PHYTOEXTRACTION OF HEAVY METALS

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ФИТОЭКСТРАКЦИЯ ТЯЖЕЛЫХ МЕТАЛЛОВ ИЗ ПОЧВ АПШЕРОНСКОГО ПОЛУОСТРОВА, ЗАГРЯЗНЕННЫХ НЕФТЬЮ

Описана методика ремедиации почв, загрязненных нефтью и тяжелыми металлами. Она предполагает фитоэкстракцию тяжелых металлов из почв путем выращивания на них специально подобранных видов высших наземных растений. Был осуществлен подбор сельскохозяйственных растений, устойчивых к воздействию нефти и способных аккумулировать широкий спектр металлов.

Ключевые слова: нефтезагрязненные почвы, фиторемедиация, тяжелые металлы, фитотоксичность

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PHYTOEXTRACTION OF HEAVY METALS FROM OIL CONTAMINATED SOILS OF THE APSHERON PENINSULA

A method for remediation of soils contaminated with oil and heavy metals has been described. It involves phytoextraction of heavy metals from soils by growing on them specifically selected species of higher terrestrial plants. Selection of agricultural plants which are resistant to oil influence and can accumulate a wide range of metals has been implemented.

Keywords: oil-contaminated soils, phytoremediation, heavy metals, phytotoxicity

Despite the fact that oil production and transportation technology has been recently improved, and the damage caused to the environment is reduced, the problem of pollution of the environment with oil and heavy metals and other pollutants accompanying them still remains the most acute ecological problem in many oil-producing countries. The history of the world oil industry began in Azerbaijan. At the beginning of the 20th century 50% of all world's oil production accounted for Azerbaijan, the majority of which was mined in the Apsheron Peninsula. Such prolonged and intensive production of oil and gas resulted in environmental contamination both by the petroleum hydrocarbon compounds and salts of heavy metals such as As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, V, Zn [1]. Unlike the hydrocarbons, heavy metals pollution is not subject to degradation processes, but only redistributed between the individual components of the environment.

In the world practice there are used different methods for cleaning up oil contaminated soils. In the recent years microbiological methods that differ by ecological safety and low cost have been more widely used. The method using combined metabolic potential of microorganisms and plants is accepted as perspective one. Owing to mutually beneficial co-existence plant-microbe associations (symbiosis) have a big advantages at surviving in unfavorable environmental conditions.

It is possible to accelerate the process of degradation of soil contamination not only by sowing of specially selected plants, but also creation of conditions for their rapid growth and increasing the metabolic activity of their rhizosphere micro biocenosis.

Plants that are used for the extraction of heavy metals from contaminated soils must meet some requirements: to be tolerant to high concentrations of metals, to be able to absorb and accumulate several metals at the same time, to effectively transform them from the root system to the ground part, to have a deeply spreading root system.

The research objective was developing a method of cleaning up and detoxifying oil and heavy metal contaminated soils with hydrocarbon-oxidizing microorganisms in association with plants able to accumulate metal ions.

EXPERIMENTAL PART

In order to select plants promising for phytoremediation some crops (oats, beans, sunflower, corn) having different sensitivity to unfavorable environmental impact factors were studied.

At the initial stage sampling of soil from different areas of Buzovna oilfield in the Apsheron Peninsula, differing by degrees of oil pollution was carried out.

To conduct a comparative analysis samples of oil contaminated soils from root zone (rhizosphere) of plants typical for territories of the oilfield area (Juncaginaceae) were selected too.

The samples of uncontaminated soils within the same area was used as a control. Some physicochemical and microbiological analyzes of the samples were conducted. The content of oil products in soils was determined by gravimetric method after extraction of hydrocarbons from soil sample with hot hexane or methylene chloride in the Soxhlet extractor [2].

The concentration of heavy metals was determined by EPA 6020 A method on the Agilent Technologies 7500 Series ICP-MS Hardware (serial # JP82802622). The number of heterotrophic microorganisms in the soil was determined by 10-fold dilution of the soil suspension [3], by the following seeding on the surface agar media: meat-peptone agar (MPA) for bacteria and wort agar (WA) for the fungi and yeasts at a temperature of 28–30 °C. Bacterial colonies were counted after 3 days, fungi and yeasts in 5 days, spore microorganisms by 4-5th day, actinomycetes by 7-10th days. The number of hydrocarbon-oxidizing microorganisms was determined by 10-fold dilution in liquid Raymond's medium with 1% of oil as a carbon source [4]. Culturing of microorganisms was carried out in Erlenmeyer flasks containing 100 ml of liquid medium on a rotary shaker (180 rev/min) at 24 °C for 10 days.

Soil phytotoxicity was evaluated by biotest - wheat, the ratio of the number of germinated and ungerminated seeds, as well as the lengths of seedlings and roots. The duration of the experiment was 30 days.

RESULTS AND DISCUSSION

Pollution of soils with oil and heavy metals causes profound changes in the physicochemical and microbiological properties, soils disturbance, rejection of them from agricultural use. In developing rational methods of cleaning up contaminated soil zonal-climatic characteristics, landscape and geo-morphological conditions, joint negative influence of oil products and accompanying pollutants (soluble salts, heavy metals and other xenobiotics) should be considered [5]. The research objects were samples of contaminated soils with different content of oil products selected from the surface layers of the soil, as well as the root zone (rhizosphere) of wild plants (Juncaginaceae), typical for the area of Buzovna oilfield and resistant to oil pollution. This plant is characterized by a strong root system and can tolerate flooded soil. The samples of uncontaminated soils within the same area were used as a control.

The selected soil samples were laid in the appropriate containers (wooden boxes). Some physicochemical parameters (Table 1) were initially identified for all types of soil.

For the further research soil containing 6,7% of oil products was used. Plants affect the number, diversity and activity of microorganisms at the expense of biologically active root exudates [6]. In the rhizosphere there are often actively developed microorganisms having enzymes required for the degradation of pollutants. To isolate groups of microorganisms from soil and to count them special methods and nutrient mediums were used. They differ depending on the biological characteristics of the isolated microorganisms. The results of microbiological studies are shown in Table 2. It can be concluded from the table that in these soils the number of bacteria exceeds greatly amount of fungi and yeasts. The number of hydrocarbon-oxidizing microorganisms in contaminated soil samples is more than in the control and it is explained by the presence of organic food in the sphere.

In general, as can be seen from the analysis of Table 2 the number of microorganisms in the rhizosphere is more than in the rest soil mass. This is obviously related to the fact that in the secretions of the roots there are organic compounds which have high physiological activity and plays a big role in the relationship of plants with microorganisms.

Table 1

Characteristics of the soil samples

***Таблица 1.* Характеристики образцов почвы**

Characteristics	Samples of oil contaminated soils				Pure soil (control)
	Version 1		Version 2		
	Rhizosphere, %	Surface layer, %	Rhizosphere, %	Surface layer, %	
Oil content, %	5.6	6.7	8.7	11.3	-
Humidity: field hygroscopic	14.7	16.3	17.6	19.2	20.0
	1.7	2.1	2.1	1.7	1.8
pH	7.6	7.3	7.8	8.2	7.2

Table 2

Quantitative count of microorganisms in the studied soils

***Таблица 2.* Количественный счет микроорганизмов в изученных почвах**

Number of microorganisms in 1 g of absolutely dry soil	Soil samples		
	Surface layer, of oil contaminated soil	Rhizosphere under *Juncaginaccae*	Pure soil
Bacteria	$27 \cdot 10^6$	$53 \cdot 10^7$	$97 \cdot 10^7$
Fungi	$17 \cdot 10^3$	$42 \cdot 10^3$	$15 \cdot 10^2$
Yeasts	$42 \cdot 10^2$	$57 \cdot 10^2$	$67 \cdot 10^3$
Actinomycetes	$15 \cdot 10^3$	$32 \cdot 10^4$	$42 \cdot 10^4$
Spores	$16 \cdot 10^3$	$42 \cdot 10^3$	$71 \cdot 10^2$
Hydrocarbonoxidizing	$21 \cdot 10^4$	$63 \cdot 10^5$	$51 \cdot 10^3$
Humidity, %	16	12	21
Oil content, %	6.7	5.6	7.0

On these soils there were planted various crops: corn, sunflower, beans. To monitor the phytoremediation process in the laboratory conditions some samples of oil contaminated soils under the test plants were additionally inoculated with suspensions of cultures of hydrocarbon microorganisms isolated from the root zone of the plants, in particular, (*Juncaginaceae*), germinating in the studied soils.

The ability of these plants to accumulate heavy metals contained in the studied oil contaminated soils has been investigated (Table 3).

Table 3

Content of heavy metals

***Таблица 3.* Содержание тяжелых металлов**

Element, g/kg	Raw oil (Buzovna)	Oil contaminated soil, (OCS) 6,7%	OCS under corn (*Zéa máys*)	OCS +mixed cultures under corn (*Zéa máys*)	In corn plant (*Zéa máys*)	OCS under sunflower (*Heliānthus*)	OCS +mixed cultures under sunflower (*Heliānthus*)	In sunflower plant (*Heliānthus*)	OCS under beans (*Phaséolus*)	OCS +mixed cultures under beans (*Phaséolus*)	In beans plant (*Phaséolus*)	In maritime arrow grass plant (*Juncaginaceae*)	Pure soil
Cr	0.0008	0.031	0.0099	0.0173	0.0160	0.0147	0.0135	0.0052	0.0143	0.0168	0.0037	0.0042	0.0501
Mn	0	0.8001	0.1145	0.1808	0.3611	0.023	0.0231	0.587	0.0311	0.0326	0.0669	0.01514	0.6907
Fe	0.0500	18.166	3.0296	4.4707	10.0933	2.371	2.9310	0.2736	2.699	2.8064	1.5627	2.0323	24.90
Co	0.0021	0.0065	0.0021	0.0027	0.0039	0.008	0.006	0.0042	0.0025	0.0008	0.0009	0.0008	0.0098
Ni	0.0179	0.020	0.0190	0.0176	0.0054	0	0.0165	0.0025	0.0431	0.0432	0	0	0.0182
Cu	0	0.0232	0.0386	0.0452	0.0152	0.021	0.0375	0.0127	0.020	0.0170	0.0206	0.0195	0.0203
Zn	0	0.0845	0.1860	0.1911	0	0.0510	0.0336	0	0	0	0	0	0.3016
As	0.0006	0.0122	0.0016	0.0021	0.0205	0.0007	0.0010	0.003	0.0031	0.0021	0.0012	0.0037	0.0090
Cd	0	0.0002	0.0003	0.0002	0.0001	0.0001	0.0003	0.0001	0	0	0.0001	0.0001	0.0002
Ba	0.003	0.2652	0.0390	0.0432	0.0425	0.030	0.0246	0.077	0.116	0.0120	0.032	0.4015	0.2175
Pb	0	0.0136	0.0182	0.0223	0.0059	0.003	0.0019	0.001	0	0	0.005	0.007	0.0133
Hg	0.001	0.0005	0.0031	0.0058	0.0016	0.012	0.0065	0.0031	0.0101	0.0040	0.0027	0.0015	0.0007

Table 4

Comparative data on reducing amount (times) of heavy metals in oil contaminated soils during the process of phytoextraction (2 months)

Таблица 4. **Сравнительные данные по восстановлению количества (времени) тяжелых металлов в почвах, загрязненных нефтью, в процессе фитоэкстракции (2 месяца)**

		Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Ba	Pb	Hg
1	Corn	3.19	28.47	8.47	11.6	8.31	1.26	2.16	9.0	2.5	20.56	3.3	0.8
2	Corn + mixed bacteria	3.33	13.7	7.54	6.75	2.25	0.91	1.92	7.7	0.5	13.7	4.04	0.1
3	Sunflower	2.97	30.9	7.32	10.12	0	1.11	1.21	12.0	5.0	7.5	4.8	0.1
4	Sunflower + mixed bacteria	3.53	27.69	8.64	11.57	0	0.82	2.12	9.81	3.3	14.9	4.48	0.05
5	Beans	3.013	20.24	8.46	8.1	3.65	0.76	0	2.11	0	18.4	0	0.1
6	Beans + mixed bacteria	2.62	19.16	7.74	9.0	3.54	0.88	0	6.00	0	16.7	0	0.2
		Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Ba	Pb	Hg
1	Corn	3.19	28.47	8.47	11.6	8.31	1.26	2.16	9.0	2.5	20.56	3.3	0.8
2	Corn + mixed bacteria	3.33	13.7	7.54	6.75	2.25	0.91	1.92	7.7	0.5	13.7	4.04	0.1
3	Sunflower	2.97	30.9	7.32	10.12	0	1.11	1.21	12.0	5.0	7.5	4.8	0.1
4	Sunflower + mixed bacteria	3.53	27.69	8.64	11.57	0	0.82	2.12	9.81	3.3	14.9	4.48	0.05
5	Beans	3.013	20.24	8.46	8.1	3.65	0.76	0	2.11	0	18.4	0	0.1
6	Beans + mixed bacteria	2.62	19.16	7.74	9.0	3.54	0.88	0	6.00	0	16.7	0	0.2

The effectiveness of phytoextraction was evaluated by the number of heavy metals removed from the contaminated areas. It can be seen from the data (Tables 3 and 4) that crops selected for the experiments can accumulate heavy metals in the studied contaminated soils. Obtained results show that these plants can be used to recover heavy metal polluted soils.

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