Remediation of soils polluted with arsenic, with use of the organo-mineral complex

Andrey Viktorovich Bogdanov, Natalia Vitalyevna Chaika, Olga Leonidovna Kachor

National Research Irkutsk State Technical University (FSBEI HPO NR IrSTU), Lermontov Str., 83, Irkutsk, 664074, Russia

Abstract. In the article we considered work results of elimination of consequences of anthropogenous impact of the accumulated mining and processing arsenic waste on the environmental objects on the example of the Angarsk Metallurgical Plant (AMP). We identified dynamics of remediation of soils from arsenic and heavy metals by various reagents-detoxicants. We took preparations used in remediation of soils, such as solution of lime milk, Humate-80 humic acids and the studied organo-mineral complex Humate-80 + lime milk as reagents-detoxicants. We fixed the level of moving forms of heavy metals and arsenic in agricultural soils of horticultural sites of MC (municipal corporation) "city of Svirsk". We selected the efficient organo-mineral complex for remediation of soils. [Bogdanov A.V., Chaika N.V.,Kachor O.L. **Remediation of soils polluted with arsenic, with use of the organo-mineral complex.** *Life Sci J* 2014;12(12s):841-844] (ISSN:1097-8135). http://www.lifesciencesite.com. 182

Key words: arsenic, heavy metals, humic acid, detoxicant, soil, remediation.

Introduction

Strategy of national security of the Russian Federation till 2020 along with achievement of the main priorities of national security: national defence, state and public security of the Russian Federation, focuses state efforts and resources on priorities of sustainable development, including the "ecology of alive systems and the rational environmental management, which is maintained by means of balanced consumption, development of progressive technologies and expedient reproduction of natural and resource capacity of the country" direction. The special attention is paid to a problem of the accumulated ecological damage from economic activity during the recent years. About 2 billion tonnes of toxic waste are accumulated across the Russian Federation. In this regard the resolution of the government of the Russian Federation #791 on 27 October 2008 approved the Federal target program "National System of Chemical and Biological Safety of the Russian Federation (2009-2013)", where one of the main planned goal was achievement of "90% share of the developed and implemented modern methods and means of protection of the population and environment from negative impacts and threats caused by factors of chemical and biological character (this index in 2009 constituted 10%)".

The special attention should be paid to the dangerous technogenic sources of mining and processing industry containing arsenic which can remain active for very long time, i.e. capable to chemical transformations and moving under the influence of natural environment. One of such sources was waste of the former Angara Arsenic Plant (AAP) on processing arsenic and pyritic ore in MC "city of Svirsk" of the Irkutsk region which during the period from 1934 to 1949 carried out production of arsenic trioxide. The industrial site of the AMP with a total area of 13 hectares contained 40 thousand tonnes of polluted soil, 6 thousand tonnes of building wastes and 40 thousand tonnes of cinders with total content of arsenic about 1600 tonnes (fig. 1). The situation is escalated also because the industrial site was located in 500 meters from the Angara River, in close proximity to a residential zone, horticultural sites, and for more than 70 years made strong anthropogenous impact on all objects of the regional environment of the upper Bratsk Reservoir with a total area of 150 km^2 [1].

Fig. 1. General view of the industrial site of the AMP before elimination, 2009.

Within the Federal target program "National System of Chemical and Biological Safety of the Russian Federation (2009-2013)", and also the regional program "Environment Protection in the Irkutsk Region" for 2006-2015 works for elimination of this source were carried out. Wastes were neutralized and buried on the special landfill Severniy 5.

However, despite elimination of the arsenic source, the adjacent territory with a total area of 25 m^2 also remains polluted by arsenic and heavy metals with excess of normative indexes. Concentration of arsenic in the soil of the region of MC "city of Svirsk" constitutes up to 150 MPC (maximum permissible concentration), of lead up to 25 APC (approximate

permissible concentration), of cadmium up to 1.5 APC, of coppers up to 4 APC (fig. 2).

Research objective is searching for the most efficient organo-mineral complex of the humic acids allowing neutralizing compounds of arsenic in soils of horticultural sites of MC "city of Svirsk" completely.

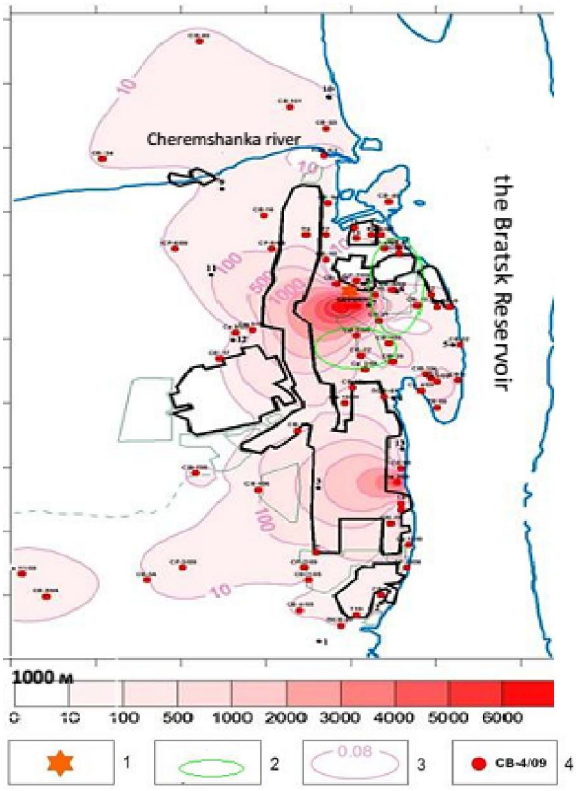

Fig. 2. Distribution of arsenic in soils around MC "city of Svirsk", 2013:

1 – location of the eliminated centre of pollution; 2 – locations of horticultural sites;
3 – isolines of arsenic in the soil; 4 – sampling points.

Object and methods

In 2012-2013 experimental and field researches on remediation of polluted soils with use of various reagents-detoxicants were conducted at the department of mineral processing and engineering ecology of FSBEI HPO NR IrSTU.

Research object is agricultural soils of horticultural sites "Astra", "Bagul'nik" and the household plot Makaryevskaya school, located in a five hundred-meter area of coverage of the former arsenic polluting industrial site of the AMP (fig. 2). Investigated polluted by arsenic and heavy metals soils, with oppressed self-cleaning ability, are thin-humous and refer to medium-textured loams.

Today the most perspective for the soils polluted by heavy metals from the point of view of ecologinomics is bioremediation, the main advantage of it is its use in extensive territories and rather low prime cost. One of directions of bioremediation is fitoremidiation, technology which means cultivation of special plants on the polluted sites during the particular period of time, which extract heavy metals and accumulate them in elevated phytomass with the subsequent cleaning and utilization [2, 3]. However the last operation is an essential drawback of this technology because it demands considerable additional costs of neutralization and utilization of the infected phytomass and is accompanied by secondary pollution of environmental objects.

Soil treatment with humin substances [4, 5], bringing to formation of stable insoluble forms of toxic compounds of heavy metals can be the alternate method deprived of the listed shortcomings. However, arsenic, possessing both metal and non-metal properties, not fully gets in touch with humic acids therefore necessary decrease in toxicity of lands is not reached [6]. By estimates of the affinity index of microcells to the humic compounds calculated by Glaskoter, studied heavy metals (copper, Zinc, lead) possess moderate affinity, and arsenic possess small affinity [7].

Research objective is searching for the most efficient organo-mineral complex of the humic acid allowing neutralizing compounds of arsenic in soils completely.

Researches were conducted in the laboratory of ecological monitoring of the natural and technogenic mediums POCC.RU 0001.518897 with use of techniques of determination of the critical concentration of micelle formation (CCM) by the Rehbinder's method (a method of determination of the maximal surface tension on the interface of fluid and gaseous phases), determination of dynamics of concentration of heavy metals and arsenic in soils at washing out by various extragents, QCA (quantitative chemical analysis) of arsenic and heavy metals, biotestings.

Results and discussion

Firstly, we determined toxicity of the humic preparation Humate-80, received from the high-oxidized brown coals, to determine the possibility of its use and its influences on growth of *Lepidium sativum* seeds (fig. 3).

We brought 20 cm^3 of the preparation with concentration 0.1-10 g/dm^3 into the Petri dish, covered it with filter paper, and spread 20 daily sprouts of *Lepidium sativum* seeds on the filter. As presented on figure 3, optimum concentration of the humic preparation is 0.3 g/dm^3, the further increase in concentration leads to decrease in germination of seeds because of its toxic action.

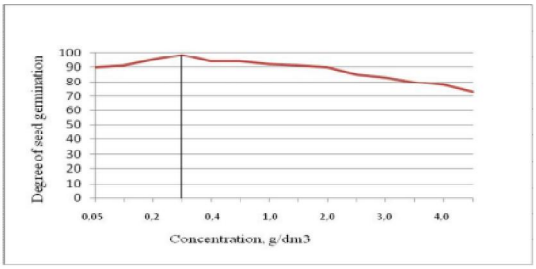

Fig. 3. Influence of concentration of the preparation Humate-80 on germination of *Lepidium sativum* seeds.

It is known that the most efficient action of humic preparations in soils during their interaction with heavy metals is shown in the dissolved molecular form prior to formation of micelles which is shown in CCM point at the maximum decrease in the surface tension on the interface "airbubble – liquid" (fig. 4) [8, 9].

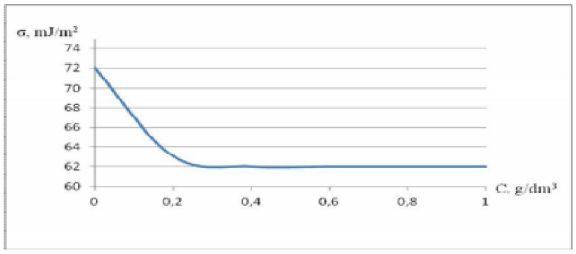

Fig. 4. Critical concentration of micelle formation Humate-80 preparation.

As presented in the fig. 4 increase in concentration of the studied humic preparation to 0.25-0.3 g/dm^3 is accompanied by decrease in the surface intention and reaches CCM point. The fixed minimum concentration of 0.25 g/dm^3 of the Humate-80 preparation was taken as optimum for carrying out further researches on detoxication of soils from arsenic and heavy metals.

We took preparations used in remediation of soils, such as solution of lime milk, Humate-80 humic acids [10] and the studied organo-mineral complex Humate-80 + lime milk as reagents-detoxicants. In figure 5 we presented results of researches on testing of reagents-detoxicants for toxicity of soils by a method of germination of *Lepidium sativum* seeds.

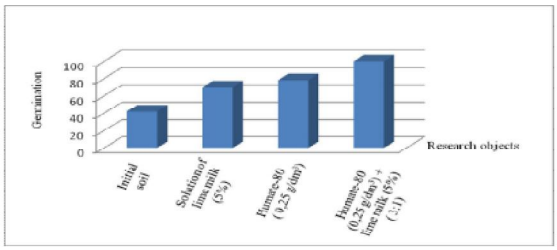

Fig. 5. Germination of seeds with reagents-detoxicants.

As shown on the fig. 5 germination of *Lepidium sativum* seeds on the initial agricultural soil of horticultural sites "Astra", "Bagul'nik" and Makaryevskaya school with the content of arsenic, copper, Zinc and lead 37; 58; 120; 347 mg\kg respectively is 42%, on the treated with lime milk soil is 63%, with Humate-80 preparation is 75%, with the organo-mineral complex Humate-80 + lime milk is 98%. The organo-mineral complex Humate-80+ lime milk is the most effective in transforming arsenic and heavy metals in water insoluble forms inaccessible for plants. More efficient formation of water insoluble forms of arsenic can happen, as due to individual effects of humic acid and lime milk, and at the expense of their accumulated effect.

On the basis of the received results we conducted researches in the field conditions on experienced sites of horticultural sites "Astra", "Bagul'nik" and Makaryevskaya school during the period from May to August, 2013. Samples for research were selected from the top humic horizon at a depth of 0-5 and 5-20 cm by an envelope method from the plots of 0.5×2.0 meters. During all vegetative period 80 tests of soil and 10 tests of vegetables grown up on the plots were selected and analysed for the content of arsenic and heavy metals. Plots in horticultural sites were divided into 4 sites, were treated with Humate-80, Humate-80 + lime milk and separately lime milk. The fourth site of the plot was not treated and served for monitoring. The interval between plot treatments was 2 weeks.

Dynamics of concentration of water-soluble forms of heavy metals and arsenic in soil at depths during the experiment on remediation is shown on the example of the horticultural site "Astra" (fig. 6).

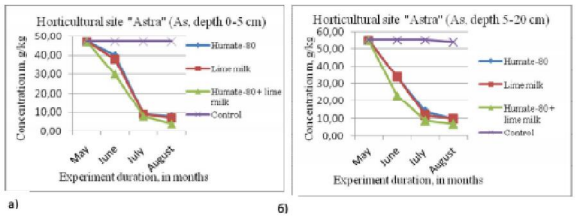

Fig. 6. Concentration of arsenic at depths: a) 0-5 cm, b) 5-20 cm.

As shown on the figure 6 a dramatic drop of concentration of arsenic in soils is observed within the first three months at both studied soil levels. Larger intensity of decrease in concentration of pollutants at the level of 0-5 cm can be related to faster penetration of reagents-detoxicants into the soil. The maximum decrease in concentration of moving forms of arsenic and heavy metals is fixed when using the organo-mineral complex Humate-80 + lime milk.

During the experiment on remediation of soils we observed increase in the content of catalase (fig. 7). The content of catalase in soils when using the organo-mineral complex Humate-80 + lime milk increased twice. More intensive increase in catalase activity at a depth of 0-5 cm can be related to faster warming up of the high layer of soils.

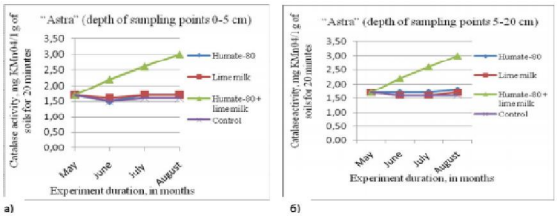

Fig. 7. Catalase activity in soils of the horticultural site "Astra" at depths: a) 0-5 cm, b) 5-20 cm.

At the same time we conducted the research on the content of toxic elements in vegetables which were grown up on the experimental plots. Vegetables were selected during the complete maturing. We analysed the upper part of cabbage and the root of beet (tab. 1).

As shown in the table soil treatment with Humate-80 + lime milk allowed to achieve the best results. The content of lead, copper, Zincum and arsenic in studied soils decreased in 12; 5.6; 6.4; 28.8 times respectively regarding the control sample and lead 6, copper 2, Zincum 23, arsenic (bulk) 2 mg/kg reached normative indexes of maximum permissible concentration of moving soils. After application of the modified humic preparation the content of arsenic and heavy metals in cabbage leaves and the root of beet decreased to normative indexes of maximum permissible concentration on arsenic 0.2, copper 5, lead 0.5, Zincum 10 mg/kg.

Table 1. The content of arsenic and heavy metals in studied soils and vegetables

Element	Bulk form (soil), mg\kg	Moving form (soil) mg\kg				Content of the element in vegetables, mg\kg							
		Without treatment	Treated with Humate-80	Treated with 5% lime solution	Treated with Humate-80+ 5% lime solution	Without treatment		Treated with Humate-80		Treated with 5% lime solution		Treated with Humate-80 + 5% lime solution	
						cabbage	beet	cabbage	beet	cabbage	beet	cabbage	beet
As	50	16	10	9	1.8	3.2	1.5	0.45	0.8	0.7	0.5	0.18	0.15
Pb	347	12	2	2	1	2.1	1.0	1.2	0.5	1.3	0.7	0.08	0.03
Cu	58	10	7	8	1.8	2.2	3.8	1.8	2.5	1.5	2.6	1.0	1.6
Zn	120	32	7	7	5	20.5	16.3	18.7	15.1	19.3	13.4	12.2	9.4

Conclusion

On the basis of the received results it is possible to make the conclusion that during remediation of soils polluted with heavy metals and arsenic, with use of the organo-mineral complex Humate-80 + lime milk (3:1), low solubility non-toxic forms of these compounds which are inaccessible for plants are formed. Effectiveness of soil and vegetable remediation from toxic elements allowed reaching normative indexes.

Corresponding Author:
Dr. Bogdanov Andrey Viktorovich
National Research Irkutsk State Technical University (FSBEI HPO NR IrSTU)
Lermontov Str., 83, Irkutsk, 664074, Russia

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