ADSORPTION OF U(VI) COMPLEXES ON ANION-EXCHANGE RESINS MODIFIED BY HYDRATED ZIRCONIUM OXIDE

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Sorption is the most widespread method for removal of uranium(VI) from diluted aqueous solutions. The development of new effective sorbents is in a focus of attention. Organic-inorganic cation-exchangers are prospective materials for sorption of uranyl cations [1-3]. These materials are characterized by higher sorption rate than the inorganic materials, moreover, they are more selective than ion exchange resins. The aim of this work is to a study of adsorption of uranium(VI) compounds from diluted aqueous solution using organic-inorganic sorbents, which were obtained by modification of anion exchange resin EDE-10P with nanoparticles of hydrated zirconium dioxide.

Morphology of the sorbents was investigated by means of transmission electron microscopy. The X-ray fluorescent method was applied to study a content of the inorganic constituent in the polymer matrix.

Several samples of the modified sorbents have been tested. They have been obtained under different synthesis conditions: concentration of the reagents, precipitation temperature and viscosity of the solvent were varied (Table). Ion exchange properties of the pristine resin have been also tested.

Table. Conditions for synthesis of organic-inorganic ion-exchangers

Sample	Concentration, mol dm^{-3}		T, K	Viscosity, mPa s	Solvent
	$ZrOCl_2$	NH_4OH			
AR-0	-	-	-	-	H_2O
AR-1	0.1	1.0	293	1.001	H_2O
AR-2	0.1	1.0	373	0.283	H_2O
AR-3	1.0	1.0	293	1.001	H_2O
AR-4	1.0	1.0	373	0.283	H_2O
AR-5	0.1	1.0	293	61.8	80% glycerol + 20% H_2O

Uranium(VI) compounds were used as sorbates, they were in 2.0×10^{-4} M solutions, which contained 0.02 mol dm^{-3} H_2SO_4 or $NaHCO_3$. The pH values were 2 (sulfate solutions) and 7 (carbonate solutions). At these pH magnitudes, uranium(VI) was in form of mixture of different forms (UO_2^{2+}, $[UO_2SO_4]^0$, $[UO_2(SO_4)_2]^{2-}$) in the sulfate solutions. Regarding the carbonate solutions, $[UO_2(CO_3)_2]^{2-}$ forms dominated [4]. Uranium-containing combining solutions of complex composition, which are models of mine water, were also used for the research. Sorption experiments were carried out under batch conditions at 293 K. The effectiveness of sorption was

estimated according to the removal degree of uranium(VI). Concentration of uranium(VI) in solutions after sorption was determined with a photometric method. Such chelating agent as Arsenazo III was applied to the analysis.

It was found that the tested sorbents remove uranium compounds more completely from the carbonate solutions (the removal degree reached 90-99.5%) comparing wit the sulfate solutions (the removal degree reached 65-70%). The rate of sorption by the modified sorbents is higher in comparison with the pristine resin. The synthesis conditions determine sorption ability towards uranium compounds. These conditions affect also a size of the embedded particles and their state in the polymer matrix (non-aggregated nanoparticles, aggregates and agglomerates). The highest rate of sorption has been found for the AR-3 sample. At the same time, the AR-5 ion-exchanger demonstrates the slowest rate. The rate of sorption of U(VI)-containing anions corresponds to the mixed diffusion mechanism. Ion exchange is complicated by chemical interaction: the kinetic curves are described by the equations of pseudo-second-order (samples AR-1, AR-3, AR-5) or pseudo-first-order (other test samples).

Composite ion-exchangers are regenerated easier and more completely than the pristine resins. The degree of uranium desorption (S_{des}) from AR-0 sample is 62% (using a 1 M KOH solution for regeneration), 72% (H_2SO_4 solution), 66% and 89% (the sorbents were treated with a $NaHCO_3$ solution one or two times respectively). The organic-inorganic ion-exchangers are regenerated more completely (S_{des}=95-99.9%) with the $NaHCO_3$ and H_2SO_4 solutions. No change of sorption degree has been found for the composites after 5 cycles of sorption-regeneration.

The obtained results can be used for the enterprises of uranium mining industry to improve technologies of the U(VI) removal from waste water.

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REMOVAL OF URANIUM(VI) FROM MODEL SOLUTIONS WITH FIBROUS ION-EXCHANGERS UNDER DYNAMIC CONDITIONS

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Purification of natural and anthropogenic waters formed during the processing of poor uranium-containing ores from natural radionuclides, in particular, Uranium(VI) compounds, is an actual environmental problem. One of the main methods for removal of Uranium compounds from diluted aqueous solutions is sorption, so it is important to search for effective sorbents. Perspective sorbents are fibrous ion-exchangers FIBAN. Earlier [1-4], we showed that fibrous ion-exchangers FIBAN effectively remove Uranium(VI) compounds from model solutions under static conditions.

This work is devoted to a study of effectiveness of removal of Uranium(VI) compounds from model aqueous solutions using fibrous ion-exchangers FIBAN under dynamic conditions.

Uranium(VI) compounds were used as sorbates, they were in model 2.0×10^{-4} M solutions, which contained one of reagents (0.02 mol dm^{-3}): HNO_3, H_2SO_4 (pH 2) or $NaHCO_3$ (pH 8). Under these conditions, Uranium(VI) was in nitrate solutions mainly in the form of cations UO_2^{2+}, in sulfate solutions as a mixture of equal amounts of UO_2^{2+}, $[UO_2(SO_4)]$ and $[UO_2(SO_4)_2]^{2-}$, and in carbonate solutions - in the form of anionic complexes of the composition $[UO_2(CO_3)_2]^{2-}$ and $[UO_2(CO_3)_3]^{4-}$. As sorbents used fibrous materials FIBAN of different nature: monofunctional strongly acidic cation exchanger FIBAN C-1 with sulfo-groups; multifunctional anion exchanger FIBAN A-6 with strongly and weakly basic amino groups; multifunctional amphoteric ion exchanger FIBAN AC-22V with carboxyl, primary and secondary amino-groups.

Sorption experiments was carried out under dynamic conditions at 290 K in column with a diameter of 20 mm and a height of 200 mm. Weighed air-dry sorbent was 1 g, the height of the filtering layer was 35 mm, the flow rate of the solution through the column was 2.5 cm^3 min^{-1}. Concentration of Uranium(VI) in solutions after sorption was determined with a photometric method using Arsenazo III. The dynamic exchange capacity of the ion-exchangers for Uranium(VI) was the main mark of the sorption efficiency.

The conducted researches have shown that the investigated fibrous ion-exchangers are effective reusable materials for the removal of Uranium(VI) compounds from model solutions of various ionic composition under dynamic conditions. In order of decreasing dynamic exchange capacity for Uranium(VI), fibrous ion exchangers can be arranged in the following series:

- sorption of U(VI) from sulfate solutions: FIBAN A-6 > FIBAN C-1 > FIBAN AC-22V;
- sorption of U(VI) from carbonate solutions FIBAN A-6 > FIBAN AC-22V >> FIBAN C-1;
- sorption of U(VI) from nitrate solutions FIBAN C-1 > FIBAN AC-22V >> FIBAN A-6.

The dynamic exchange capacity of fibrous ion-exchanger FIBAN AC-22V for Uranium(VI) has maximum value when Uranium(VI) is removed from sulfate solutions and it has minimum value when Uranium(VI) is removed from nitrate solutions. The data obtained are explained by

different mechanisms of Uranium(VI) sorption by this ion-exchanger. In the case of nitrate and carbonate solutions, Uranium(VI) is sorbed by the ion exchange mechanism, and from sulfate solutions, also by the mechanism of surface complexation.

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