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EXPANDING THE POTENTIAL OF SECOND GENERATION BIOFUEL CROPS BY USING FOR PHYTOREMEDIATION OF SITES CONTAMINATED BY HEAVY METALS: LABORATORY STAGE

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Analysis on expanding the potential of second generation biofuel crops for phytoremediation of sites contaminated by heavy metals is presented for two neighboring countries Ukraine and Slovakia. The approach has a potential for improving the state of the environment at the contaminated places, decreasing the negative effects to the human health, ensuring ecological safety and achieving sustainability. Scheme for using phytoremediation with second generation biofuel crops is overviewed. Possibility of using miscanthus, the most promisible biofuel crop of second generation, for cleaning up soil contaminated by heavy metals is discussed. Laboratory tests on cleaning up soil preliminary contaminated by two metals Cu and Co in the selected concentrations by phytoremediation with miscanthus are discussed.

Key words: biofuel crops of second generation, phytoremediation, miscanthus, heavy metals, contaminated soils.

МОЖЛИВИЙ ПОТЕНЦІАЛ ВИКОРИСТАННЯ БІОТОП ЛИВНИХ РОСЛИН ДРУГОЇ ГЕНЕРАЦІЇ ДЛЯ ФІТОРЕМЕДІАЦІЇ МІСЦЬ, ЗАБРУДНЕНИХ ВАЖКИМИ МЕТАЛАМИ: ЛАБОРАТОРНІ ДОСЛІДЖЕННЯ

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Проаналізовано можливість поширення потенціалу використання біопаливних рослин другої генерації для фіторемедіації місць, забруднених важкими металами, у двох сусідніх країнах: Україні та Словаччині. Розглянутий підхід дозволяє покращити стан довкілля на забруднених територіях, зменшити негативний вплив на здоров'я людини, підвищити екологічну безпеку і загалом сприяє впровадженню сталих підходів розвитку. Розглянуто схему використання фіторемедіації із застосуванням біопаливних рослин другої генерації. Описано можливість вирощування міскантусу як найбільш перспективної культури серед біопаливних рослин другої регенерації на ґрунтах, забруднених важкими металами. Обговорено лабораторні дослідження із вирощування міскантусу на ґрунтах, в які попередньо внесено визначені концентрації двох важких металів: міді та кобальту.

Ключові слова: біопаливні рослини другої генерації, фіторемедіація, міскантус, важкі метали, забруднені ґрунти.

PROBLEM STATEMENT**.** The increasing production and demand by society for metals indicate the mounting probability of their dispersal and contact with the environment. A metal may be dispersed from the time its ore is mined to the time it becomes a finished product [1].

In some cases the ultimate disposal of the finished product may also lead to metal dispersion. The growing world population and the importance of metals in growing economies just ensures more production of metals and the likelihood of more dispersal [2].

Ukraine and Slovakia are both among countries which have rather long traditions of metals ore production. As a result the contamination of the environment by heavy metals and supplemented substances are rather high at their territories and widely spread [3–10]. The problem of soil, water and bio resources' contamination by heavy metals and it's negative impact to the human health is listed among the most serious in both countries [5, 6, 10]. One of the possible ways for problems' solution is using phytoremediation method with effective agents [11].

Analysis regarding expanding the potential of second generation biofuel crops for phytoremediation of sites contaminated by heavy metals in Ukraine and Slovakia is actual.

This approach has a huge potential in terms of improving the state of the environment, decreasing the negative effects to the human health, ensuring ecological safety and achieving sustainability within the countries.

EXPERIMENTAL PART AND RESULTS OBTAINED. Monitoring results of soil contamination by heavy metals for Ukraine are presented in table 1. It can be concluded that the most contaminated cities were located in the Southern-Eastern part of the country (Donetsk and Dnipropetrovsk regions) and in the Central Ukraine, including capital city Kyiv and Kyiv region. In Slovakia the register of the old mining works and its information databases calculates 16,469 objects after the mining activity(including the old mining works) [6] which has led to contamination of soil including agricultural soil by different heavy metals produced.

Table 2 [9] presents data regarding content of heavy metals in the agricultural land in Slovakia which forms 47% of all territory.

Moreover there are a number of seriously contaminated brown fields places and one of the biggest is located near city Zar nad Hronom where ore production factory has been exploited during decades [12].

Table 1 – Contamination of soil by heavy metals in selected places in Ukraine (data as for year 2006) [3]

Monitoring site	Exceeding concentration of metal of annual average /max comparing to standard					
	Cd	Mn	Cu	Ni	Pb	Zn
Kostyantunivka,Donetsk oblast	4,1/31,3	1,4/2,8	1,1/4,9 0	4/0,5	11,2/62,5	4,5/14,0
Mariupol	0,2/1,0	1,4/3,7	1,3/5,4	0,3/0,6	3,7/20,4	2,1/4,6
Dnipropetrovsk	1,1/3,0	1,0/4,1	0,8/6,9	0,2/0,5	1,5/22,7	0,4/0,7
Kyiv	0,8/5,7	0,2/0,6	0,5/1,8	0,2/0,5	1,2/4,6	1,2/4,4
Fastiv, Kyiv oblast	0,3/1,6	0,3/0,6	0,7/3,0	0,2/0,9	3,9/19,8	1,5/4,6
Vishneve, Kyiv oblast	1,5/16,5	0,2/0,4	0,2/0,5	0,1/0,3	1,8/7,0	0,7/2,7
BilaCerkva, Kyiv oblast	0,0/0,3	0,3/0,6	0,2/1,1	0,2/0,4	1,1/8,6	0,9/3,1
Vasylkiv, Kyiv oblast	0,1/0,5	0,2/0,4	1,0/3,6	0,3/2,0	1,4/3,2	1,2/4,9
Orpon, Kyiv oblast	0,1/0,3	0,2/0,6	0,1/0,4	0,1/0,3	0,6/2,1	0,5/1,4
Yalta, Krum	0,1/0,5	0,7/2,8	1,6/13,5	0,5/1,2	2,1/11,7	0,9/5,7
Lutzk	0,1/0,5	0,3/0,4	0,6/5,6	0,2/1,0	0,6/6,3	1,1/3,8
Khmelnytsky	0,0/0,3	0,5/0,9	0,6/4,7	0,4/0,8	1,4/6,5	1,1/3,3
Sarnu	0,0/0,3	0,2/0,4	0,5/7,1	0,1/0,2	1,1/5,4	0,5/0,3
Chernigiv	0,0/0,0	0,2/0,6	0,1/0,6	0,1/0,4	0,5/3,8	0,3/0,9

Table 2 – The results of heavy metal determinations in agricultural soils of Slovakia (mg/kg) [9]

Heavy metals	Total content			Content in 2 mol/l HNO_3				Content in 0,05 mol/l EDTA			
	XG	min	max	*XG*	min	max	% total content	*XG*	min	max	% total content
Cd	0,285	0,050	9,05	0,169	0,010	6,85	59,3	0,088	0,010	3,60	30,9
Pb	24,9	9,5	1050	14,2	3,70	649	57,2	3,56	0,160	268	14,3
Cr	72,7	10,5	170	2,09	0,100	43,1	2,87	0,162	0,010	2,90	0,220
Ni	12,8	0,3	57.5	3,22	0,200	19,1	25,1	1,04	0,110	8,60	8,12
Cu	22,3	5,0	156	7,55	1,00	171	33,4	3,27	0,300	80,5	14,5
Zn	64,3	11,0	1070	12,3	2,05	565	19,2	2,35	0,050	126	3,66
Hg	0,075	0,009	6,69	–	–	–	–	–	–	–	–

The heavy metals pose a risk for the environment as well as for human population [13–15]. Chronic lower level intakes of toxic elements have damaging effects on human beings and animals, since there is no efficient mechanism for their elimination, and the detrimental impact becomes apparent only after several years of exposure. That is why the necessity of remediation of metal- contaminated sites, first of all brownfields, are among the main goals of environmental policy [12] and using for the process biomass crops of second generation will expand their potential [16–21].

Number of international documents and global environmental priorities are connected with this approach [22], namely:

– The Kyoto Protocol, Renewables Directive, Combined Heat and Power (CHP) Directive, Biomass Action Plan (by means of decreasing release of green gases, intensification of using biomass and implementation an integrated and coherent energy policy);

– The Waste Framework Directive, Landfill Directive (by means of diverting biodegradable waste from landfill used as compost, avoiding contaminated soil disposal as hazardous waste, and reusing spoil or made ground in voids);

– The Soil Framework Directive (by means of reusing, improving and remediating contaminated land);

– The Water Framework Directive (by soil/contaminant stabilization/sequestration to reduce diffuse source pollution entering catchments via runoff or groundwater flow)

– The Action Plan for Biodiversity (by enhanced or accelerated ecological value and biodiversity on former industrial land)

– The Strategy for Sustainable Development (by trying to meet the economic, environmental and social aspirations of sustainable development in an integrated way) [22–24].

Possibility to unite the production of biofules with using a marginal soil sounds as a sustainable solution in terms of on-going debates regarding contradictory between energy crops production and agricultural problems arise. Reusing these sites for bioenergy crop production could promote soil and contaminant stabilization or remediation and improve soil quality and biodiversity. A potential synergy exists between the need to find new markets for increasing compost production, cultivation of bioenergy crops and reclamation of plants that grow on sites with high metal concentrations [25].

One of two known mechanisms are mainly used to tolerate the toxic effects [16]. One mechanism, known as hyper-accumulation, involves the active uptake of metals and subsequent detoxification in above-ground tissue. The other, known as exclusion, is whereby the plant maintains a certain concentration in the shoot regardless of soil loadings with detoxification taking place in the roots. It is also thought that the accumulation mechanism is one that has evolved in plants that are entirely confined to metalliferous soils while exclusion is a strategy expressed by plants that have evolved some species tolerant and some intolerant to elevated soil metal concentrations. The stabilization of the contaminated sites due to plants is likely to play a larger role in the mitigation of the risk posed by contaminants.

Union of the cultivation of second generation biofuel crops and phytoremediation of contaminated and marginal lands is a perspective technology [26]. First of all, using marginal land has the benefit of providing a partial solution to the problem of the limited land bank. Secondly, reusing derelict industrial sites provides an economic advantage, since the major capital cost of land is avoided compared to using productive agricultural land. Indeed, many contaminated sites have negative asset values reflecting the costs of future remediation, or ongoing maintenance costs. In addition, this reunion could provide socio-economical benefits in areas deprived as a result of industrial decline and its detrimental environmental effects [22, 26–28].

Second generation biofuel crops usually belong to two main groups: short rotation canopy species (main representatives are willow (*Salix spp.*), poplar (*Populus spp.*), eucalyptus (*Eucalyptus spp*.), locust (*Robinia spp.*) and perennial/ annual grasses (main representatives are miscantus (*Miscanthussinensis A.*., *Miscanthussaccharіflorus M.*, *Misaccantus giganteus*), switchgrass *Panicum virgatum L.*; reed canary grass *Phalarisarundinacea L.*; common reed *Phragmitesaustralis* [19].

Using of second generation biofuel crops for phytoremediation of metal contaminated soil and

brown field sites belongs to the fastest growing areas of research and outreach, but the main part of research is about using sing of fast-growing woody plant species [22]. Less attention has been done for research on expanding the potential of second generation biofuels crops for phytoremediation of metal-contaminated soils and only a few sources reported about using this process for phytoremediation of metal-contaminated marginal land in the region of Eastern and Central Europe [29]. Positive aspects of the approach may be illustrated by scheme (Figure 1).

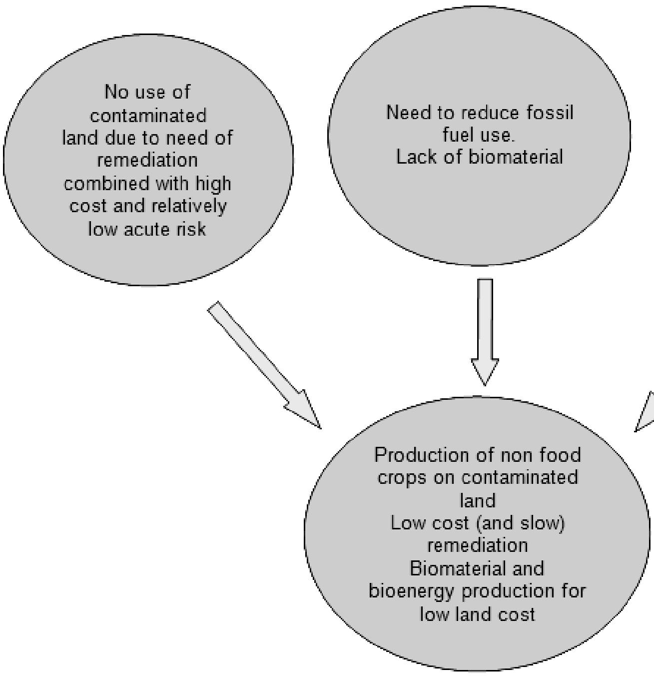

Figure 1 – Scheme for using second generation biofuels crops for phytoremediation of the soils contaminated by heavy metals and brownfield sites

The research regarding impact of two heavy metals which are in dissolved forms in the soil: Co (in the form of $CoCl_2$ x n H_2O) and Cu (in the form of $CuSO_4$ x 10 H_2O) on the process of growing miscanthus (*Miscanthus saccharіflorus* M.) have been initiated at the laboratory stage. It is planned to explore the distribution of metals within the plant, to research impact of different' concentrations of dissolved metals, their nature, soil properties and conditions to the miscanthus growing process, and to develop the conditions for the effective compilations of two processes: production of biofuels of second generation and phytoremediation of soil contaminated by heavy metals. The outcome of the laboratory research will permit to modeling both processes.

CONCLUSIONS. The increasing demands of bioenergy require land not threatening food demands, and the use of marginal low risk contaminated land offers a possible solution which is a real implementation of sustainable approaches within the countries. The potential synergy exists between two processes: growing of second generation biofuels crops and phytoremediation of metal contaminated soils and brownfields sites. Research has to be focused on the impact to both processes such factors as soils' properties, kinetic regularities, agricultural conditions, existence of supplemented substances and properties of metals.

Proposed approach is of very prospective for Ukraine and Slovakia which have number of metal-contaminated and brown fields sites across the countries.

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ВОЗМОЖНОСТЬ ИСПОЛЬЗОВАНИЯ ВЫРАЩИВАЕМЫХ БИОТОПЛИНЫХ РАСТЕНИЙ ВТОРОГО ПОКОЛЕНИЯ ДЛЯ ФИТОРЕМЕДИАЦИИ ТЕРРИТОРИЙ, ЗАГРЯЗНЕННЫХ ТЯЖЕЛЫМИ МЕТАЛЛАМИ: ЛАБОРАТОРНЫЕ ИССЛЕДОВАНИЯ

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Проанализирована возможность использования выращиваемых биотопливных растений второго поколения для фиторемедиации земель, загрязненных тяжелых металлами на территории Словакии и Украины. Рассмотренный поход позволяет улучшить состояние окружающей среды на загрязненных территориях, уменьшить их негативное воздействие на здоровье человека, повысить экологическую безопасность, и, в конечном итоге, способствует внедрению подходов к устойчивому развитию. Рассмотрена схема фиторемедиации с использованием биотопливных растений второго поколения. Обоснована возможность выращивания мискантуса как наиболее перспективной культуры среди биотопливных растений второй генерации на грунтах, загрязненных солями тяжелых металлов. Обсуждаются результаты лабораторных исследований по выращиванию мискантуса на грунтах, в которые предварительно внесены выбранные концентрации двух тяжелых металлов: меди и кобальта.

Ключевые слова: биотопливные растения второй генерации, фиторемедиация, мискантус, тяжелые металлы, загрязненные грунты.

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