J. Condensed Matter Nucl. Sci. 28 (2019) 50–52

Extended Abstract

Thermodynamic Prediction for Novel Environmental Biotechnologies of Radioactive Waste Water Purification

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Abstract

Extended Abstract is given.

Keywords: Bioremediation of ecosystems, Biotechnologies, Microorganisms, Purification of radioactive waste water, Thermodynamic prediction

Extended Abstract

The universal concept of thermodynamic justification of novel biotechnologies to purify liquid radioactive waste and for bioremediation of polluted ecosystems from a wide range of radionuclides and toxic metals has been developed. The main provisions of the concept are based on the thermodynamic prediction of the interaction of microorganisms, algae and vascular plants with radionuclides and metals of the periodic system of elements.

They are the following.

(1) Thermodynamic prediction of microorganisms and plants interaction with metals and radionuclides.
   - (a) Nonspecific reduction of metals and radionuclides to insoluble compounds.
   - (b) Metals and radionuclides accumulation due to their stereochemical analogy with macroelements.
   - (c) Integration of interaction mechanisms: nonspecific reduction and nonspecific accumulation.

(2) Application of thermodynamic prediction and concentration functions of I and II order (by V. Vernadskii) is used to estimate the theoretically permissible and effective integrated mechanisms of radionuclides accumulation.

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(3) Development of a theoretical basis of comprehensive biotechnologies for the purification of radioactive waste water and for bioremediation of ecosystems.

The nonspecific reduction of radionuclides to insoluble compounds is based on redox properties of binary systems consisting of metabolically active microorganisms and radionuclides. Microorganisms serve as the donor system and radionuclides are the acceptor system. If a potential difference between these systems is 100 mV and higher, microorganisms inevitably reduce soluble oxidized radionuclide compounds to insoluble ones:

$$^{51}\mathrm{CrO}_4^{2-} + 3\mathrm{e} + (n-1)\,\mathrm{H_2O} + 5\mathrm{H}^+ = \,^{51}\mathrm{Cr(OH)}_3\, n\mathrm{H_2O}\downarrow,$$

$$^{51}\mathrm{Cr(VI)\ soluble} + 3\mathrm{e} = \,^{51}\mathrm{Cr(III)\ insoluble},$$

$$4[\mathrm{UO_2(CO_3)_3}]_4^- + \mathrm{HS}^- + 15\,\mathrm{H}^+ = 4\,\mathrm{UO_2} + \mathrm{SO}_4^{2-} + 12\,\mathrm{CO_2} + 8\,\mathrm{H_2O},$$

$$^{238}\mathrm{U(VI)\ soluble} + 2\mathrm{e} = \,^{238}\mathrm{U(IV)\ insoluble}.$$

To implement this kind of method to remove of radionuclides from solutions, the standard redox potential of the reduction of radionuclides must be within the zone of thermodynamic stability of water (–414 < Eh < $+814$ mV). For example, ^{51}Cr(III) can not be reduced to metallic chromium, since the standard potential of its reduction reaction is more electronegative than the potential of the lower limit of water stability ($E_0' = -414$ mV):

$$^{51}\mathrm{Cr(OH)}_3\, 3\mathrm{H}^+ + 3\mathrm{e} = \,^{51}\mathrm{Cr}^0 + \mathrm{H_2O}, \quad E_0' = -1000\ \mathrm{mV}.$$

Radionuclides, for microbial reduction of which a thermodynamic inhibition takes place, will be accumulated by microorganisms due to their stereochemical analogy with macroelements. The macroelements include the ions necessary for the metabolism of microorganisms: K^+, Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, PO_4^{3-}, etc. Stereochemical analogy is the proximity or equality of ionic radii of macroelements and radionuclides. For example, $^{90}Sr^{2+}$ is the stereochemical analogue of Ca^{2+}, for which the ionic radius (IR) is 0.11 nm. The ions of $^{83}Rb^+$ (IR = 0.15 nm), $^{226}Ra^{2+}$(IR = 0.155 nm) and $^{134,137}Cs^+$(IR = 0.165 nm) are the stereochemical analogs of NH_4^+ (IR = 0.15 nm). That is why the acceptor transport systems of microorganisms intended for the absorption of macroelements are wrong and transport radionuclides together with macroelements inside cells.

The integration of two mechanisms for removal of radionuclides from aqueous solutions (reduction to insoluble compounds and accumulation due to a stereochemical analogy) provides effective purification of liquid radioactive waste.

The effectiveness of accumulation of radionuclides by living organisms (microorganisms, microalgae, algae, vascular plants, etc.) is determined by V. Vernadskii's equation for Biogeochemical Energy of Growth and Proliferation:

$$2^{n\Delta} + (\alpha + 1)^n = Nn.$$

In this equation *n* is number of days, 2 the initial number of organisms, *N* is the number of organisms after *n* days growth, α the daily increase in number of organisms (cells), and Δ the coefficient of proliferation (generations per day).

The effectiveness of radionuclide accumulation is determined primarily by the value of the index α, that is, effectiveness of growth and proliferation. For microorganisms (*Escherichia coli*) $\alpha = 2.78 \times 10^{18}$, for unicellular organisms

(*Infusoria* and *Diatomea*) $\alpha = 2.32$, and for vascular plants (*Solanum nigrum*) $\alpha = 0.03$. Obviously, microorganisms should be used in biotechnologies for the dominant extraction of radionuclides from solutions. The role of other organisms (microalgae, algae, vascular plants, etc.) lies in the deep post-treatment of liquid radioactive waste; that is to say, the extraction of radionuclides in vanishingly small concentrations.

It follows that artificial ecosystems consistently consisting of the three following blocks are the most promising for the effective purification of liquid radioactive waste.

(1) The biomass of microorganisms in artificial marshes (effectiveness of radionuclide removal – 95%).
(2) Ponds with water plants (effectiveness of radionuclide removal – 4%).
(3) Filter fields with soil plants (effectiveness of radionuclide removal – 0.999%).

Hence it is obvious that the method of thermodynamic prediction of the interaction of microorganisms and other living organisms with radionuclides makes it possible to theoretically substantiate and provide the development of novel biotechnologies for the purification of liquid radioactive waste from a wide range of radionuclides.

J. Condensed Matter Nucl. Sci. 28 (2019) 53–55

Extended Abstract

Novel Biotechnologies for Purification of Radioactive Waste Water

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Abstract

Extended Abstract is given.

Keywords: Effective biotechnologies, Extraction of radionuclides, Microbial pellets, Thermodynamic prediction

Extended Abstract

Based on our concept of thermodynamic prediction of microbial interaction with radionuclides and toxic metals, we developed novel environmental biotechnologies based on microbial pellets. The main properties of the pellets are the following:

- high stability of pellets (due to their structure) in water solutions,
- diversified microbial communities (natural and artificial),
- compounds necessary for active microbial metabolism,
- presence of Regulators of Microbial Metabolism (RMM),
- high concentration of living microorganisms (95–98% weight of pellets).

Due to these properties, the microbial communities of pellets carry out many types of interaction with radionuclides. The interactions are divided into three groups. The first group is outside the cell, the second is on the cell membrane of microorganisms, and the third is inside the cell. When radionuclides are added into a metabolically active culture radionuclides-oxidizers are reduced by microbial exometabolites-reducers to insoluble compounds ($^{51}CrO_4^{2-}$ to insoluble $^{51}Cr(OH)_3\ nH_2O\downarrow$ or $^{238}UO_2OH^+$ to insoluble $^{238}UO_2\downarrow$). Simultaneously the precipitation of radionuclides with exometabolites takes place, e.g.

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Table 1. Efficiency of extraction of radionuclides by microbial pellets from liquid radioactive waste (LRW).

Radionuclide	Activity** of radionuclides (Ki/kg)			The order of LRW activity decrease
	Initial in LRW	In Microbial Pellets	In LRW after purification	
^{51}Cr	3.90×10^{-7}	1.18×10^{-7}	*	5
^{54}Mn	6.70×10^{-8}	4.72×10^{-8}	*	4
^{60}Co	1.09×10^{-6}	5.3×10^{-6}	5.36×10^{-11}	5
^{83}Rb	6.22×10^{-7}	4.16×10^{-7}	*	5
^{90}Sr	3.52×10^{-7}	3.39×10^{-7}	*	5
^{137}Cs	1.36×10^{-5}	7.81×10^{-5}	3.36×10^{-9}	4
^{140}La	7.01×10^{-8}	9.67×10^{-8}	*	4
^{144}Ce	6.17×10^{-6}	3.50×10^{-6}	7.22×10^{-9}	3
^{226}Ra	1.21×10^{-6}	1.11×10^{-6}	7.60×10^{-8}	2

*Indicates less than sensibility of spectrometer (1.0×10^{-12} Ki/kg).
** Radioactive wastewater of the Institute for Nuclear Research (the National Academy of Sciences of Ukraine) measured by Valeriy Shevel.

$$^{194}\mathrm{Hg}^{2+} + \mathrm{CO}_3^{2-} =^{194}\mathrm{HgCO}_3^{2-}\downarrow \quad \text{and} \quad ^{60}\mathrm{Co}^{2+} + \mathrm{S}^{2-} \rightarrow^{60}\mathrm{Co}S\downarrow.$$

It is also possible to bind radionuclides with exopolysaccharides, which are excreted by cells into the external space. Furthermore, the following process occurs on the external cellular structures. Radionuclides substitute stereochemical analogues in the cell wall. Thus, $^{90}Sr^{2+}$ and Ca^{2+} have equal ionic radii (IR), 0.11 nm. Similarly, ionic radii of $^{239}Pu^{6+}$ and Mg^{2+} are equal 0.075 nm that is why $^{239}Pu^{6+}$ substitutes Mg^{2+} in the cell wall. Additional radionuclides are actively transported into cells also due to stereochemical analogy of radionuclides and macroelements. The acceptor and transport systems of microorganisms are activated to transfer radionuclides together with macroelements inside cells. For example, since $^{51}CrO_4^{2-}$ and SO_4^{2-} has equal ionic radii 0.300 nm radioactive chromium is actively transported in cells. Ions of $^{90}Sr^{2+}$ are transported in the same way, since they have the same ionic radii with

Table 2. Types of interaction of microorganisms with radionuclides.

Radionuclide	Type of interaction
$^{51}CrO_4^{2-}$	– Transport inside cells (stereochemical analogue of SO_4^{2-})
	– Reduction to insoluble Cr(III) outside and inside cells
$^{137}Cs^+$	– Transport inside cells (stereochemical analogs of K^+ and NH_4^+)
$^{83}Rb^+$, $^{226}Ra^{2+}$	– Incorporation in cell compounds (substitution of NH_2-groups in amino acids)
$^{90}Sr^{2+}$	– Transport inside cells (stereochemical analogue of Ca^{2+})
	– Precipitation by exometabolites in insoluble compounds:
	– $Sr^{2+} + CO_2 \rightarrow SrCO_3\downarrow$ (solubility index, SI = 1.1×10^{-10})
	– $Sr^{2+} + H_2S \rightarrow SrS + 2H^+ + S^o \rightarrow Sr(OH)_2\downarrow$
$^{54}Mn^{2+}$	– Transport inside cells (stereochemical analogs of Mg^{2+})
$^{60}Co^{2+}$	– Precipitation by exometabolites in insoluble compounds:
	– $Mn^{2+} + Co^{2+} + CO_2 \rightarrow MnCO_3 + CoCO_3\downarrow$(SI = 1.1×10^{-10})
	– $Mn^{2+} + Co^{2+} + 2H_2S \rightarrow MnS\downarrow + CoS\downarrow + 2H^+$ (SI = 1.0×10^{-13})
$^{140}La^{3+}$	– Transport inside cells (stereochemical analogue of Ca^{2+})
$^{144}Ce^{3+}$	– Precipitation by exometabolites in insoluble compounds:
	– $Ce^{3+} + H_2S \rightarrow Ce_2S_3\downarrow + 2H^+ + S^o$
	– $La^{3+} + H_2S \rightarrow La_2S_3\downarrow + H_2O = La(OH)_3\downarrow$

Ca^{2+}. After transfer into cells, radionuclides-oxidizers are reduced by redox enzymes to insoluble compounds, and also precipitated by metabolites.

We were able to effectively extract radionuclides using microbial pellets, from liquid radioactive waste obtained from the Institute for Nuclear Research of the National Academy of Sciences of Ukraine. The efficiency of extraction of radionuclides was high. Within three days, the activity of the solution decreased on average by 4–5 orders due to the accumulation of radionuclides in microbial pellets (Table 1).

Based on the thermodynamic predictive method, it is possible to explain the high efficiency of radionuclides extraction by microorganisms as follows (Table 2).

Thus, we have shown the possibility of using the thermodynamic predictive method to develop effective, novel biotechnologies for purification of liquid radioactive waste from a wide range of radionuclides. Obviously, the method developed by us will be effective for biotechnologies for purification of any types of liquid radioactive waste.