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Elena Elizareva
Baskir State University

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Marco Pasetti *Editors*

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Editors
Vera Murgul
Moscow State University of Civil Engineering
Moscow, Russia

Marco Pasetti
Department of Information Engineering
Università degli Studi di Brescia
Brescia, Italy

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Combining Phytoremediation Technologies of Soil Cleanup and Biofuel Production

Elena Elizareva[1,2](✉), Yulay Yanbaev[3], Nina Redkina[1], Natalya Kudashkina[4], and Alexey Elizaryev[2]

[1] Bashkir State University, 32 Validy Street, Ufa 450076, Russia
Elizareva_en@mail.ru
[2] Ufa State Aviation University, 12 K. Marx Street, Ufa 450000, Russia
[3] Bashkir State Agrarian University, 34 50-ya Oktyabrya Street, Ufa 450001, Russia
[4] Bashkir State Medical University, 3 Lenina Street, Ufa 450000, Russia

Abstract. The urgency of obtaining alternative fuels from renewable raw materials of plant origin has been substantiated. The possibility of combining the production of biofuels from rape with its use for phytoremediation of soils is considered. The contemporary state, problems and prospects for the development of phytoremediation of soils contaminated with heavy metals are analyzed. The main phytoremediation technologies have been characterized, such as rhizofiltration and phytofiltration, phytoextraction, phytostabilization, and phytoevaporation. It is shown that the tolerance index, translocation and bioconcentration factors are used in order to assess the effectiveness of using various plants for phytoremediation. Using these indicators, a logical function of selecting plants for phytoremediation was compiled depending on the utilization method of the generated biomass. The ability of rape to absorb metals was studied. It has been established that rape accumulates heavy metals mainly in the roots under conditions of high soil contamination level, which makes it possible to use it for plant stabilization. The feasibility of combining soil phytostabilization by using rape plant and biofuel production with careful control of the heavy metals content in it is shown.

Keywords: Bioethanol · Biodiesel · Phytoremediation · Rhizofiltration · Phytofiltration · Phytoextraction · Phytostabilization · Phytoevaporation

1 Introduction

In recent years, alternative fuels from renewable raw materials of plant origin found a wide spreading due to the price increase for traditional motor fuels, the tightening of exhaust emission standards, as well as due to the depletion of world oil reserves and the limitation of carbon dioxide emissions. At the present time, the following biofuels are most widely used: bioethanol, which is a product of processing almost any biomass, and biodiesel – a product of oil distillation obtained from oilseeds or animal fats (for rapeseed oil, these are methyl esters of fatty acids). Fuel production from renewable raw materials (continuous mass of plants and other organic matter from oils to wood) is a

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biocatalytic cracking. During the process, the splitting of long-chain hydrocarbons to the desired fraction of oil (diesel) fuel occurs, which is also promising in modern state [1]. Rape plant is considered the best raw material for biofuels due to its high yield and the possibility of almost waste-free use. Moreover, this culture can be cultivated in different soil and climatic zones. This article discusses the possibility of combining the production of biofuels from rape and using it for phytoremediation of soils contaminated with heavy metals. Pollution of the environment by heavy metal ions is a great danger to the biosphere. In addition to the direct toxic effects on living and plant organisms, heavy metals tend to accumulate in food chains, which increases their danger to humans. Once in the reservoirs, they are in the most dangerous ionic form for a long time, and even in a bound state (colloidal form, bottom sediments or other poorly soluble compounds) they continue to pose a potential threat for a long period of time. The increased content of heavy metals in the body leads to diseases of the cardiovascular system and causes severe allergies. In addition, heavy metals have embryotropic properties and are carcinogenic [1].

Analysis of widely used methods for removing heavy metals from such natural objects as soil cover and water bodies shows that they are associated with the formation of a large amount of toxic sludge, are expensive and difficult to perform. Therefore, searching and developing methods to extract ecotoxicants without additional burden on the environment is extremely relevant. The undoubted priority for environmental and economic efficiency is recognized by the phytoremediation method [2], which is the technology of soil and industrial wastewater purification using natural and genetically modified plants. The term is formed by a combination of two Latin words "phyto" - plant and "remedium" - to purify, restore [3]. Phytoremediation includes 4 main approaches and, is accordingly subdivided into 4 technologies: rhizofiltration and phytofiltration, phytoextraction, phytostabilization and phytoevaporation [4].

Rhizofiltration means wastewater passing through rhizofiltration facilities with hydroponically grown higher land plants. Long, fibrous and dense, covered with hairs, the root system of such plants absorbs, concentrates or precipitates heavy metals [5]. According to the same principles, wastewater is treated from heavy metal ions using higher aquatic plants (macrophytes); this method is called phytofiltration [6].

Phytofiltration of wastewater can be carried out in two ways:

(1) In the phytofiltration system by passing a stream of sewage with adjustable pH, temperature and speed through aquariums with growing macrophytes [7].
(2) The use of so-called botanical sites, which refers to a wide range of watercourses, overgrown with macrophytes in a natural way or artificially planted with them. As a rule, these are swampy areas with slower flow rates on the way to larger water bodies [8, 9].

As macrophytes become saturated with heavy metals, contaminated biomass (all or above water level) is removed or mowed.

Phytoextraction is the cultivation of specially selected plant species in contaminated areas for a certain period of time to extract heavy metals from the soil by the root system and maximize their concentration in the aboveground biomass [10, 11].

Phytostabilization (or phytorecovery) is physical and chemical immobilization of pollutants due to their sorption on roots and chemical fixation with the help of various soil additives for stabilizing toxic substances and preventing their spread by wind and water erosion. It also allows reducing the vertical migration of pollutants into groundwater. It can be used as a temporary strategy to reduce environmental risks until the selection of the most appropriate treatment technology.

Phytoevaporation is the process of adsorpting metals such as mercury and selenium from the soil by the plants, their biological transformation into a gaseous form inside the plant and their release into the atmosphere. The purification effect is due to the fact that the gaseous form of these metals is much less toxic, for example, for selenium, the toxicity decreases by 500–600 times [12, 13]. Despite the additional benefits (minimal changes in the surface being cleaned, minimal need for maintenance after planting, preventing erosion processes, no need to dispose the plant biomass), using phytoevaporation, unlike other phytoremediation technologies, makes it impossible to control the migration of pollutants entering the environment during the process. Therefore, phytoevaporation is the most controversial phytoremediation technology. Additional characteristics of phytoremediation technologies are shown in Table 1.

From Table 1 it follows that each specific phytoremediation technology involves the use of plants with certain properties. Thus, according to Baker's theory, 3 following groups of plants are distinguished by the mechanisms of metal extraction: accumulators, indicators and excludors [14]. In accumulators, the extraction of metals by roots and their transport to aerial parts are balanced, while in excludors, which do not have the ability to regulate the extraction of metals, the transport to shoots is limited. Thus, accumulators extract a large amount of metals and transport them to the aboveground part in a logarithmic relation between the metal concentration in the soil and the metals concentration in the shoots.

In addition, Baker introduced the term of hyper-accumulator, the assignment criterion for which is the following metal content in the aerial part: more than 100 mg of Cd/kg, 1000 mg of Ni or Cu/kg, more than 10,000 mg of Zn or Mn/kg of dry weight [7]. In excludors, the concentration of metals in shoots is small and constant over a wide range of soil metal concentrations until a certain value is reached, above which unlimited transport appears. Indicators reflect the concentration of metal in the soil. Thus, indicators can be effectively used for monitoring pollution with heavy metals, accumulators for phytoextraction processes, and excluders for phytostabilization. Plants used for rhizofiltration or phytofiltration processes should have properties opposite to those of accumulators, they should accumulate metals in the roots.

In order to assess the effectiveness of using various plants for phytoremediation, the following indicators are used: tolerance index, translocation and bioconcentration factors, the characteristics of which are presented in Table 2.

Table 1. Characteristics of phytoremediation technologies.

Heading level	Plant selection	Cleaning object
Rhizofiltration and phytofiltration	(1) For phytofiltration - a combination of various macrophyte types (floating, partially or completely submerged) for cleaning all layers of the water flow [14] (2) For rhizofiltration - land plants that create an extremely large contact surface with the medium being cleaned due to an extensive root system. Such plants also must be tolerant to metals [15] Selecting the pants according to translocation properties is determined by the method of disposal of the resulting contaminated biomass	Rhizofiltration is especially effective for the remediation of large wastewater volumes containing relatively low concentrations of various heavy metals Thus, for example, according to [16], regulatory wastewater treatment can be achieved by rhizofiltration if the initial concentration of heavy metals does not exceed 20 MCL for copper, 5… 6 MCL for zinc and cadmium, 2 MCL for manganese and cobalt
Phytoextraction	Tolerance to high concentrations of metals. The ability to absorb and accumulate high concentrations of several metals or their particular forms simultaneously. Efficient translocation of metals from the root system to aboveground biomass [17]. High growth rate, large biomass, deeply growing root system High resistance to plant diseases and pests. The ability to grow with the use of conventional farming	Applicable for the remediation of large land areas, the contamination of which does not extend to great depths. In addition, high concentrations of metals can be lethal to plants, so the contamination degree should be low or medium [18] The soil surface should be free from obstacles such as fallen trees or stones, and be characterized by topography that allows the use of agricultural machinery
Phytostabilization	The plants or substances they secrete should have the ability to stabilize pollutants in the soil by binding them with lignin on the cell wall ("lignification"), absorption by soil humus using plant or microbial enzymes ("humification"), binding by organic substances or using other mechanisms [19]. Absence (or low level) of translocation of pollutants from root biomass to aboveground. High growth rate, dense aboveground and root biomass, tolerance to metals	Most effective for fine soils with high organic content. Most often used for large areas with low or medium pollution
Phytoevaporation	Some macrophytes have a good ability to convert easily volatile metals into gaseous form. In addition, it seems quite effective to use woody vegetation with a developed root system, long life expectancy and intensive production of bedding from fallen leaves, which contributes to the availability of metals in the soil. Genetically modified plants are used for phytoevaporation of mercury, developing such plants for phytoevaporation of arsenic is in progress [20]	It is recommended to use this technology far from populated areas and in places with meteorological conditions that facilitate rapid decomposition of volatile substances [21, 22]

elizareva_en@mail.ru

Table 2. Indicators for assessing the performance of various plants for phytoremediation.

Performance indicators	Formula	Gradation
Tolerance to metals	Tolerance index: $TI = \frac{M_{Me}}{M_c} \times 100\%$, where M_{Me} is the dry weight of a plant biomass grown with the addition of metals, g; M_c is the dry weight of a control plant biomass grown in Hoagland solution, g The tolerance index is calculated for shoots (STI), roots (RTI) and the whole biomass in total (BTI)	TI > 100% - stimulating effect; TI = 100% - no effect; TI < 100% - the inhibitory effect of the analyzed concentrations of heavy metals on plant growth; TI = 50% is the minimum desirable volume of biomass when grown on a polluted environment [23]
Metal translocation inside the plant	Translocation factor: $TF = \frac{C_s}{C_r}$, where C_s is the concentration of metal in shoots, mg/g; C_r - metal concentration in the roots, mg/g where is the concentration of metal in shoots, mg/g;	The value of TF < 1 indicates the accumulation of metals mainly in the roots, TF > 1 – in the shoots
The ability to accumulate metals (individually and mixed)	Bioconcentration factor: $BCF = \frac{C_{pl}}{C_{sol}}$, where C_{pl} is the concentration of the metal in the plant, mg/g; C_{sol}- concentration of metal in solution, mg/l Bioconcentration factor is calculated separately for shoots (BCF_s) and roots (BCF_r)	A BCF > 1000 value is a criterion for classifying a plant as a proper accumulator [24]

Using the indicators given in Table 2, the phytoremediation potential of rapeseed on real soils adjacent to the territory of metallurgical enterprises was investigated.

2 Materials and Methods

Soils adjacent to the territory of three following enterprises were selected for the research: Karabashmed (at a 1.5 km distance from the plant), Satkinskiy chugunoplavil'nyy zavod (at a 2 km distance from the plant) and Uchalinskiy gorno-obogatitel'nyy kombinat (1.2 km from the plant). Soil samples were taken using the "envelope" method from the upper humus-containing horizon. A sample taken on the territory of the winter garden of the Bashkir State Agrarian University (sample Ufa) was chosen as a background soil test.

Rape was grown on selected soils in a greenhouse for 90 days. Mineral fertilizers in the form of nitroammophoska were applied to all variants of the experiment (including the control ones) at the rate of N120P120K120.

The grown biomass was weighed in each experiment. In the experiment with soils from Satka, seed germination did not occur. It should be noted that in the experiment with soils from Karabash, the mass of the aboveground part of the grown plants was significantly less than in the experiments with the Uchaly and Ufa soils. This is probably due to the high contamination level of these soils with heavy metals.

The concentrations of heavy metals (manganese, iron, copper, zinc) in the soil and plant samples were determined by atomic absorption spectrometry (AAS). The metal ion content was calculated in milligrams per kilogram of dry weight (mg/kg).

3 Results

The heavy metals (HM) content in soils before and after growing plants is shown in Table 3.

Table 3. Gross concentrations of HM in the studied soil samples before and after growing plants and approximate permissible concentrations (APC), mg/kg.

Location of soil collection	Fe		Zn		Cu		Mn	
	Before	After	Before	After	Before	After	Before	After
Ufa	22484	12016	30	31	24	15	590	385
Uchaly	33438	33625	393	330	637	181	742	770
Karabash	48750	25437	3388	2551	10720	2829	423	505
Satka	29938	–	59	–	74	–	854	–
APC	25000[a]		55		33		1500	

Notes: [a]Percentage abundance in the crust; the excess of the APC is highlighted in the table.

It can be seen from Table 3 that the content of heavy metals in the background sample (Ufa) in all respects does not exceed the approximate permissible concentration of gross forms. The manganese content does not exceed the standards in all soils.

Comparing the gross concentrations of iron, zinc and copper before and after the cultivation of rape shows that the HM concentration in soil samples taken in the city of Uchaly and Karabash did not reach APC values. The copper content in soils decreased the most, 1.5 times in Ufa, 3.5 times in Uchaly, 3.8 times in Karabash. The concentration of zinc also decreased: 1.2 times in Uchaly, 1.3 times in Karabash, but practically did not change in Ufa. The iron content fell 1.8 times in the soils of Ufa and Karabash, but remained on the same level in Uchaly. The manganese content in the soil of Ufa decreased by 1.5 times, but slightly increased in the soils from Uchaly and Karabash. Seeds had been sown in the soil of Satka didn't grow. The dried rapeseed biomass grown in the soil of Karbash was not enough for analysis. Probably, the level of soil contamination with heavy metals turned out to be too high.

The content of HM in rapeseed is presented in Table 4. The calculation results of the translocation and bioconcentration factors are shown in Table 5.

Table 4. The accumulation of heavy metals by rape seed.

Location of soil collection	Plant part	Content of dry matter, mg/kg			
		Fe	Zn	Cu	Mn
Ufa	Leaves	430	25.38	3.78	23.7
	Roots	603	28.6	2.61	11.2
Uchaly	Leaves	247	154	9.34	29
	Roots	768	298	16.9	32

Table 5. Performance indicators of using the various plants for phytoremediation.

Indicators	Ufa				Uchaly			
	Fe	Zn	Cu	Mn	Fe	Zn	Cu	Mn
TF	0.71	0.89	**1.45**	**2.12**	0.32	0.52	0.55	0.91
BCF_s	0.02	0.86	0.16	0.04	0.01	0.39	0.01	0.04
BCF_r	0.03	0.97	0.11	0.02	0.02	0.76	0.03	0.04

According to the data obtained, rape is prone to translocation of copper and manganese to shoots with a low HM content in soil. Zinc, iron and cadmium mainly accumulate in the roots. With a higher level of soil contamination, all metals accumulate in the underground part of the plant.

4 Discussion

Based on the data obtained, the options for the rape use for phytoremediation and options for the possible use of the resulting biomass are considered. Using the indicators given in Table 2, let us set the efficiency criterion for using one or another plant for the purposes of phytoremediation in the form of a logical function $E = f(BTI, TF, BCF_s, BCF_r)$ shown in Fig. 1.

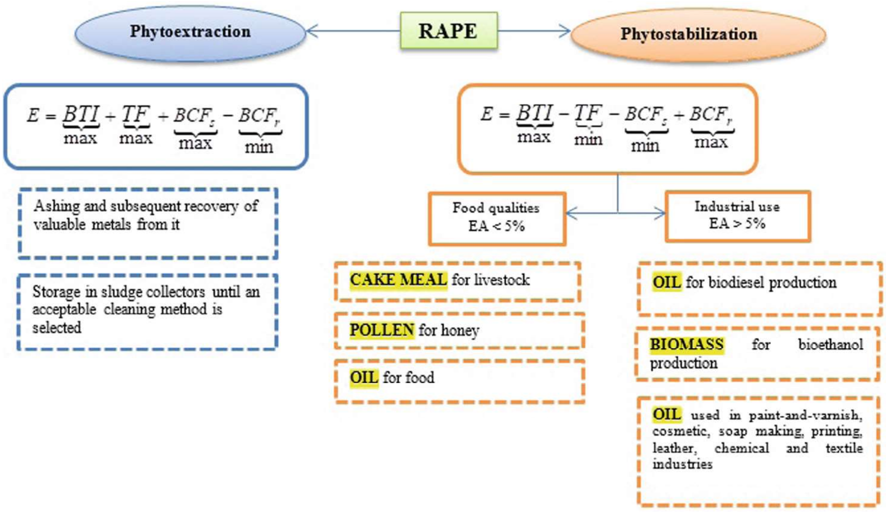

Fig. 1. Efficiency function of phytoremediation technology, depending on the method of biomass utilization.

The indicator included in the formula with the sign "+" should tend to the maximum, with the sign "−" to the minimum. It should be noted that E function is not a mathematical relationship and is only qualitative. Nevertheless, this approach may be useful in substantiating the choice of a specific plant for a particular phytoremediation method with the most suitable method of utilizing the resulting biomass.

One of the main effectiveness components of any environmental protection technology is zero waste. Phytoremediation technologies lead to the formation of biomass contaminated with heavy metals, so the possibility of its utilization is an important task. The definition of further biomass use after phytostabilization for food or technical purposes depends on the content of erucic acid (EA) in rape seeds, which belongs to omega-9-unsaturated fatty acids. Rape with an erucic acid content of less than 5% is used for food purposes such as the production of oils, margarines, mayonnaise, confectionery fats, etc. When an erucic acid content is more than 5%, it is used for technical purposes like soap making, production of fuel and lubricants, plastics, in the paint-and-varnish, metallurgical, printing, cosmetic industry, in the production of biodiesel.

According to the "Energy Strategy of Russia for the period until 2030" the expansion of the production and use of new fuel types derived from various biomass types is one of the priorities of scientific and technological progress in the energy sector [25]. In this regard, the option of obtaining biofuels from rapeseed is preferred.

The following advantages of biofuel obtained from rape should be noted:

– almost complete biodegradability;
– eco-friendly production;
– reduction of emissions of hydrocarbons, soot, nitrogen oxides due to lowering the combustion temperature;

– extremely low content of sulfur compounds;
– the absence of polycyclic aromatic hydrocarbon-carcinogens in the exhaust gases of the engine;
– adaptability to transportation and storage at the gas stations;
– renewability.

The results of domestic studies and the experience of foreign firms indicate that mixed biofuels based on rapeseed oil or rapeseed biodiesel help to save oil fuels, improve the environmental performance of diesel engines and solve a number of social problems when using rape processing by-products [1, 17]. However, it should be noted that the distribution of heavy metals in the organs of agricultural crops is selective and decreases in the following order: leaves > stalks > roots > fruit coat > seeds. Despite this, biofuel obtained from rapeseed used for phytostabilization of soils is necessary to be carefully checked for the HM content, in order to prevent secondary pollution.

5 Conclusions

The results of experiments on cultivating the rapeseed on real soils contaminated with HM and selected in the influence zone of metallurgical production testify to the effectiveness of using rapeseed for phytostabilization.

An algorithm for selecting the most efficient method of using rapeseed biomass is proposed. The biomass is formed during the process of soil phytostabilization, as a logical function that takes into account the values of the tolerance index, translocation factor, bioconcentration factor and erucic acid content. It is shown that one of the most promising areas of biomass utilization is the production of biofuels subject to strict control of heavy metals content in it.

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