was no water turbidity what is very important for experiments in column and application under real conditions.

The natural and Fe(III)-modified zeolite before and after encapsulation were characterized byXRPD analysis and patterns are shown in Figure 1.

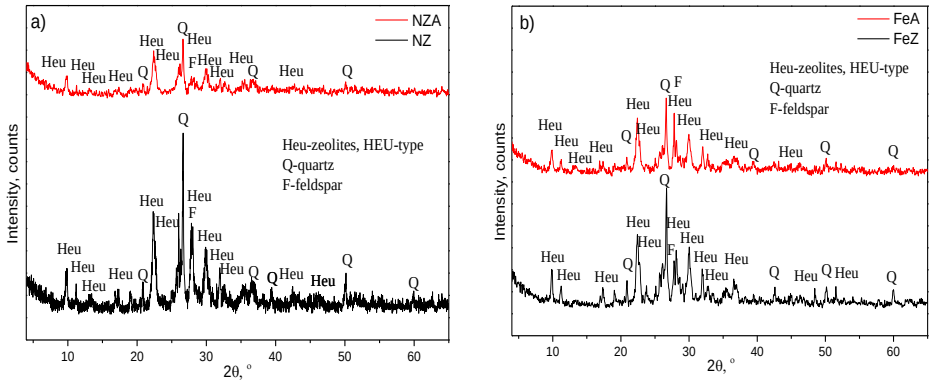

Figure 1. XRPD patterns of: a) NZ and NZA; b) FeZ and FeA.

As can be seen from Figure 1, Fe(III)-modified zeolite is characterized by lower crystallinity than the NZ. It seems that theFeZ maintain the main characteristic peaks of starting zeolite, but with the significantly lower intensity.However, additional Fe-oxidic or oxo-hydroxidic crystalline phases were not observed at X-ray diffractograms. In spectra of the NZA and FeA decreasing of intensities of all peaks were also obtained indicating lowering of the crystallinity of the parent samples. Also, after modification with alginate additional peaks were not observed, meaning that there are no new crystalline phasesin NZA and FeA.

For practical application it is also important that applied modification has no negative effect on adsorption properties of the starting samples. From that reason removal of leadfrom water solutions by NZA and FeA was investigated for different initial lead concentrations and results are shown at Figure 2.As can be seen from Figure 2 for NZA as well as for FeA, adsorbed amount of lead increased with increasing its initial concentration. However, even both adsorbents were modified under same conditions, for all initial concentrations higher amount of removed lead ions was obtained for FeA.Thus, for initial concentration 1.6 mmol/dm^3 adsorbed amounts of lead ions were 0.15mmol/dm^3 for NZA and 0.17mmol/dm^3 for FeA, while for initial concentration of 15.1mmol/dm^3 adsorbed amounts were 0.50 and 0.66mmol/dm^3 for NZA and FeA, respectively. Since both adsorbents were treated with the same amount of alginate, obtained differences in adsorption

properties indicated that beside alginate, adsorption of lead also occurred on active centers on NZ in NZA and FeZ in FeA. Comparing the results obtained in this study for NZA and FeAwith those for NZ and FeZ (0.32 and 0.64 mmol/dm3, respecitevely) [1] showed that encapsulation with Na-alginate has positive influence on removal of lead ions from water solutions by both, NZ and FeZ.

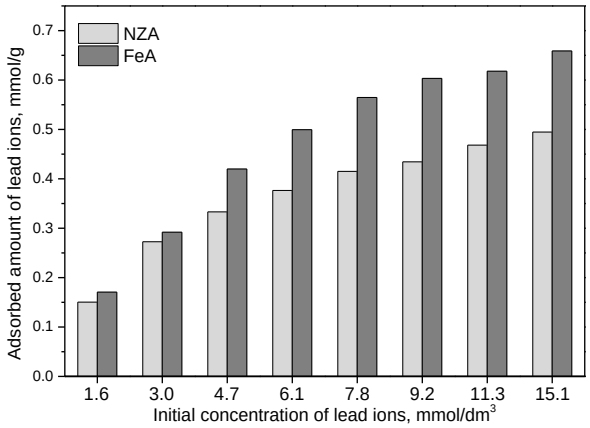

Figure 2. Adsorption of lead by NZA and FeA for different initial concentrations

CONCLUSION

From presented results it can be concluded that modification of the NZ or FeZ with Na-alginate improved adsorption properties of the starting materials. For both samples, adsorbed amount of lead increased with increasing its initial concentration in solution. For all initial concentration adsorbed amount of lead by FeA was higher than by NZA.

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REFERENCES

[1] M. Kragović, A. Daković, Ž. Sekulić, M. Trgo, M. Ugrina, J. Perić, G. Diego Gatta, Appl. Surf. Sci. 2012, **258**, 3667–3673.
[2] M. Kragović, A. Daković, M. Marković, J. Krstić, G.D. Gatta, N. Rotiroti, Appl. Surf. Sci. 2013, **283**, 764–774.
[3] R. Cheraghali, H.Tavakoli, H. Sepehrian, Sci. Iran. 2013, **20**, 1028-1034.
[4] F. Wang, X. Lu, X. Li, J. Hazard. Mater. 2016,**306**, 75-83.
[5] G. Yan, T. Viraraghavan, Bioresour. Technol. 2001, **78**, 243–249.