среды Республики Беларусь [Электронный ресурс]. – 2019. – Режим доступа: http://www.nsmos.by/content/402.html – Дата доступа: 03.05.2020.

3. Федорова, А.И. Практикум по экологии и охране окружающей среды: учебное пособие / А.И. Федорова, А.Н.Никольская; под ред. Ю.Г. Королева. – Москва: ВЛАДОС, 2003. – 364 с.

4. Санитарно-микробиологический анализ питьевой воды. Методические указания МУК РБ № 11-10-1-2002. – Минск, 2002. – 43с.

УДК 579.695

THERMODYNAMIC APPROACH TO REMOVE TOXIC METALS AND RADIONUCLIDES FROM INDUSTRIAL SEWAGE AND POLLUTED ECOSYSTEMS

O.B. Tashyrev[1], V.M. Hovorukha[1], O.A. Havryliuk[1], A.V. Sachko[2], G.V. Gladka[1]
[1]*Zabolotny Institute of Microbiology and Virology of the NASU,*
Acad. Zabolotnogo Str., 154, Kyiv, 03143, Ukraine
[2]*Yuriy Fedkovych Chernivtsi National University*
2 Kotsjubynskyi Str., Chernivtsi, 58012, Ukraine
e-mail: tach2007@ukr.net

At the end of the 20th century, our planet was suggested to be on the brink of ecological disaster. In the 21st century, this environmental disaster has already erupted. Our planet is littered with waste and flooded with toxic sewage. The volumes of toxicants in ecosystems are increasing. The lack of a universal approach that theoretically substantiates and practically implements the optimal biotechnology of detoxification of metals and radionuclides is the methodological problem of waste treatment [1, 2, 3, 4].

We developed the concept of thermodynamic prediction of the interaction of microorganisms with metals and radionuclides. This concept makes it possible to create new effective environmental biotechnologies and, in some cases, to obtain valuable products from waste such as metal concentrate and pure water.

We consider the main classes of xenobiotics as extreme factors. They include solid and liquid organic waste, toxic metals and radionuclides. The thermodynamic prediction allows choosing the optimal reaction and metabolic pathway for the detoxification of metals and radionuclides by microorganisms and plants. Further, a microbiome detoxifying xenobiotics is selected and tested. Then a pilot project for wastewater treatment or bioremediation of ecosystems is created basing on the obtained experimental data. Finally, industrial biotechnology is being created at the last stage. It provides not only wastewater treatment and ecosystem bioremediation, but also makes it possible to obtain valuable products from toxic waste.

The main provisions of our Concept are as follows:

1. Non-specific microbial reduction of xenobiotics-oxidants (metals, radionuclides);
2. Non-specific microbial accumulation of metals and radionuclides due to their stereochemical analogy with macroelements;
3. Integration and combination of metabolic pathways of microorganisms for simultaneous implementation of multiple mechanisms of xenobiotics detoxification.

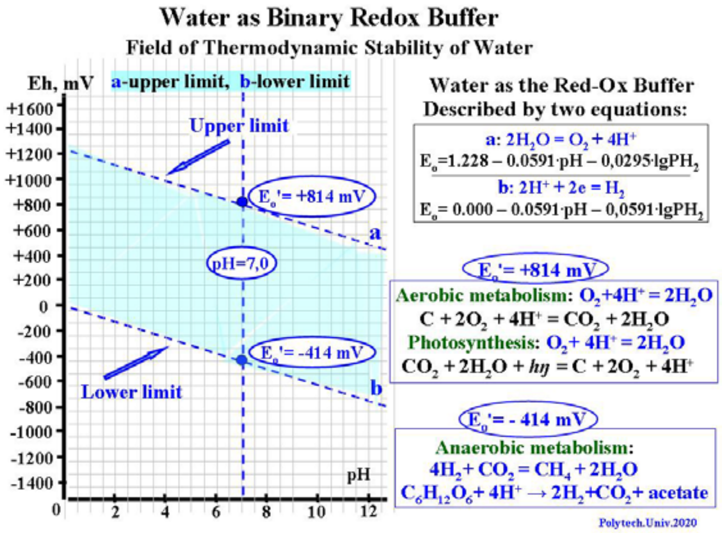
These provisions are used to develop the biotechnology for:

- sewage treatment from metals and radionuclides;

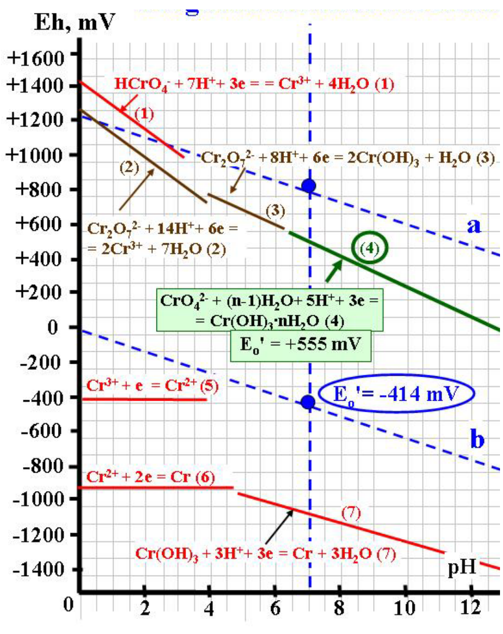
- bioremediation of aqueous and soil ecosystems polluted with metals and radionuclides.

To predict the pathways of microbial interaction with metals we used equations and diagrams of the elements stability in aqueous solutions in the coordinates of «pH-Eh» according to Purbaix [5].

We postulated that all metabolic oxidative-reductive reactions carrying out during vital processes take place inside the zone of water stability (Fig. 1).



A



B

Fig. 1 The thermodynamic prediction of microbial interaction with metals:
A – the thermodynamic stability of water and microbial metabolism;
B – the prediction of chromium compounds reduction by microorganisms. Reactions 1, 5, 6, 7 are impermissible, since their Eh is out of the zone of water stability. Reactions 2, 3 are possible, but unsuitable, because reduced Cr^{3+} is soluble. Only one reaction, 4 is suitable, because $Cr(OH)_3 \cdot nH_2O$ is insoluble.

This zone is limited by two oxidative-reductive reactions. The first one is proton reduction to molecular hydrogen and the second is oxidation oxygen of water (or hydroxyl ion) to molecular oxygen:

$$1).\ O_2+4H^+ + 4e = 2H_2O;\ E_o' = +814\ mV;$$
$$Eh = 1,228 - 0,0591 \cdot pH - 0,0295 \cdot lgPH_2;$$

$$2).\ 2H^+ + 2e = H_2;\ E_o' = -414\ mV;$$
$$Eh = 0,000 - 0,0591 \cdot pH - 0,0591 \cdot lgPH_2,$$

where E_o' – standard redox potential of reaction (Eh, mV) at pH=7 and 1M concentration of both oxidized and reduced forms of reacting compounds; PH_2 – partial pressure of molecular hydrogen (1 atm).

Water is a thermodynamically stable dissolvent between these values. A width of Eh value zone inside which water is thermodynamically stable does not depend on pH and is equal to 1,228 V. On the diagram, the Eh-pH dependence is inclined line, because redox potentials of both reactions are linear functions of pH [5, 6]. The zone of oxidative-reductive water stability is enclosed between potentials – 414 and + 814 mV at pH = 7.

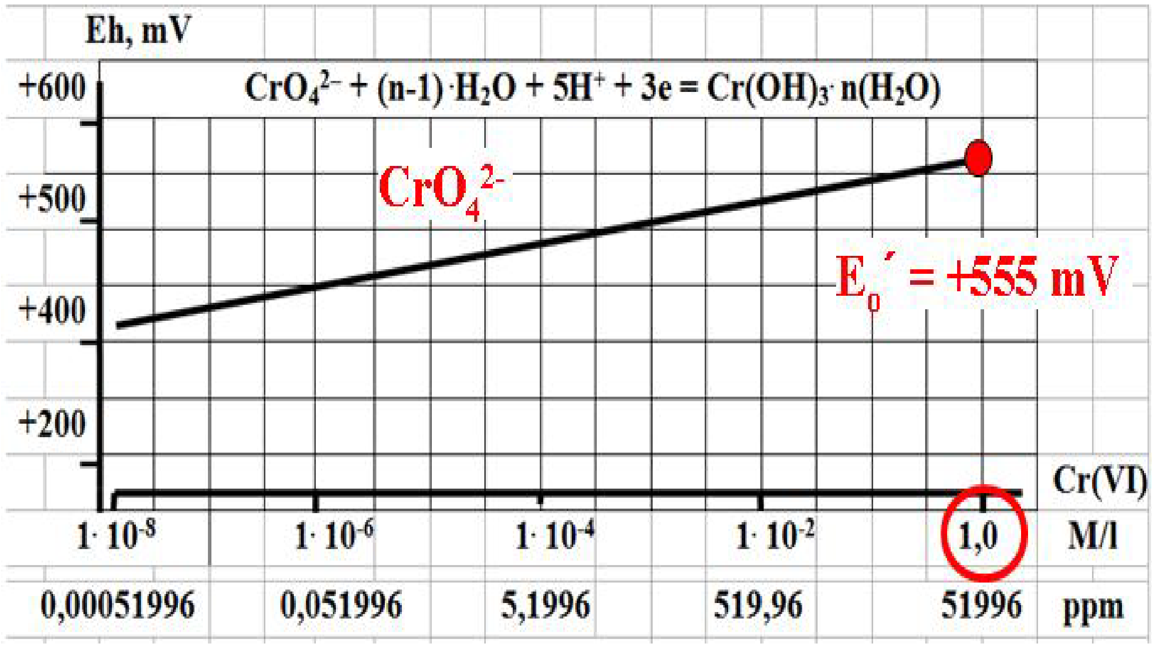
Toxicity of metal depends on the redox potential value of solution defined by the presence of oxidative-reductive system, formed by the oxidized and the reduced metal compounds and the position of this value regarding the limits of water thermodynamic stability zone. Microorganisms effectively use energy obtained from oxidative-reductive reactions which take place inside the zone of water stability (Fig. 1) [7]. Respectively, catabolic oxidative-reductive enzyme systems, starting from high potential oxygenases and cytochromes and ending with ferredoxins and hydrogenases with low redox-potentials, function within the limits of water thermodynamic stability zone [8, 9]. Thus, we supposed that microorganisms can interact with external redox systems and carry out oxidative-reductive reactions with their participation, including metals-oxidizers, upon condition that these reactions are within the zone of water stability thermodynamic.

In accordance with the prediction, we divided all the metals of the periodic system of elements into two groups (see explanations on the example of chromium compounds at Fig. 1, B). The first group includes metals that cannot be reduced by microorganisms. The second one includes metals that can be reduced by microorganisms. The reduction reactions of these metals can be used to remove metals from industrial sewage.

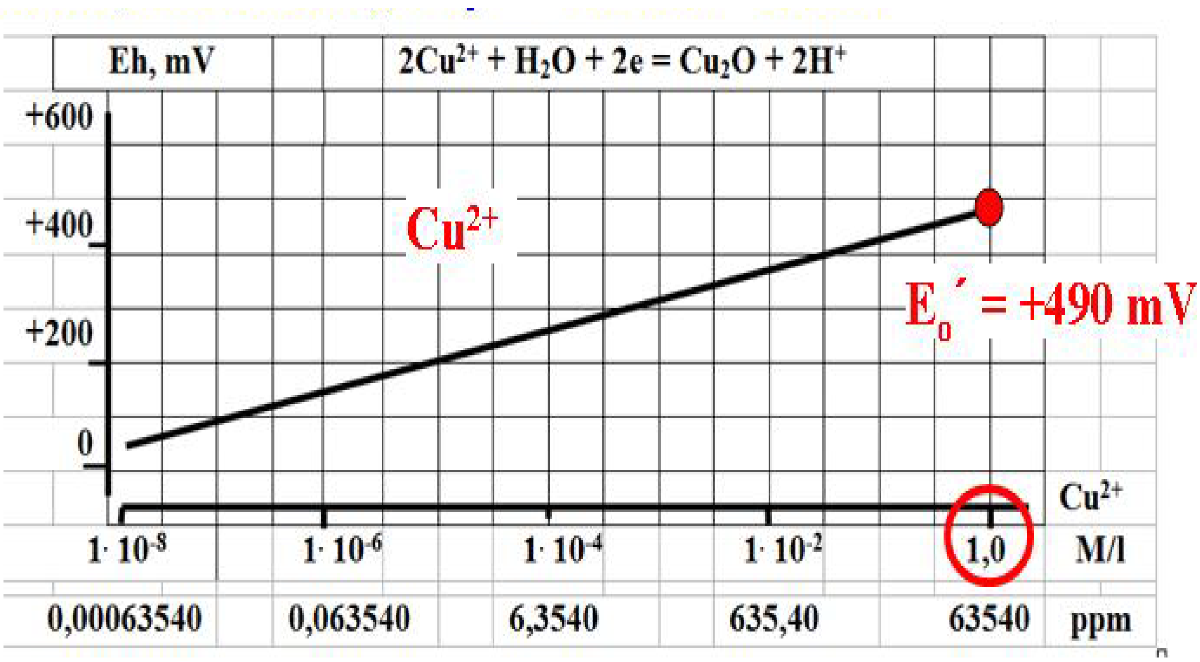
The possibility of the growth of microorganisms at ultrahigh concentrations of metals-oxidizers and interaction with them is one of the consequences of the theory. For example, even at 1M concentration of CrO_4^{2-} and Cu^{2+}, the redox potentials of the reactions of their reduction are inside the zone of water thermodynamic stability (Fig. 2. A, B; Fig. 3). Therefore, microorganisms can not only grow in the presence of ultrahigh concentrations of chromate and copper, but also reduce them to insoluble (and therefore non-toxic) compounds. We confirmed experimentally this seemingly fantastic hypothesis.

Thus, the thermodynamic prognosis allows isolating microorganisms to develop novel biotechnologies for the removal of metals-oxidizers in a wide concentration range.

The concept of the stereochemical analogy of metals and macroelements is promising for the development of environmental biotechnology. The stereochemical analogy implies the proximity or the equality of the ionic radii of macroelements and toxic metals (Fig. 4, A). Microorganisms actively absorb macroelements, i.e. ions necessary for microorganisms. Simultaneously with macroelements (Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-} etc.) microorganisms can transport toxic metals inside cells (Cu^{2+}, Hg^{2+}, CrO_4^{2-} etc.), for example, Mg^{2+} and Cu^{2+}(Fig. 4, B).



A



B

Fig. 2. Dependence of the redox potential of reactions on the concentration of metals- oxidizers: A – CrO_4^{2-}, B – Cu^{2+}.

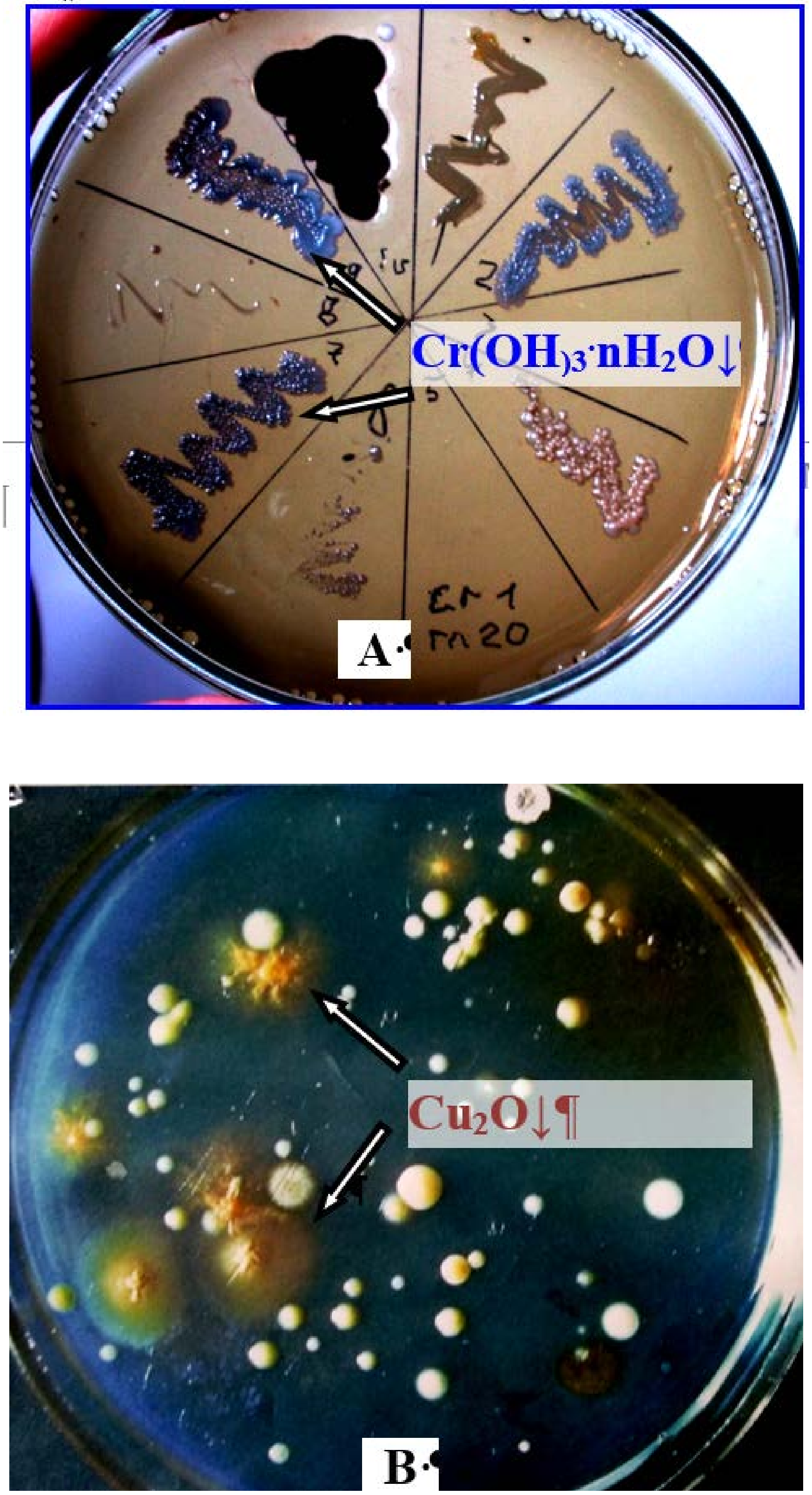
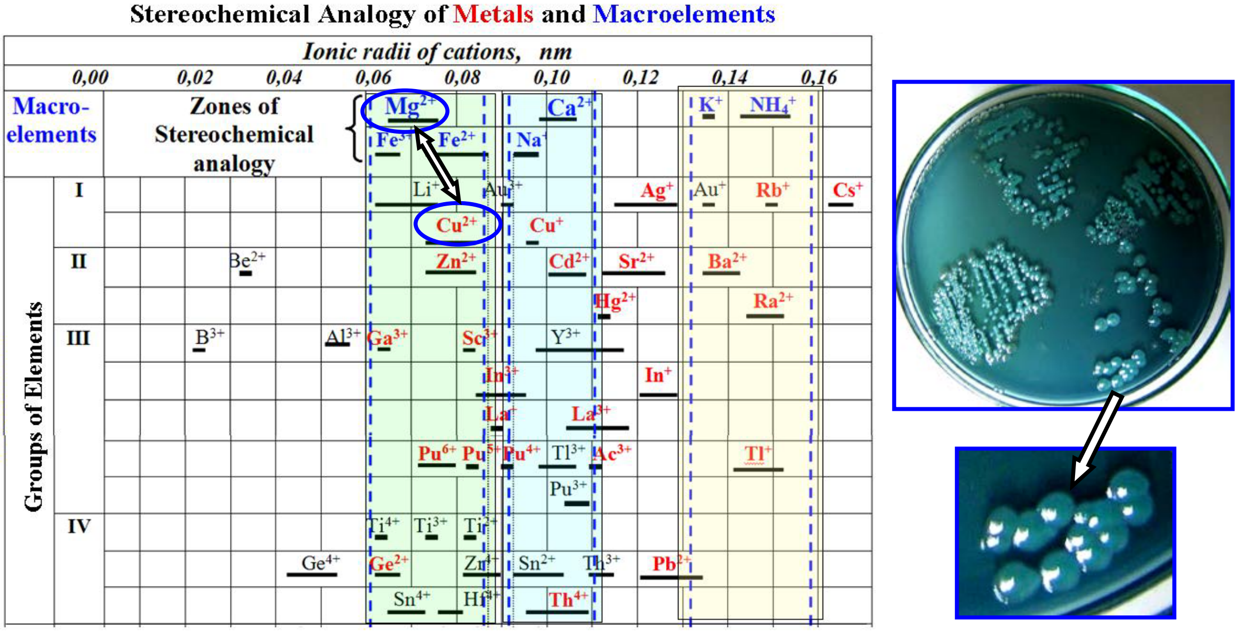


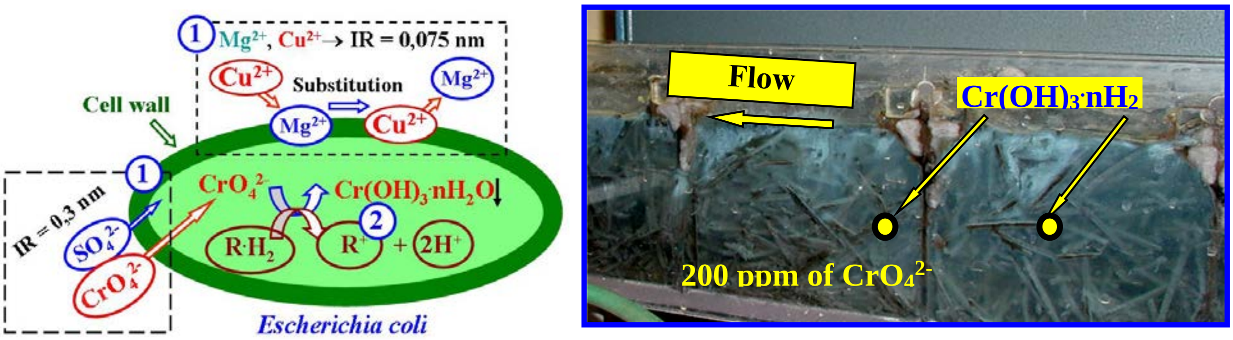
Fig. 3. Reduction of toxic metals to insoluble compounds:
A - CrO_4^{2-} to $Cr(OH)_3 \cdot nH_2O\downarrow$; B – Cu^{2+} to $Cu_2O\downarrow$.



A **B**

Fig. 4. The concept of the stereochemical analogy of metals and macroelements:
A – the calculations of the stereochemical analogy of metals and macroelements;
B – accumulation of Cu^{2+} inside bacterial colonies due to it stereochemical analogy with Mg^{2+}.

The simultaneous implementation of the reductive transformation of metals and their accumulation due to the stereochemical analogy (Fig. 5, A) allows developing universal biotechnologies for wastewater treatment (Fig. 5, B).



A **B**

Fig. 5. Development of the universal biotechnologies for wastewater treatment:
A – combined mechanisms of microbial interaction with metals;
B – purification of CrO_4^{2-} galvanic sewage by Granulated Microbial Preparation in the direct flow plant

For the purification of ecosystems from metals, we use phytobacterial biotechnology (Fig. 6. A, B).

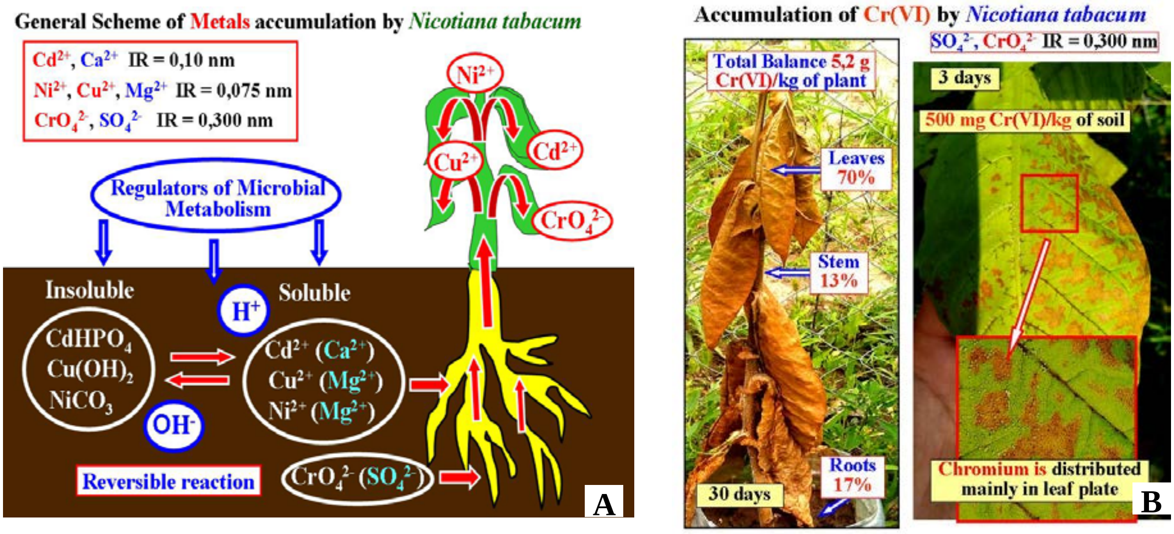


Fig. 6. The backgroung for soil bioremediation biotechnology:
A – combined mechanisms of phytobacterial bioremediation of soil,
B – the accumulation of CrO_4^{2-} in *Nicotiana tabacum*

Conclusions:

1. The thermodynamic prognosis is the universal approach that allows theoretically substantiating and implementing all types of microbial interaction with xenobiotics (metals, radionuclides);
2. The developed the biotechnologies based on the thermodynamic calculations are ready for the implementation to purify different types of wastewater with obtaining of valuable products (pure water, metal concentrate);
3. We invite scientists and industrial companies for the collaboration in the field of environmental biotechnologies.

References:

1. De Clercq D. Biomethane production potential from restaurant food waste in megacities and project level-bottlenecks: A case study in Beijing / D. De Clercq, Z. Wen, F. Fan, L. Caicedo, // Renew. Sust. Energ. Rev. – 2016. – Vol. 59. – P. 1676-1685.
2. Fu F. Removal of heavy metal ions from wastewaters: A review / F. Fu, Q. Wang // J. Environ. Manage. – 2011. – Vol. 92. – P. 407-418.
3. Grimm N.B. Global Change and the Ecology of Cities / N.B. Grimm, S.H. Faeth, N.E. Golubiewski, C.L. Redman, J. Wu, X. Bai, J.M. Briggs // Science. – 2008. – Vol. 319. – P. 756-760.
4. Hudson-Edwards K. A. Mine Wastes: Past, Present, Future / K.A. Hudson-Edwards, H.E. Jamieson, B.G. Lottermoser // Elements. – 2011. – Vol. 7, No. 6. – P. 375-380.
5. Pourbaix M. Atlas of Electrochemical Equilibria in Aqueous Solutions. – Oxford: Pergamon press, 1963. – 320 p.
6. Nikolsky B.P., editor. Handbook of chemistry. Leningrad: Khimia. – 1971. – 827 p.
7. Gottschalk G. Bacterial Metabolism. Springer-Verlag New York XIII. – 1979. – 359 p.
8. Schlegel, G., General Microbiology, 6th ed., Cambridge: Cambridge Univ. Press. – 1986. – 655 p.
9. Bacterial Energy Transduction, ed. by A. Christopher. – London-Toronto: Acad. press. – 1988. – 517 p.