

Dedicated to professor Gh. Marcu at his 80th anniversary

ON THE DEPOLLUTION OF SOME RADIOACTIVE EFFLUENTS

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ABSTRACT. In this review, parts of our recent analyses in the depollution of the radioactive wastewaters are reported. The studies were focused in two main directions: (1) laboratory analyses on biodepollution of low radioactive waste waters, both in the absence and in the presence of the ionic competition and (2) chemical treatment of the radioactive waste waters using microporous titanosilicates and calix[4]arene/ *p*-(*tert*-butyl)calix[4]arene. In some cases, different aspects of the chemical reactivity, the kinetic of the reactions and the thermodynamic properties are presented.

1. Introduction

The problems of environmental radioactivity pollution are of crucial concern to state and local authorities responsible for environmental protection and control of nuclear wastes and weapons. In principle, there are two sources of environmental radioactivity, namely natural and manmade [1].

The pathways of radionuclides through the environmental waters are extremely complex. Transportation by water contaminates soils and water sources (rivers, lakes and the sea), many of which are situated far away from the release point. This is why in the Laboratory of Radiochemistry of "Al.I. Cuza" University of Iași a reinforced research in this matter started about ten years ago.

2. Recent analyses of bioaccumulation using plant species and microorganisms

Application of bacteria, fungi, algae or even plants to clean up surface and ground water contaminated by radionuclides has been increasingly applied. Hence a large number of studies on bioaccumulation or biosorption of $^{51}\text{Cr}^{3+}$, $^{60}\text{Co}^{2+}$, $^{90}\text{Sr}^{2+}$, $^{137}\text{Cs}^+$, $^{204}\text{Tl}^+$, Th(IV), U(VI) from liquid wastes on different biocollectors has been reported.

2.1. Bioaccumulation of uranium using different strains of *Saccharomyces cerevisiae*

Under conditions of a natural aqueous systems, the insoluble uranium rapidly corrodes forming yellow uranyl compounds, where the linear $[\text{O}=\text{U}=\text{O}]^{2+}$ entity forms the characteristic structural elements. Most notably, the solution chemistry of

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U(VI) is relatively complex, with numerous mono- and polynuclear uranyl-hydroxide and uranyl-carbonate complexes being formed.

The possibility of bioaccumulation of uranium species in beer yeast was investigated [2]. The behaviour of the *S. cerevisiae* – UO_2^{2+} system was studied versus contact time, pH and anion nature without ionic competition. Analysis of the obtained data revealed the following optimal working conditions: 1 h contact time, pH = 6.5 and 0.1 M $\text{UO}_2(\text{CH}_3\text{COO})_2$ solution as uranyl source; as result, the maximum degree of bioaccumulation attends a value nearly 8.75 mmol UO_2^{2+} /g yeast. Both scanning electron microscopy and amino acid determinations lead to the conclusion that the uranyl nitrate solution may devastate the yeast cells provoking membrane damage and the release of the cell constituents (including the bioaccumulated uranium species).

However, in natural contaminated waters, the uranium series decay products and the non-radioactive cations influence uranium bioaccumulation process. Consequently, five different strains of *S. cerevisiae* were tested to analyze the bioaccumulation of U(VI) from waste water containing competitive ions [3]. Samples of water passing out from a previous uranium mill were used. The accumulation capacities of the tested strains were different. The kinetics of bioaccumulation, the leaching degree, the influence of cell density and their origin were analyzed. Under the applied working conditions, more than a half of the total activity could be accumulated after 1 h contact time of 1 ml *S. cerevisiae* suspension and 5 ml of water. The heavy metals effectively competed the uranium accumulation.

2.2. Decontamination of radioactive liquid wastes by hydrophytes vegetal organisms

The bioaccumulation of some radioactive ions from contaminated waste solutions, on hydrophytic vegetal organisms. In order to follow the distribution of radioactive ions $^{51}\text{Cr}^{3+}$ [4], $^{60}\text{Co}^{2+}$, $^{137}\text{Cs}^+$ [4,5] and $^{65}\text{Zn}^{2+}$ [6] in various cell components extracted from *Spirulina platensis*, *Porphyridium cruentum*, *Scenedesmus quadricauda*, *Lemna minor*, *Elodea canadensis*, *Pistia stratiotes*, *Riccia fluitans* and *Azolla caroliniana* the plants were "cultivated" in radioactive solutions.

The formed complexes were extracted with acetone or acetic acid and were chromatographically separated. The results show an intense activity of the polysaccharide and lipid fractions in the bioaccumulation process. The unusually high removal activity of lipids was probably due to the partial hydrolysis into the fatty acids and triglycerides, with a greater chelating action of the cations. An example of thin layer radiochromatography experiment is presented in Fig. 1.

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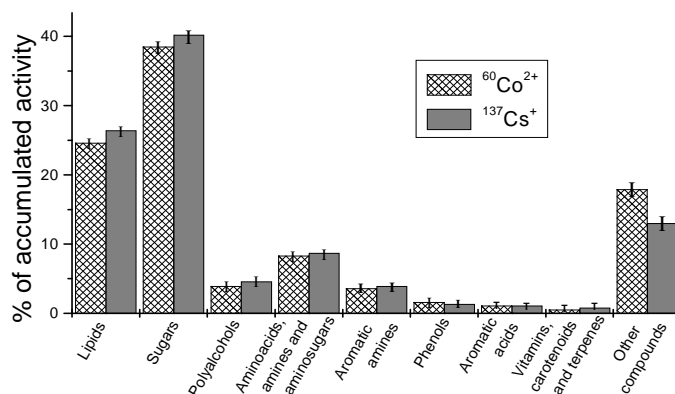


Fig. 1. The amount of ¹³⁷Cs⁺ and ⁶⁰Co²⁺ – radioactive ions localized in different biochemical components of the living fern *Azolla caroliniana* Willd.

3. Chemical treatment of the low radioactive wastewaters

3.1. Sorption of ⁶⁰Co²⁺, ¹¹⁵Cd²⁺, ¹³⁷Cs⁺ and ²⁰⁴Hg²⁺ on ETS-4 and ETS-10 microporous titanosilicates

ETS-4 (synthesized from gel with following molar composition: 2.0Na₂O: 0.3TiO₂: 0.6KF: 2.56HCl: 1.49SiO₂: 39.5H₂O) and ETS-10 (synthesized from gel with following molar composition: 1.0Na₂O: 1.49SiO₂: 0.2TiO₂: 0.6KF: 1.28HCl: 39.5H₂O) were subjected to sorption of radioactive cations ⁶⁰Co²⁺, ¹¹⁵Cd²⁺, ¹³⁷Cs⁺ and ²⁰⁴Hg²⁺ from aqueous solution, in the absence of ionic competition [7,8]. The uptake of these radiocations was compared by means of the distribution coefficient (K_d) versus contact time, determining their cationic exchange capacity at equilibrium.

Table 1.

The distribution coefficients of ⁶⁰Co²⁺, ^{115m}Cd²⁺ and ²⁰³Hg²⁺ on ETS-4 and ETS-10 titanosilicates.

Radioactive ion	Temperature, K	K _d , ml/g	R, meq/g
⁶⁰ Co ²⁺	277	436	3.03
	293	733	4.23
	313	760	4.31
¹¹⁵ Cd ²⁺	277	631	3.87
	293	791	4.43
	313	811	4.48
¹³⁷ Cs ⁺	277	1258	3.83
	293	1636	4.50
	313	1670	4.55
²⁰⁴ Hg ²⁺	277	341	2.54
	293	627	3.85
	313	808	4.45

For all sorption systems and the considered radiocations, a rapid increase of K_d in the first minutes of contact can be observed. The higher the exchange temperature, the higher the value of K_d ; further, the equilibrium value is established more quickly. The maximum sorption capacity at equilibrium, stated in ml/g (K_d) and meq/g (exchange capacity – R), are summarised in Table 1. The values of ΔH° , ΔS° and ΔG° for the considered sorption systems were given in Table 2.

Table 2.

Thermodynamic parameters for the sorption of M^{n+} radiocations on ETS-4 and ETS-10 titanosilicates.

Cation	Titanosilicate	$K_d, \text{cm}^3/\text{g}$			
		277 K	293 K	313 K	333 K
Co^{2+}	ETS-4	536	593	625	649
	ETS-10	436	733	760	_{-b}
Cd^{2+}	ETS-4	583	651	693	750
	ETS-10	631	791	811	_{-b}
Hg^{2+}	ETS-4	644	778	801	810
	ETS-10	341	627	808	_{-b}

3.2. Use of some calixarenes as cleaning agents for low radioactive waste waters

Calixarenes are products of the condensation of phenol *p*-substituted with formaldehyde in an alkaline medium. One of the most important practical applications of this class of compounds is the environmental decontamination of waters containing ions of the heavy metals like Cs^+ , Ag^+ , Au^+ , Hg^{2+} , Pb^{2+} , Cd^{2+} etc.

In order to clean some low radioactive contaminated waters containing $\beta+\gamma$ -active cations ($^{55+59}\text{Fe}^{3+}$, $^{60}\text{Co}^{2+}$, $^{65}\text{Zn}^{2+}$ and $^{137}\text{Cs}^+$), calix[4]arene and *p*-(*tert*-butyl)calix[4]arene has been used [9]. Experiments were performed in the absence of ionic competition, at 277, 293 and 313 K. Whatever the temperature and the sorbent used, the capacity of retaining the $\beta+\gamma$ -active cations varies as follows: $^{55+59}\text{Fe}^{3+} > ^{60}\text{Co}^{2+} \geq ^{65}\text{Zn}^{2+} > ^{137}\text{Cs}^+$ (the capacity of sorption decreases with the increasing ionic radius and decreasing cationic valence).

In the uranium case, the interaction is a chemical one, a new 1:1 UO_2^{2+} : *p*-*tert*-butylcalix[4]arene complex being synthesised [10] in acetone. The combination metal: ligand ratio was determined by mass spectrometry and by the Job method. The chemical binding of uranium was proved by FT-IR spectroscopy and by a leaching study. The mass spectrum of the UO_2^{2+} :*p*-*tert*-butylcalix[4]arene complex (Fig. 2) indicates that the molecular peak appears at $m/z = 908$ a.m.u. which correspond to a combination ratio M:L = 1:1 (650÷700 K). The most intense peaks appears at $m/z = 56$ a.m.u. (solvent) and $m/z = 648$ a.m.u. (*p*-*tert*-butylcalix[4]arene ligand). Although other significant peaks do not appear in the 648÷908 u.a.m. m/z range, we cannot conclude that the prepared compound is pure, because a part of ligand may be still unreacted.

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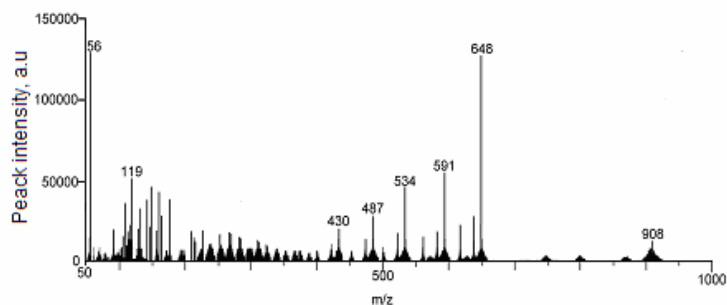


Fig. 2. Mass spectrum of the 1:1 UO_2^{2+} :p-*tert*-butylcalix[4]arene complex.

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