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Biosorption of Uranium (VI) from Natural Water

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1. Introduction

Uranium mining and reprocessing industry, atomic energetics, nonsanctioned disposal of waste water, technogeneous catastrophes are the main factors of radio-uranium contamination of the environment including natural water which provide chemical elements' migration in biosphere. In recent year a new additional factor "dirty" bombs with nonriched U-238 has appeared and used by USA and NATO troops in Iraq and Serbia. Hemogenesis and excretion organs of human and animal beings are the most sensitive to uranium but the toxic symptoms can be manifested after a long latent period. The uranium concentration in river water can vary in wide range from 10^{-4} to $5x10^{-5}$ mg/dm^3 [25]. At the same time the maximum permissible concentration of uranium for drinking and household water basins are 1,0 and 0,5 mg/dm^3 respectively [24, 25]. There are four valencies of uranium oxidation in water solution and the most stable form is U(VI) [2, 6, 7, 11, 28, 34]. Because of high hydrolysis and complex forming ability, uranium U(VI) exists in natural water in the form of organic, mainly fulvinate, complexes and their part can achieve 60% [6, 11, 28, 30, 32–34]. In the processes of water ecosystems' self-cleaning microorganisms play an important role. It is established that essentially all microorganisms are able in a specific extent to sorb UO_2^{2+} ions from water solutions [3, 4, 7–9, 12–16, 18–21, 23]. But a possibility of biosorption of uranyl organocomplexes which are the most typical for natural waters metal compounds hasn't been studied up to now. Besides, all mentioned above investigations were fulfilled on pure microbial mono cultures. But real biological processes are accomplished by the combination of microorganisms with the different properties adapted to the coexistence under specific conditions (microbiocenosis). The cheapest and widespread microbocenosis is activated sludge (by-product of biological treatment of municipal west waters).

The goal of our work is the comparative study of the sorption of ions, as well as fulvinate complexes of uranium (VI) by widely available activated sludge from natural river water.

2. Materials and methods

A natural water of the Dnieper River was used in our experiments. The water of pH 6.8 and hardness 7 mg-eq./dm^3 consists of (mg/dm^3): sulfates – 500; chlorides – 350; ferrous – 0.3; manganese – 0.1; copper – 1.0; aluminum – 0.5; dry residue – 1000. The system pH value was adjusted with 0,1 M HCl and NaOH solutions and controlled by potentiometry. The water was contaminated by the solutions of uranyl nitrate $UO(NO_3)_2$ or uranyl fulvinate. The last was synthesized at mass ratio UO_2^{2+} : fulvic acid = 1 : 1 and contact time for 2 days. [UO_2 – FA] is a stable water soluble complex with a constant of formation $6 \cdot 10^7$ and a constant of dissociation $1{,}2 \cdot 10^{-6}$ [2, 15, 31]. Uranium (VI) concentration was measured colorimetrically using Arsenazo III dye.

As a model biosorbent of uranium (VI) the syntrophic microbial association “activated sludge” used all over the world at the station for biological treatment of municipal waste water was tested. It contains all known representatives of microbiota of aqueous ecosystems combined into the aggregates (bioflocks) due to the polysaccharides of *Zoogloea ramigera* which is the most characteristic member of activated sludge microbocenosis. Activated sludge bioflocks possess a highly developed surface and ability to rapid sedimentation [8, 16, 27, 31]. Activated sludge was concentrated by settlement and dosed as a suspension. Biomass concentration in the handling suspension was measured by the gravimetry after drying at 105°C.

Uranium compounds’ uptake by bioflocks (biosorption) was studied by the method of adsorption from solution. For this purpose the suspension of activated sludge microorganisms contaminated with U(VI) was stirred during the time necessary to attain the sorption equilibrium.

The range of initial U(VI) concentrations was 0.1 - 0.8 mM, acting concentration of microorganisms – 1 g/dm^3 (as dry mass). The separation of used bioflocks from a liquid phase was performed by settlement during 30 min sufficient for a whole division of the suspension. The uranium (VI) removal from a liquid phase was estimated by its residual concentration expressed as a percents of the initial one:

$$a = \frac{C_i - C_e}{m} \text{ (mmole/g)} \tag{1}$$

where C_i и C_e are the initial and equilibrium metal concentration in solution (mM), m is the biosorbent concentration (g/dm^3).

Freundlich proposed the formula [1, 3, 5, 9, 12, 17, 19-22, 26, 29], describing adsorption process

$$a = kC_e^{\frac{1}{n}} \text{ (mmole/g)} \tag{2}$$

where a – adsorption, k, $1/n$ – constants.

Freundlich formula uses along with the constant k (depending mainly on the solution temperature and adsorbent's surface) the constant n which is a temperature function. The constant n is always more than one. The Freundlich isotherm equation is widely applied for a description of adsorption from diluted water solutions. In a linear form the equation (2) can be written as

$$\lg a = \lg k + \frac{1}{n}\lg C_e \tag{3}$$

When analyzing uranium (VI) biosorption dependence on its equilibrium concentration in solution, the Langmuir equation [9, 12, 16, 17, 21, 23, 26, 29].

$$a = \frac{a_{\max} K C_e}{1 + kC_e} \tag{4}$$

was used in the linearized form [1, 9, 10, 21].

$$\frac{C_e}{a} = \frac{1}{a_{\max}} K + \frac{C_e}{a_{\max}} \tag{5}$$

where $a_{\max}$ – the limiting sorption of U(VI), mmole/g, K – constant proportional to the affinity of U(VI) for a biosorbent [9, 26].

The equation (4, 5) doesn't take into account interactions between uranium molecules. The form of the equation (5) is used for a description of adsorption processes for *l*-type isotherms in the C_e/a coordinates as the C_e function [21]. Within the bounds of applicability of the equation (5) one can obtain a straight line with a slope $1/a_{max}$ and the section $1/a_{max}{\cdot}K$ on the axis C_e/a.

When studying uranium (VI) desorption, biosorbent (activated sludge) loaded by uranium (VI) was covered with a fresh portion of pure natural water or 0.1 M $NaHCO_3$ solution. Then the suspension was stirred for 30 min, the bioflocks were allowed to settle and in water phase uranium (VI) concentration was detected and compared with the one, early sorbed from a challenge volume.

3. Results and discussion

One of the most important controllable factors that are responsible for the behavior of uranium (VI) in water solution is the pH value. In this connection, we studied the influence of the pH value on the efficiency of the metal sorption by microbocenosis at 40 min contact time sufficient for sorption equilibrium attainment (Fig. 1). Maximum interaction occurs at pH 4-5 when the metal is present in the form of water-soluble cations UO_2^{2+} [9, 18, 21, 32, 33]. Some decrease in uranyl biosorption at the neutral pH values within the range of the pH value 6-7 in comparison with more acid medium can arise from the formation at these conditions hydroxocomplexes $[UO_2OH]^+$, $[(UO_2)_3(OH)_5]^+$, $[UO_2(OH)_2]$ [2, 28, 31, 33]. A specific feature of the pH dependence of uranyl biosorption is its significant inhibition at pH≥8 when U(VI) is present in the form of negatively charged water soluble compounds – uranite ions UO_4^{2-}, polyuranite ions $U_2O_7^{2-}$, $U_3O_{10}^{2-}$ and carbonate complexes of uranyl $[UO_2(CO_3)_3]^{4-}$ [2, 28, 32, 33]. The data obtained (Fig. 1, curve 2) show that within the studied range of the pH value from 4 to 9 a sorption of uranyl fulvic complexes slightly depends on the level of water acidity and substantially less effective than a sorption of a free uranyl-ion.

The dependence of a specific sorption of uranium (VI) compounds in the form of ions, hydroxo- and fulvinate complexes by activated sludge microbocenosis on equilibrium (residual) metal concentration was studied in the range of their initial concentrations from 0.1 to 0.8 mM (Fig. 2). The curves obtained (Fig. 2) have the shape of Langmuir isotherms with steep initial plot, indicating a high affinity of studied uranyl forms to the challenge biosorbent and chemosorption character of interaction in the system uranium (VI) – activated sludge microbocenosis. It is established, that the better fit occurred with the Langmuir linear isotherm with high correlation coefficient values (r^2), 0.9882 (UO_2^{2+}), 0.9903 ($[UO_2OH]^+$, $[(UO_2)_3(OH)_5]^+$, $UO_2(OH)_2$), 0.9874 ([UO_2-Fulvinate]) which can be observed in tab. 1. At the same time the r^2 values for Freundlich isotherm were ($r^2 = 0.9645$ (UO_2^{2+}), $r^2 = 0.9720$ ($[UO_2OH]^+$, $[(UO_2)_3(OH)_5]^+$, $UO_2(OH)_2$), $r^2 = 0.9653$). The values of the correlation coefficient r^2 calculated as a measure of agreement of experimental data with the isotherms models.

The calculated Langmuir equation coefficients (Table 1) show that a limiting sorption of uranium (VI) by activated sludge microbiocenosis under optimal conditions can be very high $a_{\max} = 0.636$ mmole/g = 151.4 mg/g. This is much higher than the corresponding values for bacterial monocultures – 100 mg/g, for activated carbon – 80 mg/g [18] and for ion-exchange resins – 20 mg/g [16]. We can notice that activated sludge microbocenosis is able to sorb more than 0.26 mmole/g = 61 mg/g of uranium (VI) even in the form of weakly active fulvinate complex. A possibility of high uranyl uptake from natural water by activated sludge is supported by the sorption indexes calculated after Freundlich approach (Table 1a).

The experiments on U(VI) adsorption from activated sludge by natural water (Table 2) showed that at the initial handling U (VI) concentration in adsorption cycle ~0.2 mM the metal, regardless of the form being in water, is strongly bound by the microorganisms. However, upon the action of HCO_3^- ions (at pH level increases to > 8) uranium sorbed as hydroxocomplex can transfer into aqueous phase after transformation into carbonate complex at these conditions.

Table 1. Characteristics of uranium (VI) adsorption from natural water by microbocenosis of activated sludge (by Langmuir equation)
Tabela 1. Charakterystyka adsorpcji uranu (VI) mikrobiocenozą osadu czynnego z wody naturalnej (według równania izotermy Langmuira)

Uranium (VI) form	pH	$a_{\max}$		K	r^2
		mmole/g	mg/g		
UO_2^{2+}	4.0÷4.3	0.636	151.39	98.98	0.9882
$[UO_2OH]^+$ $[(UO_2)_3(OH)_5]^+$ $UO_2(OH)_2$	6.0÷6.3	0.373	88.79	160.0	0.9903
$[UO_2\text{-ΦK}]$	6.4÷6.8	0.260	61.89	10.70	0.9874

Table 1a. Characteristics of uranium (VI) adsorption from natural water by microbocenosis of activated sludge (by Freundlich equation)
Tabela 1a. Charakterystyka adsorpcji uranu (VI) mikrobiocenozą osadu czynnego z wody naturalnej (według równania izotermy Freundlicha)

Uranium (VI) form	pH	k		1/n	n	r^2
		mmole/g	mg/g			
UO_2^{2+}	4.0÷4.3	0.244	58.13	0.269	3.720	0.9645
$[UO_2OH]^+$ $[(UO_2)_3(OH)_5]^+$ $UO_2(OH)_2$	6.0÷6.3	0.187	44.54	0.183	5.464	0.9720
$[UO_2\text{-ΦK}]$	6.4÷6.8	0.031	7.33	0.440	2.272	0.9653

Table 2. Efficiency of uranium (VI) desorption from the biosorbent
Tabela 2. Efektywność desorpcji uranu (VI) z biosorbentu

Desorbing solution	pH	U (VI) form	a mmole/g	C_e mM	Desorption, %
Natural water	6.6	Hydroxocomplexes Fulvinate complex	0.197 0.120	0.0 0.0	0.0 0.0
0,1 M $NaHCO_3$ solution	8.2	Hydroxocomplexes Fulvinate complex	0.198 0.122	0.182 0.0	92.0 0.0

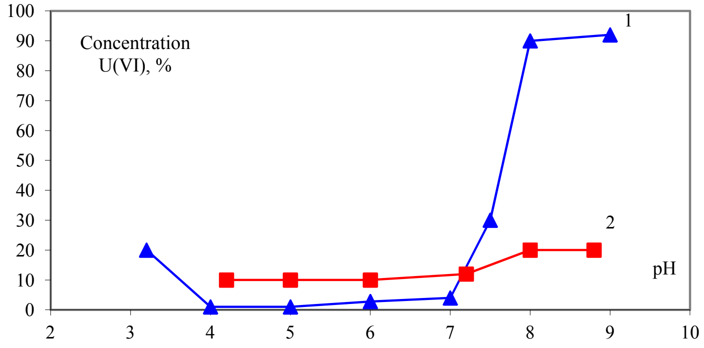

Fig. 1. Dependence of the uranium (VI) concentration in natural water on pH in the course of biosorption process: 1 – ion-form, 2 – fulvinate complex form, initial uranium concentration – 0,2 mM

Rys. 1. Zmiany stężenia równowagowego uranu (VI) w wodzie naturalnej w procesie biosorpcji dla różnych wielkości pH: 1 – forma jonowa, 2 – fulwokompleks

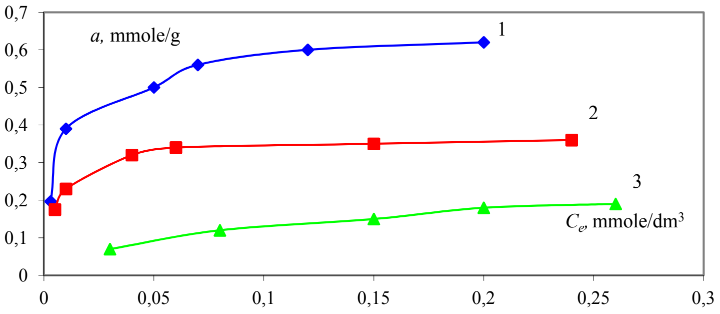

Fig. 2. Isotherms of uranium (VI) biosorption from natural water in the form of ions at pH 4.0÷4.3 (1), hydroxocomplexes at pH 6.0÷6.4 (2), fulvinate complexes at pH 6.0÷6.4 (3)

Rys. 2. Izotermy biosorpcji uranu (VI) w wodzie naturalnej w formie jonowej dla pH 4.0÷4.3 (1), hydrokompleksu dla pH 6.0÷6.4 (2), fulwokompleksu dla pH 6.0÷6.4 (3)

The previous investigation [4, 7–9, 12–16, 18, 20, 21, 23] showed that the microbial monocultures had been able to sorb efficiently U(VI), both as simple ions and hydroxocomplexes, but in the form of organocomplexes (fulvinates, humates, citrates) it hadn't interacted with cells. So, cheap and widely available activated sludge, by-product of biological waste water treatment plants, capable to sorption U(VI) in different forms, can be considered as a promising biosorbent for heavy metals removal from aqueous systems.

Therefore, implementation of complex microbocenosis of activated sludge can open the new prospects in the rehabilitation of water systems contaminated by uranium compounds in different forms (the ions, inorganic and organic complexes). The results of this study can serve as a base for the development of ecological approaches to the remediation of water ecosystems contaminated by heavy metals.

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Biosorpcja uranu (VI) z wody naturalnej

Streszczenie

Celem pracy było zbadanie sorpcji różnych form uranu (VI) przez mikroorganizmy z naturalnej wody. W procesach samooczyszczenia wodnych ekosystemów ważną rolę odgrywają mikroorganizmy. Ustalono, że praktycznie wszystkie mikroorganizmy mogą adsorbować jony UO_2^{2+} z roztworów wodnych, jednak możliwość biosorpcji najbardziej charakterystycznych dla naturalnej wody organicznych kompleksów uranylu do chwili obecnej nie została zbadana.

W badaniach wykorzystywano wodę z Dniepru o pH = 6.8 i następujących zanieczyszczeniach (w mg/dm^3): siarczany – 500; chlorki – 350; żelazo – 0,3; mangan – 0,1; miedz – 1,0; glin – 0,5; sucha pozostałość – 1000. Stężenie uranu w wodzie Dniepru jest zmienne i wynosi około $5x10^{-5}$ mg/dm^3 – jednak w wodach innych rzek i zbiornikach wodnych Ukrainy wynosi ono od 10^4 do $5x10^{-5}$ mg/dm^3. Do eksperymentu wykorzystywano wodę z rzeki do której dodawano związki uranu.

Jako biosorbent uranu (VI) zastosowano mikroorganizm osadu czynnego wykorzystywane w stacji oczyszczania ścieków komunalnych z charakterystyczną dla osadu czynnego znaczącą ilością bakterii *Zoogloea ramigera*. Kłaczki osadu czynnego posiadają rozwiniętą strukturę porowatą, a więc i stosunkowo wysoką pojemność adsorpcyjną oraz zdolność do sedymentacji. Stężenie biomasy w zawiesinie określano poprzez wysuszenie w temperaturze 105°C.

Jednym z najważniejszych czynników determinujących zachowanie się związków uranu (VI) w wodzie i jego adsorpcja z roztworów wodnych jest jej pH. W pracy zbadano wpływ pH na efektywność sorpcji. Równowagę sorpcyjna ustalono na 40 min. Maksymalny efekt wzajemnego oddziaływania obserwowano dla pH = 4,0÷4,3 gdy metal znajdował się w postaci rozpuszczalnych kationów UO_2^{2+}. Dla wartości obojętnych pH = 6,0÷6,8 następowało zmniejszenie biosorpcji uranylu, w porównaniu z środowiskiem bardziej kwaśnym, na co wpływały powstające hydrokompleksy z mniejszym ładunkiem – $[UO_2OH]^+$, $[(UO_2)_3(OH)_5]^+$, $[UO_2(OH)_2]$.

Cechą charakterystyczną zależności biosorpcji uranylu od $pH \geq 8$ jest wzrost stężenia uranu (VI) w formie ujemnie naładowanych jonów rozpuszczalnych w wodzie: jonów UO_4^{2-}, $U_2O_7^{2-}$ i $U_3O_{10}^{2-}$ oraz kompleksów węglanowych uranyl $[UO_2(CO_3)_3]^{4-}$. Wyniki eksperymentu przedstawione na rys. 1 (krzywa 2) wskazują, że w przedziale pH = 4÷9 sorpcja fulwokompleksu uranylu jest tylko nieznacznie zależna od kwasowości wody i znacznie mniej efektywna niż wolnego jonu uranylu.

Wykonane badania potwierdziły, że bakterie osadu czynnego efektywnie adsorbują uran (VI) w postaci jonów i hydrokompleksów, jednak w formie organicznych kompleksów nie obserwowano wzajemnego oddziaływania, interakcji uranu z komórkami.