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Original scientific paper

URANIUM(VI) ADSORPTION ON NATURAL AND MODIFIED CLINOPTILOLITE MINERAL

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Abstract: In this paper the investigation results of adsorption of uranyl ion on unmodified and acid modified clinoptilolite are presented. Adsorption was investigated at different amounts of adsorbents in suspension, different concentrations of uranyl ion in solution, as well as at different pH values.

Keywords: Zeolite, Adsorption, Uranyl ion

1 INTRODUCTION

Uranium is the most important element for the nuclear industry. It has a long half-life and is observed to have a coordination chemistry consisting of multiple stable oxidation states and stable solid and aqueous forms within the ecosphere. Under standard environmental conditions, uranium typically occurs in the hexavalent form as the mobile, aqueous uranyl $(UO_2)^{2+}$ ion (Sylwester, Hudson and Allen, 2000).

Adsorption of uranium (VI) ion onto various solids is important from purification, environmental and radioactive waste disposal points of view. In the last decades, the adsorption of uranium (VI) on activated carbon, metal oxides, as well as on natural and modified aluminosilicate adsorbents, has been the subject of many investigations (Seaman, Meehan and Bertsch, 2001, Chisholm-Brause et al.2001, Bors, Dultz and Riebe, 1999).

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2 EXPERIMENTAL

X-ray diffraction (XRD) was employed for the identification of the mineral composition of the starting sample (Phillips PW/1710). The quantitative chemical analysis of the samples was conducted by the silicate method, SiO_2 content and I.L. (loss on annealing at 1000°C) were determined gravimetrically, while the oxide content Na_2O, K_2O, Fe_2O_3, CaO, MgO after destruction of the sample by melting, were determined by analyzing the content of their cations in the solution using the method of atomic absorption spectrometry (AAS).

The cation exchange capacity (CEC) of clinoptilolite was measured by the method of ion exchange with ammonium chloride (Matijašević et al., 2006), while its external cation exchange capacity (ECEC) was determined using the method of Ming and Dixon (Ming and Dixon, 1987). The suspensions were filtrated and the concentrations of exchanged Ca^{2+}, Mg^{2+}, Na^+ and K^+ were measured in the supernatants using AAS. Results expressed in centimole of charge per kg, represents the total CEC (ECEC). Hydrochloric acid (1M) was used for the preparation of the acid-modified zeolite (H-zeolite). The constant quantity of zeolitic tuff (100 g) was mixed with 1000 ml of acid solutions in a turbo mixer at 6000 rpm for 60 minutes at 50°C. The H-zeolite was rinsed with distilled water until Cl- ions were no longer detected and then dried at 60°C.

Adsorption of uranium(VI) on a natural zeolitic mineral as well as on H-zeolite was carried out by the batch technique. Uranium(VI) solutions were prepared using uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$) (Sigma-Aldrich Co).

The preliminary batch studies were carried out by shaking known amounts of each adsorbent (natural and modified zeolite) and uranium (VI) solution, at room temperature for at least 24 h, at pH 6. In order to investigate the influence of the amount of adsorbents in suspension on uranium (VI) adsorption, at pH 6, the experiments were performed as follows: the volume of solution (50 ml) and the concentration of uranium (VI) (50 mg/l) were kept constant while the amount of adsorbent varied from 0.5 to 2.5 g. The suspensions were shaken for 2 h, at room temperature. After the reaction time, the solids were separated by centrifugation and in supernatants, the remaining uranium (VI) concentration was determined.

In order to investigate uranium (VI) adsorption isotherms on H-zeolite, to each tube 0.125 g of adsorbent and 50 ml of uranium (VI) solution were added at concentrations of 10, 20, 25, 30, 40, 50 mg/l. The adsorption of uranium (VI) ion on H-zeolite was studied at different pH values, with each sample being done in duplicate. The amount of uranium (VI) adsorbed on H-zeolites was calculated from the differences between the initial uranium (VI) concentration and the uranium (VI) concentration in solution after equilibrium. Since, at pH higher than 8.5, precipitation of yellow uranyl carbonate complex was noticed, all experiments were done in pH region from 3 to 8. The pH was adjusted with HNO_3 and NaOH. The samples were shaken for 2 h, centrifuged at 10000 rpm for 10 min and uranium(VI) concentration was measured in supernatants.

Uranium (VI) concentration in solutions were determined using fluorometric method based on the fluorescence of U in fused mixture of NaF, Na_2CO_3 and K_2CO_3 (Rathore, 2008).

3 RESULTS AND DISCUSSION

The starting material used in these experiments was a natural zeolitic mineral from Beočin deposit (Fruška Gora, Serbia). Based on the qualitative mineralogical analysis, the content of clinoptilolite was over 80%, while the accessory minerals were quartz, feldspar, mica, calcite and clay minerals. The starting material had the following chemical composition: SiO_2–56.00%, Al_2O_3–14.40%, Fe_2O_3–1.86%, CaO–6.20%, MgO–2.64%, Na_2O–0.52%, K_2O–2.67%, I.L.–15.71%, while H-zeolite had:SiO_2–81,22%, Al_2O_3–10,85%, Fe_2O_3–1,51%, CaO–1,31%, MgO–0,35%, Na_2O–0,48%, K_2O–2,51%, I.L.–1.77% (AAS Perkin Elmer 703).

The cation exchange capacity (CEC) of the zeolitic tuff was 168 cmolc/kg (H-zeolite was 30.62 cmolc/kg) and the external cation exchange capacity (ECEC) was 10.4 cmolc/kg.

In order to determine the equilibrium time for uranium(VI) adsorption on H-zeolite, the kinetics of adsorption was investigated. It was found that adsorption begins very fast and that the most of uranium(VI) ion is adsorbed in less than 2 hours (>95%). Practically there were no changes in adsorption within the next 48 h. Based on these results subsequent adsorption experiments were conducted with 2 hours reaction time.

Preliminary uranium(VI) ion adsorption experiments on natural unmodified zeolitic mineral at mass ratio adsorbent: uranium(VI) ion 1000: 1, at pH 6, showed that uranium(VI) adsorption index was 34.8% (0.34 mg uranium(VI)/g adsorbent), while uranium(VI) adsorption on H-zeolite, at pH 6, was 95.3% (0.92 mg uranium(VI)/g adsorbent). At mass ratio adsorbent : uranium(VI) ion 400: 1 adsorption index was 93.1 (2.25 mg/g) on H-zeolite and at mass ratio adsorbent: uranium(VI) ion 200:1 index was 63% (3.04 mg/g) on H-zeolite (Fig.1).

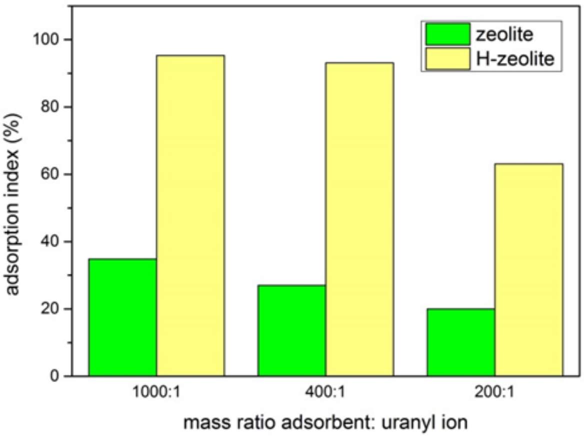

Figure 1 Adsorption index of uranium(VI) at different mass ratio adsorbent: uranyl ion

Acid modified zeolite with hydrochloric acid significantly increases adsorption of uranyl ion. The acid treatment eliminates the impurities of the zeolite through the replacement of natural zeolite cations with H^+ cations and raises the surface area and microporosity (Oztas, Karabakan and Topal, 2008, Castaldi et al.,2008, Matijašević et al., 2016).

Further results at mass ratio adsorbent: uranium(VI) 50:1 and at three different pH are shown at Figure 2.

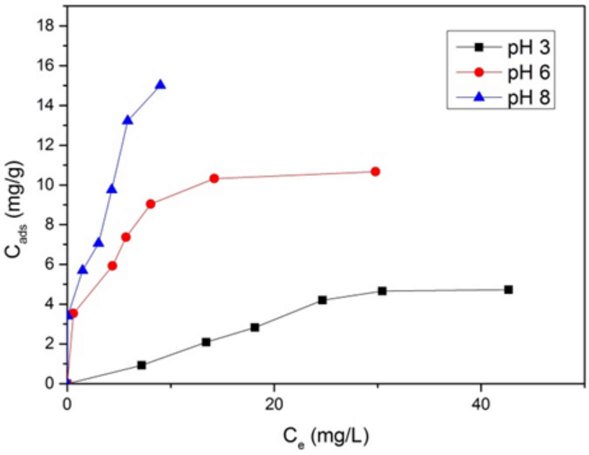

Figure 2 Adsorption index of uranium(VI) at three different pH for acid modified zeolite

As can be seen from Fig. 2, uranium(VI) adsorption on H-zeolite, at pH 3 and pH 6 according to IUPAC classification, is well described by the Langmuir type of isotherm (Type I) while adsorption at pH 8 is described by Type V isotherm.

The adsorption maximum calculated from linear plots gives estimates of the H-zeolite adsorption capacity for uranium(VI) ion. The calculated maximum is 4.72 mg/g at pH 3, 10.48 mg/g at pH 6 and 15.01 mg/g at pH 8. Results demonstrated that presence of H-ions in zeolite improve adsorption of uranium(VI) ion and that adsorption increases in following order pH 8> pH 6> pH 3.

4 CONCLUSION

The results reported in this paper demonstrated that H-zeolites obtained by acid modification of zeolitic mineral clinoptilolite are effective for the removal of uranium(VI) from water solution. The availability of clinoptilolite, their low cost and simple procedure for preparation of H-zeolites are the main advantages for production of large quantities of these materials. Concerning all this, H-zeolites as adsorbents, provide promising materials for removal of uranium(VI) from contaminated soils and groundwater systems.

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