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SORPTION REMOVAL OF URANIUM (VI) COMPOUNDS WITH ORGANIC-INORGANIC ION-EXCHANGERS

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Abstract. Organic-inorganic composites based on ion exchange resins containing zirconium hydrophosphate (cation-exchanger) and hydrated zirconium dioxide (anion-exchanger) were applied to removal of soluble U(VI) compounds from modeling solutions. The advantages of the composites over the pristine resins are more significant sorption capacity, higher sorption rate and more facile regeneration.

Keywords: *organic-inorganic ion-exchangers, zirconium hydrophosphate, hydrated zirconium dioxide, uranyl ions, waste water treatment.*

Introduction. Purification of liquid wastes after processing of poor uranium-containing ores [1] is an actual ecological problem (maximal allowable concentration of soluble uranium compounds in waste waters is 0.015 – 0.6 mg dm^{-3} [2, 3]). Sorption is the most widespread method for removal of these highly toxic impurities from diluted aqueous solutions, the development of new effective sorbents is in a focus of attention. In addition to sorbents investigated earlier [4-6], organic-inorganic ion-exchangers are rather prospective [7]. These materials are characterized by higher sorption rate than the inorganic materials, moreover, they are more selective than ion exchange resins. The aim of the research is to estimate a possibility to use organic-inorganic cation- and anion-exchangers for removal of uranium (VI) compounds from modeling solutions of different composition.

Experimental. Aqueous solutions of uranium (VI) acetate were used (2.0·10^{-4} mol dm^{-3}). Additionally the solutions contained acid or salt (0.02 M H_2SO_4 or HCl or $NaHCO_3$). These reagents are used for treatment of uranium-containing minerals. Under these experimental conditions, uranium was in a form of cations in the chloride solution (98.3% of UO_2^{2+} and 1.6% of $[UO_2Cl]^+_2$) [8]. The sulfate solution contained anionic and neutral complexes, such as $[UO_2(SO_4)]$ (46.3%) and $[UO_2(SO_4)_2]^{2-}$ (6.5%) and also UO_2^{2+} cations (46.3%). There were $[UO_2(CO_3)_2]^{2-}$ (87%) and $[UO_2(CO_3)_3]^{4-}$ (13%) in the carbonate solution. The modeling solutions were also used (g dm^{-3}): I – U(VI) (0.05),

$FeCl_3$ (0.25), HCl (0.73) (modeling waste waters of monazite processing), II – U(VI) (0.007), Cl^- (0.14), $NaHCO_3$ (0.46), Ca^{2+} (0.01), Mg^{2+} (0.07), SO_4^{2-} (0.04) (modeling carbonate mine waters), III – U(VI) (0.1), Ca^{2+} (0.5), Mg^{2+} (0.5), Fe^{3+} (0.5), Al^{3+} (2), SO_4^{2-} (15) (modeling technological solutions that are formed during the autopsy of poor uranium ores).

Dowex HCR-S cation exchange resin (*CR*) and EDE-10P anion exchange resin (*AR*) were applied to the investigations. Organic-inorganic sorbents, which had been obtained by modification of these resins with nanopartilces of zirconium hydrophosphate (*CR-ZHP*) or hydrated zirconium dioxide (*AR-HZD*), were also used. The synthesis conditions are given in Table 1.

Table 1. Modification Conditions and Sorption of U(VI) Compounds from Sulfate, Chloride and Carbonate Solutions (Sorbent Dosage Was 2 g dm^{-3})

Sorbent	**Reagents for modifications**	*S*, %	$t_{1/2}$, **min**	t_{eq}, **min**	$k \times 10^4$, s^{-1}
		Chloride solution			
CR	-	99.5±0.5	44	120	3.00
CR-ZHP-1	0.1 M $ZrOCl_2$ 1 M H_3PO_4	99.5±0.5	15	80	9.67
CR-ZHP-2	1 M $ZrOCl_2$ 1 M H_3PO_4	99.5±0.5	16	100	5.17
		Carbonate solution			
AR	-	99.5±0.5	25	300	2.35
AR-HZD-1	0.1 M $ZrOCl_2$ 1 M NH_4OH	99.5±0.5	40	390	2.00
AR-HZD-2	1 M $ZrOCl_2$, 1 M NH_4OH	99.5±0.5	20	300	2.52
		Sulfate solution			
AR	-	70.0±0.5	70	210	1.22
AR-HZD-1	0.1 M $ZrOCl_2$ 1 M NH_4OH	65.5±0.5	140	300	6.17
AR-HZD-2	1 M $ZrOCl_2$, 1 M NH_4OH	70.5±0.5	60	240	8.50

Sorption experiments were performed under static conditions with continuous shaking at 20±2^{0}C during 15–1800 min. The sorbent dosage was 2–10 g dm^{-3}. The solutions after sorption were analyzed with a photometric method using arsenazo III [9]. Sorption degree was calculated as:

$$S = \frac{C_0 - C}{C_0} \times 100,\% \qquad (1)$$

where C_0 and C are the initial and final concentration of uranium (VI) in the solution.

Desorption experiments were carried out by similar manner using 1 M H_2SO_4 or $NaHCO_3$ solutions. Desorption degree was determined via:

$$S_{des} = \frac{C_{des}}{C_0 - C} \times 100,\% \quad , \tag{2}$$

where C_{des} is the concentration of uranium (VI) in the solution after desorption.

Results and discussion. Pristine ion exchange resins and organic-inorganic materials remove uranium (VI) compounds practically completely from chloride and carbonate solutions (see Table 1) as well as from the modeling solution II (Table 2), when the sorbent dosage is 2 g dm^{-3}. No additional correction of the pH is needed.

Table 2: Sorption of Uranium (VI) Compounds from Modeling Solutions

Sorbent	Sorbent dosage, g dm^{-3}	pH	S, %	$t_{1/2}$, min	t_{eq}, min	$k \times 10^4$, s^{-1}
Modeling solution I						
CR	5	2	60.0±0.5	57	>1800	3.70
		4	99.5±0.5	20	180	4.03
	10	2	99.5±0.5	33	480	7.02
CR-ZHP-2	5	2	60.5±0.5	240	>1800	3.17
		4	99.5±0.5	28	150	5.08
	10	2	99.5±0.5	36	1440	8.67
Modeling solution II						
AR	2	8	99.5±0.5	25	120	6.58
AR-HZD-1			77.5±0.5	40	150	5.97
AR-HZD-2			99.5±0.5	25	120	5.28
Modeling solution III						
AR	5	2	79.0±0.5	35	100	4.72
AR-HZD-1			47.5±0.5	-	80	7.68
AR-HZD-2			76.5±0.5	40	120	4.55

The residual U(VI) content decreases down to maximal allowable concentration by this manner. More complete removal of U(VI) species from the model solution I requires optimization of sorption conditions: it is necessary to increase either the pH (up to 4) or the sorbent dosage. This optimization causes not only an increase of the S value, but also sorption acceleration. Sulfate solutions contain anionic and neutral complexes of U(VI) as well as uranyl cations. These species are not able to interact with anion exchange functional groups of the polymer constituent of the sorbents. Thus, the maximal sorption degree is not reached in the sulfate solutions, particularly from the modeling solution III.

Following kinetic characteristics for sorption of uranium (VI) compounds are given in Table 2: half-time of exchange ($t_{1/2}$), time of equilibrium (t_{eq}), constant of sorption rate (k) that was calculated using the first order equation:

$$ln\frac{C_t}{C_0} = -k \times t\,, \tag{3}$$

where C_t is the concentration under predetermined time.

The *CR-ZHP-1* sample, which was impregnated with a 0.1 M $ZrOCl_2$ solution before ZHP precipitation, is the most attractive from the point of view of sorption kinetics (in the case of chloride solutions). Regarding sorption of anions, the sample that have been saturated with more concentrated $ZrOCl_2$ solution for following ZHD deposition, is the most effective.

Composite ion-exchangers are regenerated easier and more complete than the pristine resins. The degree of uranium desorption from *CR* is 85 (using H_2SO_4 solution for regeneration) and 50% ($NaHCO_3$ solution). The S_{des} values are 90 (H_2SO_4) and 66% ($NaHCO_3$) for the *AR* sample. At the same time, the organic-inorganic ion-exchangers are regenerated more completely (S_{des}=90%) with the $NaHCO_3$ solution and the most completely (S_{des}=100%) with the H_2SO_4 solution. No change of sorption degree has been found for the composites after 5 cycles of sorption-regeneration.

Conclusions. Organic-inorganic ion-exchangers containing ZHP and HZD demonstrate more significant sorption ability towards soluble U(VI) compounds than the pristine resins. Depending on modification conditions, the composites show also higher sorption rate despite the inorganic constituents. This was shown particularly for the solutions, which model liquid wastes of uranium processing or mine waters. Other advantages of the organic-inorganic ion-exchangers are more facile regeneration and, as a result, a possibility of multiple application.

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СОРБЦІЙНЕ ВИЛУЧЕННЯ СПОЛУК УРАНУ (VI) ОРГАНО-НЕОРГАНІЧНИМИ ІОНІТАМИ

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Резюме. Органо-неорганічні композити на основі йонообмінних смол, які містять гідрофосфат цирконію (катіоніт) та гідратований діоксид цирконію (аніоніт) застосовані для вилучення розчинних сполук U(VI) з модельних розчинів. Перевагами композитів у порівнянні з вихідними смолами є вища сорбційна ємність, більш висока швидкість сорбції, а також полегшена регенерація.

Ключові слова: органо-неорганічні іоніти, гідрофосфат цирконію, гідратований діоксид цирконію, йони уранілу, очистка стічних вод.