V.I. Vernadskii Institute
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MEMBRANE AND SORPTION MATERIALS AND TECHNOLOGIES: PRESENT AND FUTURE

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CHAPTER 9

POLYMER-INORGANIC CATION-EXCHANGERS CONTAINING ZIRCONIUM HYDROPHOSPHATE. REGENERATION OF URAIUM-LOADED FORM

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Abstract. *It has been found that polymer-inorganic cation-exchangers, which contain nanoparticles of zirconium hydrophosphate, can be used many times for sorption of uranyl cations from diluted solutions. This is due to the possibility of practically complete regeneration of the loaded sorbents with diluted solutions of $NaHCO_3$ or EDTA. The sample that includes the smallest embedded particles shows the highest regeneration rate.*

Keywords: *organic-inorganic cation-exchangers, zirconium hydrophosphate, uranyl, regeneration of sorbent, polymer-based composite*

Introduction. In practice, sorption is the main effective method for the recovery of valuable and toxic components from water. As opposed to membrane separation, the choice of selective sorbent allows us to extract one or other ionic component from the solutions containing high amount of salts. Economical efficiency of sorption processes is determined particularly by optimal conditions for regeneration of sorption materials and processing of effluents. This is necessary for the repeated use of sorbents on the one hand and, in the case of processing of liquid industrial wastes, to return valuable components back to the technological process.

Last years organic-inorganic ion-exchangers are used for sorption of heavy metal ions [1]. These ion-exchangers are characterized by selectivity towards heavy metal ions comparing with commercially available ion exchange resins. In comparison with inorganic sorbents, much higher sorption rate is attributed to the composites of mentioned type.

As shown in [2-3], the composites based on gel-like strongly acidic ion exchange resin, which contains both non-aggregated and aggregated nanoparticles of zirconium hydrophosphate (ZHP), effectively extract uranyl

cations. The main advantage of these composites is the possibility of multiply usage after regeneration with a 1 M H_2SO_4 solution. The disadvantages of this reagent is its significant danger and high chemical activity providing equipment corrosion. Moreover, the use of sulfuric acid is limited at the legislative level.

The aim of the work is to establish some regularities of the regeneration of uranyl-loaded forms of polymer-based ion-exchangers containing ZHP nanoparticles. The solutions of $NaHCO_3$ and EDTA were applied to investigations. .The choice of these low-cost reagents is due to their availability and low selfishness. Moreover, they form strong complexes with uranyl-iions in solutions [4].

Experimental. Aqueous solutions of uranium (VI) acetate were used ($2.0 \cdot 10^{-4}$ mol dm^{-3}). Additionally the solutions contained 0.02 M HNO_3. Полученные растворы имели pH 2.2-2.5. Under these experimental conditions, uranium was in a form of cations in the nitrate solution (98.3% of UO_2^{2+} and 1.7% of $[UO_2NO_3]^+$) [4].

As sorbents, the samples based on Dowex HCR-S resin were used. The polymer was modified with ZHP particles according to [1-3]. The samples marked as *1*, *2* and *3*, they differed in synthesis conditions (concentrations of $ZrOCl_2$ and H_3PO_4, Table 9.1), which determine diameter of grains, and the size of embedded aggregated and non-aggregated particles. The composition of sorbents affects their functional properties, namely .sorption ability towards uranyl ions and facility of regeneration of uranium forms.

Table 9.1. Synthesis conditions and some characteristics 0f polymer-inorganic cation-exchangers [2-3]

Sample	**Synthesis conditions**		**Size of embedded ZHP particles, nm**	**Average diameter of grains, μm**
	C($ZrOCl_2$), M	C(H_3PO_4), M		
1	1	0,01	10-20; 400-600	800
2	1	1	50; 200-300	624
3	0.3	1	2-10;<100	640

Sorption experiments were performed under static conditions with continuous shaking at 20 ± 2^0C during 30–180 min. The sorbent dosage was 2 g dm^{-3}. The solutions after sorption were analyzed with a photometric method using arsenazo III [5]. Sorption degree was calculated as:

$$S = \frac{C_0 - C}{C_0} \times 100,\% \qquad (9.1)$$

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

The sorbent loaded with uranyl-ions was separated from liquid, washed with deionized water and dried down to constant mass. utanyl-loaded forms of ion-exchanger was obtained by this manner. Namely these sorbents were regenerated for 30-240 min shaking with 0.01-1 M $NaHCO_3$ solutions or 0.01-0.4 M EFTA solutions. These reagents were well proven for the regeneration of uranium forms of other ion exchangers of different nature, particularly composites [6, 7]. The efficiency of sorbent regeneration was estimated as uranium desorption degree ($S_{des.}$):

$$S_{des.} = \frac{C_{des}}{C_0 - C} \times 100,\% \ , \qquad (9.2)$$

where C_{des} is the concentration of uranium (VI) in the solution after desorption. The rate constant for uranyl desorption ($k_{des.}$) was found by graphically solving the equation:

$$\ln (C_{ads.} - C_{des.}) = \ln C_{ads.} - k_{des.} \times t \ , \qquad (9.3)$$

where $C_{ads.}$ ($C_{ads.} = C_0 - C$) is the concentration of uranium in a sorbent.

Results and discussion. The investigations have shown that the efficiency of regeneration (degree of uranium desorption, time and rate of sorbent regeneration) depends on properties of organic-inorganic ion-exchangers, as well as nature and concentration of the solution for regeneration (Figures 9.1).

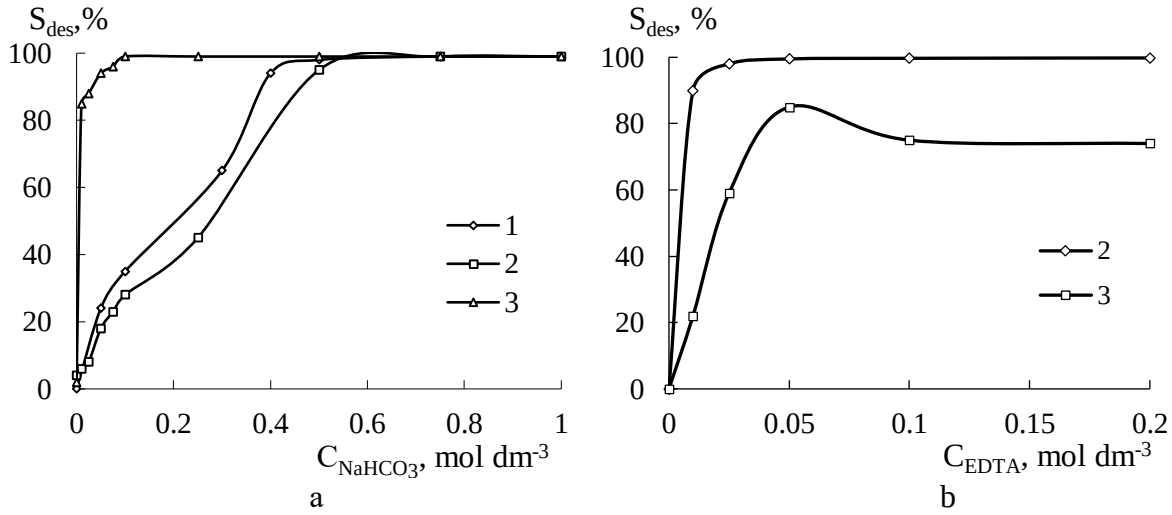

Fig. 9.1. *Degree of desorption ($S_{дес.}$) for uraniun (VI) from uranium forms of polymer-inorganic cation-exchangers as a function of concentration of $NaHCO_3$ (a) and EDTA solutions (b).*

Increasing in the concentration of $NaHCO_3$ and EDTA solutions up to a certain value, which is determined by the properties of sorbent, causes the efficiency of uranium desorption (Table 9.2). Regeneration of samples *1* and *2*

requires 0.5 M $NaHCO_3$ solution. Less concentrated solution (0.1 M) is desirable for regeneratiion of sample *3*. Even a 0.05 M EDTA solution allows us to reach high desorption degree of uranyl ions and maximal desorption rate. It is necessary to note that EDTA is the most effective reagent for sample *2*: higher quantitative desorption rates were found in this case. Regarding sample 3, s $NaHCO_3$ solution is more desirable.

Table 9.2. Kinetics of uranium (VI) desorption with $NaHCO_3$ and EDTA solutions

C, M	Sample *1*			Sample *2*			Sample *3*		
	t, min	k ×10^4, s^{-1}	R^2	t, min	k ×10^4, s^{-1}	R^2	t, min	k ×10^4, s^{-1}	R^2
$NaHCO_3$									
0.01	—	—	—	210	0.05	0.98	150	2.53	0.94
0.025	—	—	—	180	0.03	0.97	120	2.93	0.89
0.05	180	0.25	0.94	180	0.15	0.98	150	3.54	0.89
0.075	—	—	—	180	0.20	0.99	150	4.11	0.97
0.10	180	0.48	0.97	180	0.25	0.99	150	4.43	0.99
0.25	180	0.88	0.99	180	0.55	0.99	120	4.90	0.92
0.50	90	3.97	0.88	150	4.51	0.96	90	5.53	0.99
0.75	90	4.55	0.95	120	5.50	0.99	90	5.68	0.98
EDTA									
0.01	—	—	—	210	2.50	0.98	180	0.23	0.99
0.02	—	—	—	210	2.41	0.99	180	0.75	0.97
0.05	—	—	—	210	3.48	0.99	150	2.07	0.99
0.10	—	—	—	—	—	—	150	0.83	0.99
0.20	—	—	—	—	—	—	150	1.15	0.96
0.40	—	—	—	—	—	—	150	1.05	0.95

* *t* is the desorption time, R^2 is the correlation coefficient of line (3).

The sorbents, which are completely regenerated with a 0.5 M $NaHCO_3$ solution, completely restore their original form and the sorption capacity for uranium (the degree of sorption of uranium reaches 99.9 ± 0.5%) after 5th cycles of sorption-regeneration. During further cycles, the degree of sorption decrease Further cycles reduce the degree of uranium sorption by 3-5%. The sorbents regenerated with a 1 M $NaHCO_3$ solution save their sorption capacity after 10th cycle of sorption-regeneration.

Conclusions. The obtained results are explained with composition and properties of organic-inorganic materials being regenerated. The samples *1* and *2* contain larger non-aggregated and aggregated ZHP particles. they are located in void between gel field of polymer blocking them. This evidently makes it difficult diffusion of exchanged ions inside the grains. Moreover, the modifier particles are also able to sorb ions. In the case of particle diffusion, increase of the size of embedded particles slow down the sorption rate. When the movement of ions is limited by chemical reaction, the deceleration is caused by high

amount of functional groups of ZHP. Smaller embedded particles accelerate ion exchange (sample 3), this is most expressed in the case of $NaHCO_3$ solutions.

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ОРГАНО-НЕОРГАНИЧЕСКИЕ КАТИОНИТЫ, СОДЕРЖАЩИЕ ГИДРОФОСФАТ ЦИРКОНИЯ: ОСОБЕННОСТИ РЕГЕНЕРАЦИИ УРАНОВОЙ ФОРМЫ

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Резюме. *Встановлено, що полімер-неорганічні катіоніти, що містять наночастинки гідрофосфату цирконію, можуть бути використані багаторазово для сорбції катіонів уранілу з розбавлених розчинів. Це зумовлено ефективною регенерації уранової форми цих сорбентів розбавленими розчинами $NaHCO_3$ або ЕДТА. Найвищу швидкість десорбції знайдено для композиту, який містить найменші частинки модифікатору.*

Ключові слова*:органо-неорганічні катіоніти, гідро фосфат цирконію, уранілюни, регенерація сорбенту, композит на основі полімеру.*