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EQUILIBRIUM OF URANIUM RECOVERY WITH ION-EXCHANGE RESINS FROM THE SOLUTION SIMULATED RADIOACTIVELY CONTAMINATED GROUNDWATER

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Abstract. The paper presents the research results of the uranium recovery equilibrium by granular ion exchange resins from the solution that simulated radioactively contaminated groundwater accumulated in the Centralnyi Yar radioactive tailing site at the former Prydniprovsk Chemical Plant (Kamianske, Ukraine), one of the largest Soviet uranium ore processing facilities. This site was among the oldest tailing facilities at this plant; it was commissioned without any engineering protection of the bottom resulting in migration of water contaminated with radionuclides into the local aquifer. Radioactive waste accumulated in it features a strong acidic reaction (pH 2.5 to 4.0). Based on the preliminary study of uranium sorption by different types of sorption materials, ion exchange resins with quaternary ammonium, benzylpyridinium, and iminodiacetic acid functionalities were selected to study the recovery equilibrium. Uranium recovery was studied in a batch mode using the different portion technique by contacting sorbent portions with 20 cm^3 of the acidic solution that simulated radioactive water in the Centralnyi Yar tailing facility. Recovery was carried out during for 24 hours at a temperature of 20±2 °C. Uranium concentration in the aqueous phase was measured by photocolorimetry with Arsenazo III at a wavelength of 655 m; uranium content in solid phase was calculated by mass balance. The moisture content in sorbents and the simulated solution acidity were measured according to general procedures. Equilibrium experimental data were processed by Freundlich, Langmuir, and Sips models using non-linear regression; determination factor value was used as a criterion for selecting the best one. Based on the experimental data, it was revealed that ion exchange resin AM-p with quaternary ammonium functionalities and Lewatit MDS TP 208 with iminodiacetic ones featured the highest sorption capacity. Experimental data were also processed using the linearized form of the Dubinin-Radushkevich equation. Sorption characteristic energy (14.87 kJ/mole to 21.68 kJ/mole) has indicated that the ion exchange mechanism involved chemisorption. Basic parameters of uranium equilibrium sorption (constants of mathematical models, maximum sorption capacity, heterogeneity factors) were calculated based on the models used.

Keywords: uranium, sorption, equilibrium, ion exchange resins, simulated solution.

1. Introduction

Processing residues of uranium-containing ores and other mineral raw materials accumulated in tailing sites at the industrial site of former Prydniprovsk Chemical Plant, one of the largest Soviet uranium ore processing facility, and adjacent territories feature an increased content of uranium-thorium radionuclides; they are sources of human exposure and environmental pollution [1, 2].

Centralnyi Yar tailing site is among the oldest tailing facilities at Prydniprovsk Chemical Plant. It was commissioned in the early 1950s. The tailing site was located in a natural ravine on the upper terrace of the Dnipro River without any engineering protection of its bottom that resulted in the infiltration of radionuclide-contaminated groundwater from the tailing site into the local aquifer. The waste accumulated in the tailing site features a strong acidic reaction (pH is 2.5 to 4.0) [3].

Previously, we studied [4] uranium recovery from uranium-contained solutions that simulated the contaminated groundwater in the Centralnyi Yar tailing site and the one accumulated in the basement of building No. 103 at former Prydniprovsk Chemical Plant using granular ion exchange resins and sorbents produced by modification of vegetal raw materials. The uranium distribution factor was calculated for the wide range of granular sorbents and phosphorylated apricot kernel and walnut shell.

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This research aimed to study the equilibrium of uranium recovery with ion exchange resins from the solution that simulated the radioactively contaminated groundwater formed in the Centralnyi Yar tailing site.

2. Experimental part

Materials and reagents. We have selected domestic and foreign ion exchange resins with different functionalities [5–7] based on the previous study results [4]:

- quaternary ammonium: Puromet MTA6002PF, Ambersep 920U, AM-p, AM-p-2, Lewatit MonoPlus M 500;
- benzylpyridinium: AMP;
- iminodiacetic acid: Lewatit MDS TP 208, Puromet MTS9300.

To measure parameters of the uranium equilibrium sorption from radioactively contaminated water with ion exchange resins, we prepared the acidic solution that simulated radioactive water in the Centralnyi Yar tailing facility based on the data given in [4]: U – 20.0 mg/dm^3, NO_3^- – 7.81 mg/dm^3, $MgCl_2$ – 93.3 mg/dm^3, $CaCl_2$ – 332 mg/dm^3, KCl – 19.1 mg/dm^3, $MgSO_4$ – 1 535 mg/dm^3, Na_2SO_4 – 297 mg/dm^3, H_2SO_4 – 68.4 mg/dm^3, pH = 3.0. Chemicals used during the measurement were at least reagent grade.

Experimental procedure. We studied uranium equilibrium distribution between the sorbents and the simulated solution using the different portion technique in a static mode by contacting sorbent portions with 20 cm^3 of the solution during 24 hours at a temperature of 20±2 °C using the 357-type temperature-adjusted mixer (Elpan, Poland). Solid and liquid phases were separated after sorption. Uranium concentration in the aqueous phase before and after uranium sorption was measured using photocolorimetry procedure [8] with Arsenazo III at a wavelength of 655 nm. Uranium content in sorbents was calculated by mass balance. The moisture content in sorption materials and the acidity of simulated solution were measured according to the procedures described in [4].

3. Results and discussion

Resin equilibrium capacity (q, mg/g) was calculated by the difference of uranium concentrations in the aqueous phase before and after sorption using the formula:

$$q = \frac{\left([U]_{ini} - [U]_{eq}\right) \cdot V}{m}, \qquad (1)$$

where $[U]_{ini}$ and $[U]_{eq}$ are uranium initial and equilibrium concentrations in the aqueous phase, correspondingly, mg/dm^3; V is the simulated solution volume, dm^3, m is the resin portion weight on an oven-dry basis, g.

Experimental data were processed by the most widely used Freundlich (2), Langmuir (3), and Sips (4) mathematical models [9] using the non-linear regression analysis to calculate quantitative parameters of the uranium recovery equilibrium with ion exchange resins from the simulated solution:

$$q = K_F \cdot [U]_{eq}^{1/n_F} \tag{2}$$

where K_F is the constant, (mg/g)(mg/dm^3)$^{-1/n}$; n_F is an empiric factor; $[U]_{eq}$ is the uranium equilibrium concentration, mg/dm^3;

$$q = \frac{q_m \cdot K_L \cdot [U]_{eq}}{1 + K_L \cdot [U]_{eq}} \tag{3}$$

where q_m is the maximum sorption capacity, mg/g; K_L is the constant, dm^3/mg; $[U]_{eq}$ is the uranium equilibrium concentration, mg/dm^3;

$$q = \frac{q_m \cdot K_S \cdot [U]_{eq}^{n_S}}{1 + K_S \cdot [U]_{eq}^{n_S}} \tag{4}$$

where q_m is the maximum sorption capacity, mg/g; K_S is the constant, dm^3/mg; $[U]_{eq}$ is the uranium equilibrium concentration, mg/dm^3; n_S is the heterogeneity factor.

The OriginPro 2016 software package (demo version) was used to process experimental data and find the equation factors. Tables 1–3 contain the results of the experimental data processing for the specified uranium concentration range when recovering uranium sorption.

Table 1 – Experimental data processing results using the Freundlich equation

Resin	Parameters		
	K_F, (mg/g)(mg/dm^3)$^{-1/n}$	n_F	R^2
AMP	18.48	1.561	0.9967
AM-p	52.52	2.869	0.9477
AM-p-2	14.73	1.876	0.9855
Lewatit MonoPlus M 500	18.41	2.276	0.9765
Puromet MTA 6002 PF	33.73	3.657	0.8718
Lewatit MDS TP 208	51.18	2.537	0.9289
Puromet MTS9300	28.18	2.400	0.9543
Ambersep 920U	17.65	2.183	0.9600

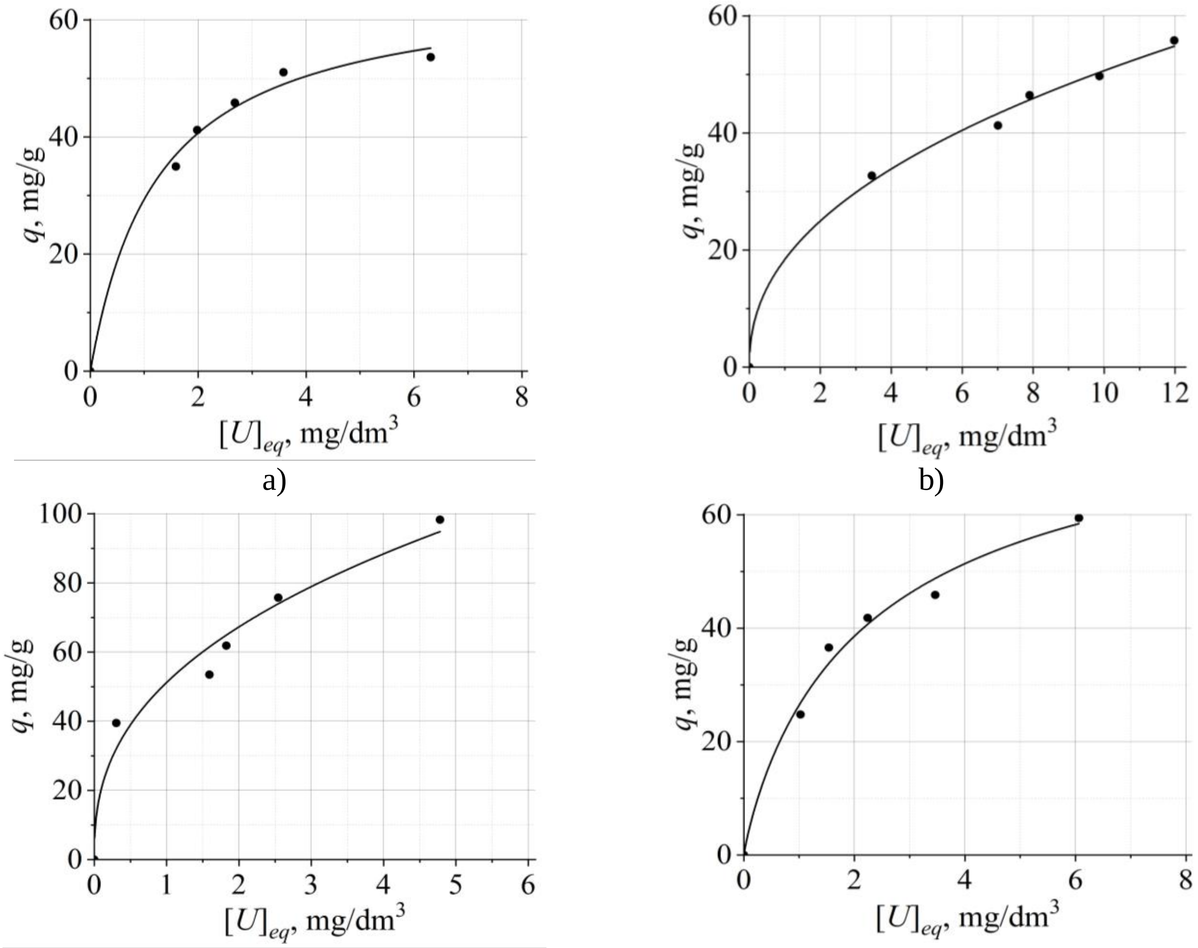
Table 2 – Experimental data processing results using the Langmuir equation

Resin	Parameters		
	q_m, mg/g	K_L, dm^3/mg	R^2
AMP	117.8	0.1593	0.9867
AM-p	88.24	1.626	0.8824
AM-p-2	88.96	0.1296	0.9929
Lewatit MonoPlus M 500	77.03	0.1926	0.9424
Puromet MTA 6002 PF	66.15	0.7985	0.9495
Lewatit MDS TP 208	116.6	0.7464	0.7536
Puromet MTS9300	76.85	0.5108	0.9643
Ambersep 920U	74.03	0.2079	0.9803

Table 3 – Experimental data processing results using the Sips equation

Resin	Parameters			
	q_m, mg/g	K_S, dm^3/mg	n_S	R^2
AMP	2 679	$6.93 \cdot 10^{-3}$	0.6504	0.9966
AM-p	4 765	$1.115 \cdot 10^{-2}$	0.3527	0.9474
AM-p-2	83.97	0.1306	-1.056	0.9930
Lewatit MonoPlus M 500	2 298	$8.04 \cdot 10^{-3}$	0.4476	0.9762
Puromet MTA 6002 PF	55.43	0.6401	-2.148	0.9940
Lewatit MDS TP 208	27 970	$1.83 \cdot 10^{-3}$	0.3951	0.9287
Puromet MTS9300	84.50	0.4551	0.8845	0.9649
Ambersep 920U	64.46	0.2025	-1.221	0.9822

The determination factor value (R^2) was used as the criterion for selecting the sorption equilibrium model. Figures 1–2 show experimental data as well as the plots of isotherm models with the highest determination factor for the studied sorbents.

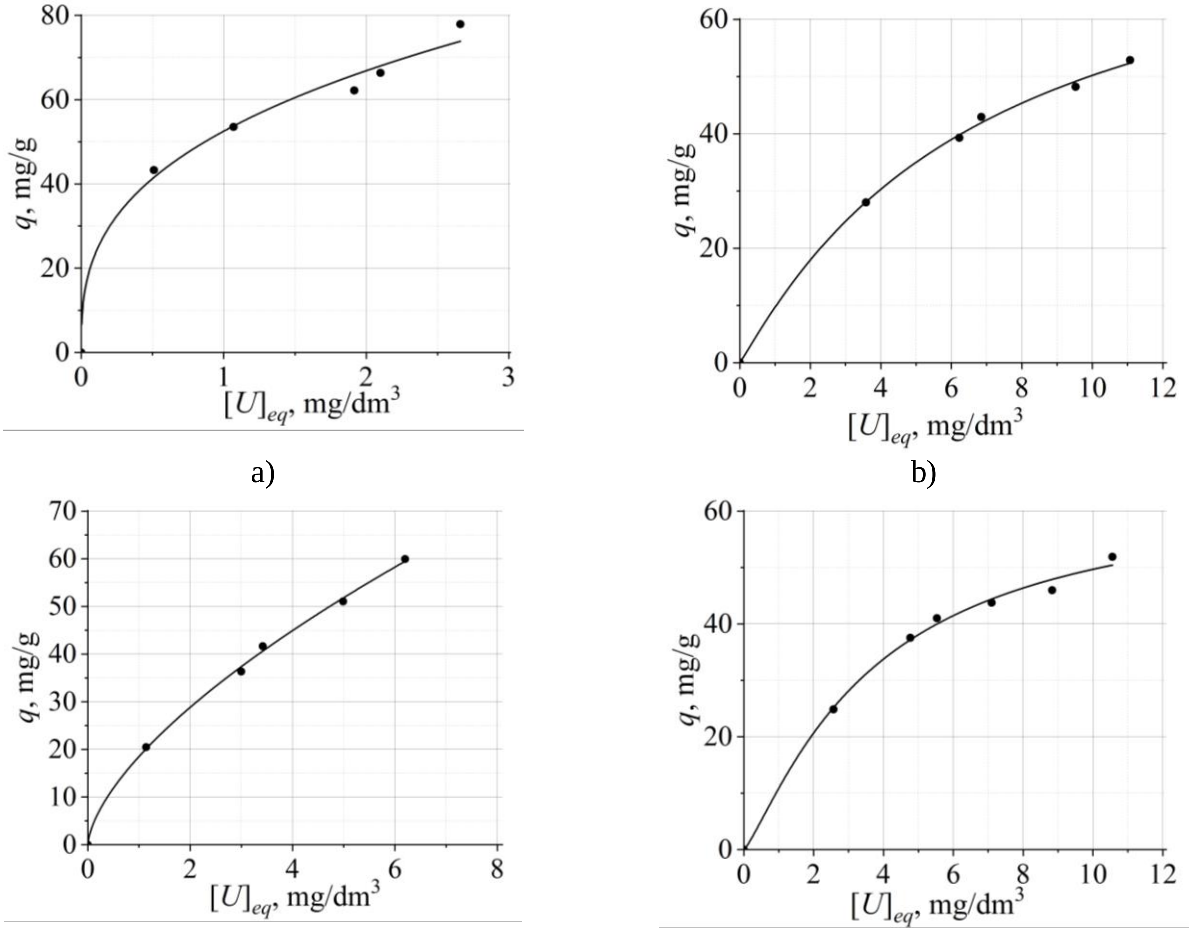


a) b)

c) d)

a) – Puromet MTA 6002 (Langmuir equation), b) – Lewatit MonoPlus M 500 (Freundlich equation), c) – Lewatit MDS TP 208 (Freundlich equation), d) – Puromet MTS9300 (Sips equation)

Figure 1 – Isotherms of uranium recovery from the acidic simulated solution



a) b) c) d)

a) – AM-p (Freundlich equation), b) – AM-p-2 (Sips equation),
c) – AMP (Freundlich equation), d) – Ambersep 920U (Sips equation)

Figure 2 – Isotherms of uranium recovery from the acidic simulated solution

It may be seen from the above data that the following ion exchange resins – AM-p with quaternary ammonium functionalities and Lewatit MDS TP 208 with iminodiacetic groups – feature the highest sorption capacity within the studied range of uranium concentration.

Experimental data were also processed with the Dubinin-Radushkevich model in the linearized form [10]:

$$lnq = lnq_m - \frac{R^2T^2}{E^2}[ln(1+\frac{1}{[U]_{eq}})]^2 \tag{5}$$

where q_m is the maximum sorption capacity, mmole/g; E is sorption characteristic energy, J/mole; $[U]_{eq}$ is the uranium equilibrium concentration, mg/dm^3; T is temperature, К.

Table 4 presents maximum equilibrium capacity and sorption characteristic energy.

Table 4 – Parameters of the Dubinin-Radushkevich equation

Resin	E, kJ/mole	q_m, mmole/g	R^2
AMP	14.87	5.314	0.9960
AM-p	21.32	1.746	0.9555
AM-p-2	15.23	3.068	0.9893
Lewatit MonoPlus M 500	17.46	1.616	0.9730
Puromet MTA 6002	21.34	1.054	0.8878
Lewatit MDS TP 208	21.68	1.674	0.8892
Puromet MTS9300	17.61	2.305	0.9401
Ambersep 920U	16.23	2.262	0.9667

Values of sorption characteristic energy (14.87 kJ/mole to 21.68 kJ/mole) indicate ion exchange mechanism of the recovery process involving chemisorption [10].

4. Conclusions

Based on experimental data, it was revealed that ion exchange resins AM-p with quaternary ammonium functionalities and Lewatit MDS TP 208 with iminodiacetic groups featured the highest sorption capacity within the studied uranium concentration range when recovering it from the acidic solution, which simulated radioactively contaminated water formed in the Centralnyi Yar radioactive waste tailing facility.

The basic parameters of the uranium equilibrium recovery were calculated (model constants, maximum capacity, heterogeneity factor) for the studied sorption materials using Freundlich, Langmuir, Sips, and Dubinin-Radushkevich sorption equilibrium models. It was found that the uranium recovery mechanism involved chemisorptions.

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Conflict of interest

Authors state no conflict of interest.

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РІВНОВАГА ВИЛУЧЕННЯ УРАНУ ІОНООБМІННИМИ СМОЛАМИ З РОЗЧИНУ, ЩО МОДЕЛЮЄ РАДІОАКТИВНО ЗАБРУДНЕНІ ПІДЗЕМНІ ВОДИ

Коровін В., Погорєлов Ю, Кортіна Х.Л., Шестак Ю., Валяєв О.

Анотація. У статті наведені результати дослідження рівноваги вилучення урану гранульованими іонообмінними смолами з розчину, який моделював радіоактивно забруднені підземні води у хвостосховищі радіоактивних відходів «Центральний Яр» колишнього виробничого об'єднання «Придніпровський хімічний завод» (м. Кам'янське, Україна). Це сховище було одним з найстаріших на цьому підприємстві; воно було введене в експлуатацію без будь-якого інженерного захисту днища, що призвело до міграції забруднених радіонуклідами вод у місцевий водоносний горизонт. Радіоактивні відходи, накопичені в ньому, мають сильнокислу реакцію (pH від 2,5 до 4,0). На основі попереднього дослідження сорбції урану різними типами сорбентів було обрано смоли з четвертинними амонієвими, бензилпіридинієвими та імінодіацетатними функціональними групами. Рівновагу вилучення урану вивчали у статичному режимі методом різних наважок шляхом контактування порцій сорбенту з 20 см^3 модельного розчину протягом 24 годин при температурі 20±2 °C. Концентрацію урану у водній фазі вимірювали фотоколориметричним методом. Рівноважні експериментальні дані обробляли за допомогою моделей Фрейндліха, Ленгмюра та Сіпса методом нелінійного регресійного аналізу, критерієм вибору найкращої моделі слугувало значення коефіцієнта детермінації. На основі експериментальних даних визначено, що іонообмінна смола АМ-р з четвертинними амонієвими групами та Lewatit MDS TP 208 з імінодіацетатними групами мають найвищу сорбційну ємність. Експериментальні дані обробляли за допомогою рівняння Дубініна-Радушкевича в лінеаризованій формі. Енергія сорбції (від 14,87 до 21,68 кДж/моль) вказує на іонообмінний механізм, що включає хемосорбцію. На основі використаних моделей розраховані основні параметри рівноважної сорбції урану (константи математичних моделей, максимальну сорбційну ємність, коефіцієнти гетерогенності).

Ключові слова: уран, сорбція, рівновага, іонообмінні смоли, модельний розчин.