

## Selenium or sulfur based aminofurazan *N*-hydroxyamidine materials as sorbents for removal of uranium from liquid media

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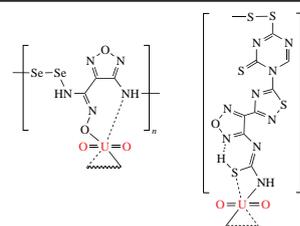
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DOI: 10.1016/j.mencom.2020.09.007

Reactions of *N*'-hydroxy-1,2,5-oxadiazole-3-carboximidamide with SeO<sub>2</sub> or thiourea afford complex materials containing elements of the reactants and diselenide or disulfide bridges, respectively. These materials were tested as agents for U<sup>VI</sup> extraction from liquid media in the range of pH 6–9 including technological and sea water.



**Keywords:** uranium, amidoximes, sorption, 1,2,5-oxadiazoles, diselenides, disulfides, polymerization.

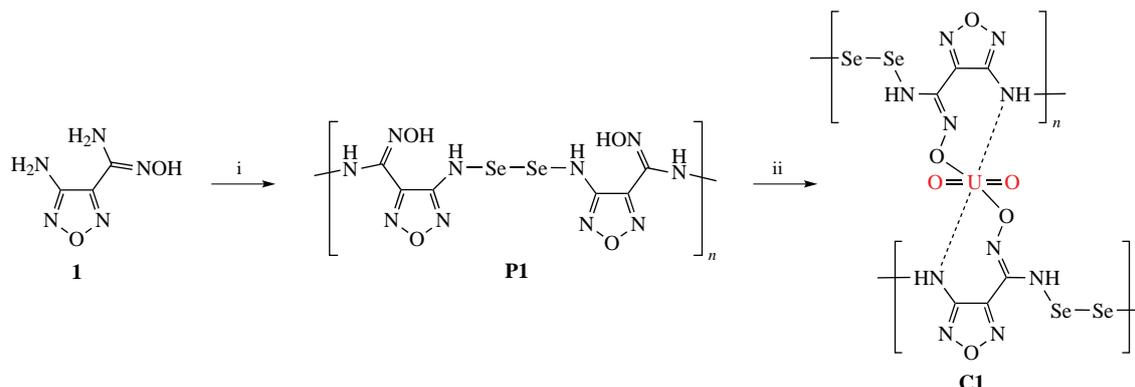
Solid and liquid radioactive wastes containing natural uranium and other radionuclides are accumulated in the course of mining and processing of mineral uranium raw materials required for the development of nuclear power industry. The processing would cause the environmental spread of uranium being an element with high migration capacity. Obviously, the search for efficient ways to concentrate and isolate it from contaminated natural and man-made waters is topical.

For quantitative removal of uranium from aqueous media, sorption methods<sup>1</sup> using various natural and synthetic sorption materials (titanosilicates,<sup>2</sup> phosphorosilicates,<sup>3,4</sup> synthetic cation exchange resins,<sup>5</sup> and some other<sup>6</sup>) are applied. However, conventional sorbents are normally efficient only in a narrow range of the pH values (2.0–4.5)<sup>7,8</sup> and tend to be destructed with subsequent desorption of the radionuclide, which complicates the technological process. Unlike the sorbents mentioned above, the ones containing amidoxime functional groups exhibit high selectivity towards U<sup>VI</sup> compounds in a wide (6–9) pH range.<sup>9</sup> A specific feature of such sorbents

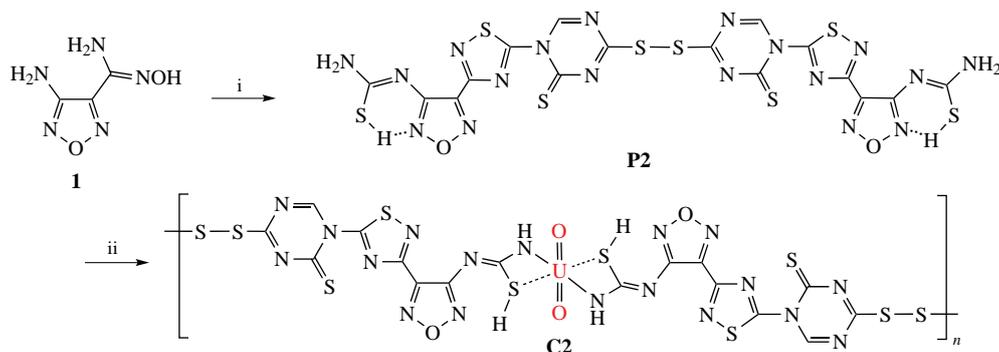
consists in the fact that amidoxime amino groups provide removal of uranyl ions through both the ion exchange and the complexation. Despite a significant progress in fabricating materials based on amidoximes and oximes, polymers and large molecules comprising Se and S atoms as cross-linking units were not previously studied.

The present study describes new synthesis of sorbents highly selective towards uranyl ions by introducing heteroelements with high coordination capacity such as S and Se into the starting *N*'-hydroxy-1,2,5-oxadiazole-3-carboximidamide **1**, which contributes to the formation of polymer materials with a developed structure and high content of ion-exchange groups (amino and hydroxyl groups). Schemes 1 and 2 demonstrate the proposed structures of materials **P1** and **P2**, respectively, which is in concord with their IR spectra, XPS and reported data<sup>10</sup> (for experimental details, see Online Supplementary Materials).

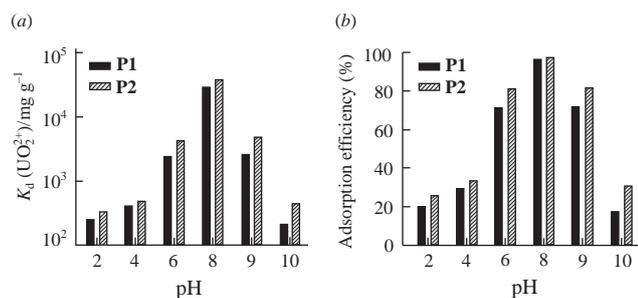
The dependence of the extraction efficiency of uranyl ions on the pH for the model solution showed that the new sorbents



**Scheme 1** Reagents and conditions: i, SeO<sub>2</sub>, AcOH, reflux, 80–100 min; ii, UO<sub>2</sub><sup>2+</sup>, H<sub>2</sub>O, competing cations.



**Scheme 2** Reagents and conditions: i,  $(\text{H}_2\text{N})_2\text{C}=\text{S}$ , neat, 220–250 °C, 60–80 min; ii,  $\text{UO}_2^{2+}$ ,  $\text{H}_2\text{O}$ , competing cations.



**Figure 1** Dependency diagrams: (a) distribution coefficients of  $\text{UO}_2^{2+}$  vs. pH of the medium; (b) the adsorption efficiency of  $\text{UO}_2^{2+}$  vs. pH of the model solution.

were efficient in the pH range from 6 to 9 (Figure 1), while the maximum DC values for **P1** and **P2** were from  $5 \times 10^3$  to  $4 \times 10^4$  ml  $\text{g}^{-1}$ , respectively.<sup>†</sup> In solutions with  $\text{pH} > 9$ , there was a decrease in extraction efficiency due to the adsorption of uranium on the walls of glass or polypropylene containers, which was recorded in the test experiment with no sorbent. In acidic media ( $\text{pH} < 6$ ), uranium absorption did not occur, which was related to the protonation of the imidamide moieties. High degree of adsorption is apparently stipulated for a large number of sorption sites in materials **P1** and **P2**, such as Se–Se and S–S, respectively, as well as *N*-hydroxyimidamide moieties. The resulting materials appeared to be resistant to abrasion and were not soluble in the most common organic and inorganic solvents.

The study of the sorption of uranyl ions in the presence of  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  ( $0.1 \text{ mol dm}^{-3}$ ) showed that the highest values of SEC and DC were achieved at pH 6 (Table 1). The decrease of the SEC and  $K_d$  value at pH 6 was related to the formation of carbonate and sulfate complex uranium ions in

alkaline media, which prevented the extraction of uranyl ions. Despite the decrease of SEC values at pH 4 and pH 8, the adsorption exceeds 80%.

The greatest negative effect on the sorption of uranyl ions was imposed by bicarbonate ions as a result of the formation of stable anion complexes of the  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  and  $[\text{UO}_2(\text{CO}_3)_2]^{2-}$  types.<sup>11</sup> The presence of inorganic anions in the solution reduces the value of SEC in the next sequence:  $\text{NO}_3^- < \text{SO}_4^{2-} < \text{HCO}_3^-$ ; however, in all cases the sorption efficiency is more than 80%, which indicates a high affinity of sorbents for  $\text{UO}_2^{2+}$ . The best distribution coefficients were achieved in the presence of  $\text{NO}_3^-$  ions:  $46.7 \times 10^{-3}$  and  $11.9 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$  for **P1** and **P2**, respectively.

The limiting adsorption value was calculated using the Sips equation and, in the presence of nitrate ions ( $100 \text{ mg dm}^{-3}$ ) and at pH 8, was 370 and 460  $\text{mg g}^{-1}$  for the **P1** and **P2**, respectively. The obtained values indicate a high sorption capacity, which is important in decontamination of liquid media with high concentrations of uranium. Based on the obtained XPS spectra of materials after sorption (see Online Supplementary Materials), an assumption was made about the mechanism of extraction of uranyl ions, which is based on the complexation reaction (see Schemes 1 and 2, structures **C1** and **C2**, respectively).

To conclude, simple synthetic procedure for efficient polymer sorbents has been herein developed. The materials are characterized by good mechanical and chemical stability and high affinity for uranyl ions in the pH range from 6 to 9. The removal efficiency at the  $V/m$  ratio of  $1000 \text{ ml g}^{-1}$  was higher than 80%.

This work was supported by the Russian Foundation for Basic Research (project no. 19-33-90148\19 Graduate students).

**Table 1** The effect of inorganic anions ( $0.1 \text{ mol dm}^{-3}$ ) on the extraction of  $\text{U}^{\text{VI}}$ .

Material	pH 4			pH 6			pH 8			
	Anion	Ads (%) <sup>a</sup>	SEC <sup>b</sup>	$K_d \times 10^{-3c}$	Ads (%) <sup>a</sup>	SEC <sup>b</sup>	$K_d \times 10^{-3c}$	Ads (%) <sup>a</sup>	SEC <sup>b</sup>	$K_d \times 10^{-3c}$
<b>P1</b>	$\text{HCO}_3^-$	–	–	–	91	31	9.6	81	28	3.8
<b>P1</b>	$\text{SO}_4^{2-}$	88	38	6.2	95	41	16.5	86	38	7.7
<b>P1</b>	$\text{NO}_3^-$	98	73	39.5	98	75	46.7	87	71	40.7
<b>P2</b>	$\text{HCO}_3^-$	–	–	–	89	32	10.0	74	27	5.4
<b>P2</b>	$\text{SO}_4^{2-}$	83	33	4.4	95	40	15.3	89	39	7.8
<b>P2</b>	$\text{NO}_3^-$	91	69	9.5	94	81	11.9	93	71	11.8

<sup>a</sup> Ads (%) is sorption efficiency (%). <sup>b</sup> SEC is static exchange capacity ( $\text{mg g}^{-1}$ ). <sup>c</sup>  $K_d$  is uranium distribution coefficient ( $\text{cm}^3 \text{ g}^{-1}$ ).

<sup>†</sup> Sorption experiments. The sorption of the  $\text{U}^{\text{VI}}$  macro-quantities was performed under static conditions at a ratio of the volume of the solution to the weight of the sorbent of  $1000 \text{ ml g}^{-1}$  in the presence of  $\text{NaNO}_3$  ( $100 \text{ mg dm}^{-3}$ ). The contact time of the phases was 48 h, and the initial

concentration of uranium was  $50 \text{ mg dm}^{-3}$ . The content of  $\text{U}^{\text{VI}}$  was determined by the spectrophotometric analysis in the presence of Arsenazo III, and then the sorption efficiency (Ads), static exchange capacity (SEC), and distribution coefficients (DC) of uranyl ions were calculated.

*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.09.007.

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Received: 14th April 2020; Com. 20/6193