Studia Periegetica nr 1(25)/2019
DOI: 10.26349/st.per.0025.07

Yelizaveta Chernysh*

An Environmental Friendly Solution for Stimulating Protective Properties of the Soil

Abstract. The development of soil management at the local and regional level is faced with challenges associated with an increasing level of soil contamination in urbanized systems. Thus, intensive soil use in Ukraine in recent years has resulted in a significant loss of humus, which is accompanied by negative changes in agrophysical, physico-chemical and biological properties of the soil. The aim of the study was to model a stimulating process of natural protective properties of the soil complex thanks to the influence of biocomposite based on sewage sludge and phosphogypsum under conditions of sulfate reduction. The chemical fractions were extracted from contaminated soil before and after the treatment. Surface images of the treated soil were obtained by means of X-ray diffractometry and microscopic analysis. The mineral composition of soil samples after processing by biocomposite was also mapped. Finally, the technological concept of a two-stage process of soil remediation was proposed involving the stage of aerobic soil treatment with biocomposite and the phyto-remediation stage for additional treatment.

Keywords: protective properties, soil, heavy metals, biocomposite, phosphogypsum, sewage sludge

1. Introduction

The development of soil management at the local and regional level is faced with challenges associated with an increasing level of soil contamination in urbanized systems. Thus, intensive soil use in Ukraine in recent years has resulted in a significant loss of humus, which is accompanied by negative changes in agrophysi-

* Sumy State University, Department of Applied Ecology, Sumy, Ukraine, e-mail: e.chernish@ssu.edu.ua, phone: +380 991 421 477, orcid.org/0000-0003-4103-4306.

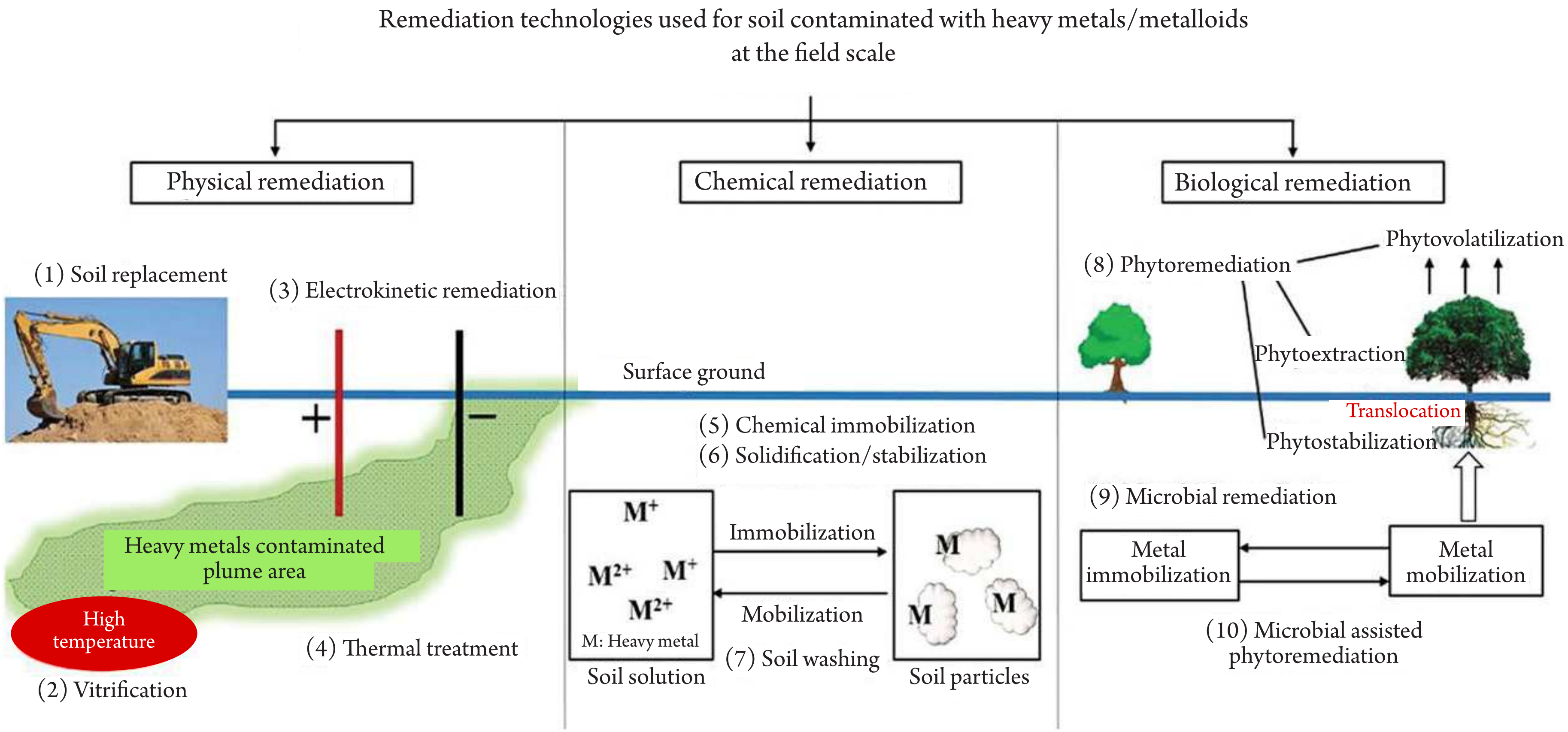


Figure 1. Remediation technologies for contaminated soil

Source: Yanyan Gong et al. 2018: 440-460.

cal, physico-chemical and biological properties of the soil. Correspondingly, the efficiency of agricultural methods and the productivity of agricultural crops are decreasing [Dadenko et al. 2013: 1274-1277].

Nowadays, it is still difficult to solve the problem of reducing levels of heavy metals in plant systems. Migration and accumulation of heavy metals is facilitated by the secretion of root exudates that moisten soil aggregates and bind cations of two- and polyvalent metals with the help of carboxyl and hydroxyl groups of polysaccharides, amino acids and carboxylic acids in complex compounds and concentrate these cations, resulting in the toxication of land ecosystems.

Among measures aimed at reducing the impact of pollutants on the soil one should highlight the following ones: chemical, physical and biological. Figure 1 shows various methods of soil remediation.

Many studies [Derome 2000: 79-88; Anderson et al. 2013: 1-21; Goulding 2016: 390-399] investigated the impact of liming and different kinds of fertilizer (phosphate, nitrogen, potash and organic fertilizers) treatments on heavy metal (Cu, Ni) and macronutrient (Ca, Mg, K) availability in the organic layer of soil. Widely used in the practice of agriculture has the technique of liming acidic soils [Derome 2000: 79-88], that not only helps to create better conditions for plant growth, but also reduces the flow of heavy metals from the soil into plants. The introduction of lime and lime materials is possible only on acidic soils. On alkaline soils, their enrichment with calcium can be carried out due to gypsum. For all types of soil, and especially for sandy and easily loamy, the enrichment of the horizon with organic fertilizers is quite important. However, in this case we mean manure, humus, peat, composts, pond silt and other types of local fertilizers.

From the point of view of biomineralization, bacterial metabolism affects the oxidation-reduction reaction in the soil medium and the rate of release of nutrients and deposition of heavy metals [Zachara et al. 2002: 179-207; Konhauser et al. 2012: 105-130], respectively, in the process of their fixation in a complex biogenic organomineral fraction of the soil. In the process of metabolic induced bio-mineralization, secondary minerals are formed as by-products of microbial metabolism containing metals in a chemically bound form, respectively, the extraction of the latter from the cycle of substances in the ecosystem [Chernysh 2017: 131-133].

The distribution of heavy metals in the soil is also regular, such as exogenous mainly in the soil surface between 0-5 cm; heavy metals are included to chelate complexes in the soil. Accumulation of the main part of heavy metals is observed mainly in the humus-accumulative soil horizon, where they are bound by aluminosilicates, and non-silicate minerals, organic substances due to various interaction reactions. Redistribution and migration in soil depends on the content of organic matter, particle size distribution, type of water regime, reaction of soil solution, temperature of individual horizons. Thus, high content of humus and free iron oxides, which are the main carriers of heavy metals, weakly acid reaction of the soil ensures fixation of trace elements and their relative property in the soil profile. Quantitative indicators of the adsorption of heavy metals largely depend on the pH of the medium. The processes of adsorption of metals can change, namely, reduce the pH value of soil solutions. According to [Chang Pan et al. 2018: 012113], the causes of this phenomenon are the release of protons during the hydrolysis of heavy metal salts, the displacement of cations during the specific adsorption of metals.

Phosphogypsum is a mechanically destroyed rock, treated with sulfuric acid with the addition of lime mortar after extraction with P_2O_5; it has a significant content in the composition of the product of insoluble compounds (CaO, SO_3,

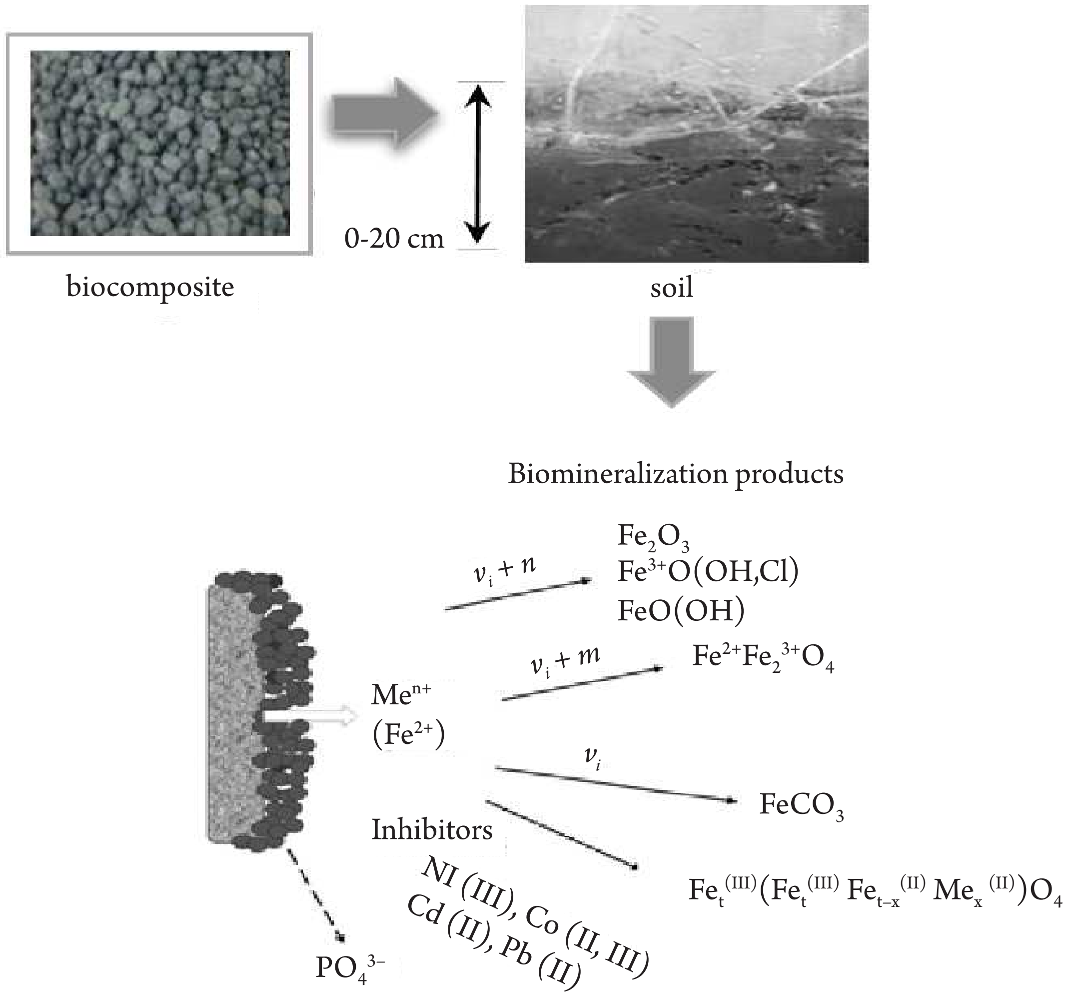


Figure 2. Schematic process of biocomposite introduction to soil

Source: based on Chernysh 2017: 131-133.

Al_2O_3, Fe_2O_3, SiO_2, MgO). The physicochemical properties of phosphogypsum affect the process of mineralization and humification of organic matter in the soil complex. A number of studies have revealed that when fertilizers are added with the addition of such qualitative transformations: the content of mineral colloids in the soil increases; soil aggregation increases; more moisture accumulates and remains; the remains of maize, sunflower and other plant waste that is difficult to degrade are more intensively decomposed. It has been revealed that phosphogypsum can be a stimulating additive for plant growth [Hentati 2018: 80-89].

Thus, the study of laws and mechanisms of the biochemical transformation of heavy metals in natural and artificial ecosystems for optimization and balancing of nutrition of crops remains relevant. The applied nature of this problem can also be considered from the perspective of the development of biotechnological systems and biotechnical means of natural mechanisms for stimulating soil complex protection while rehabilitating natural and anthropogenic landscapes contaminated by heavy metals. And the problem solving of phosphogypsum treatment is very important today.

Thus, the most important task of environmental research is to find ways to stimulate the natural protective properties of soils under condition of intensive anthropogenic load.

The study purpose is to research the effect of biotechnological treatment on the localization of heavy metals in the soil complex.

To achieve this aim it is necessary to solve the following tasks:

– study of the effect of organo-mineral biocomposite based on sewage sludge and phosphogypsum on soil detoxification;

– development of a technological scheme for the biotechnological treatment of soil remediation.

2. Materials and methods

2.1. Method of microfield experiment

In Chernysh [2018] was determined the features of quantitative and qualitative changes in the soil complex after biocomposite treatment (Fig. 2).

The experiment was carried out in plexiglass blocks with a perforated bottom area of 0.20 m^2 (0.5 × 0.4 × 0.5 m). The blocks were filled with gray forest soil taken from an area with a high level of anthropogenic load, containing 17.6-21.2 mg/kg (total form) of lead.

Perennial grasses were grown in blocks using increasing biocomposite doses. Natural vegetation which grew in blocks was mowed and removed from the soil surface every season. The soil in blocks was dug over at a depth of 0-20 cm and partially removed from the blocks, mixed and put again into blocks at random. In this case, the perennial grasses used in crop rotation (alfalfa, clover, espartset, their mixtures with cereals) were applied. The ambient temperature in the room was maintained at 22-25 °C.

During the experiment biocomposite was introduced at an increasing rate of: 1) 2.5 kg/m^2; 2) 5.0 kg/m^2; 3) 7.5 kg/m^2. The biocomposite containing sewage sludge and phosphogypsum was mixed with the soil layer of 0-20 cm. The experiment was repeated three times. X-ray diffractometry of the mineral constituent were carried out. The analysis was carried out with the help of automated diffractometer DRON-4-07 (JSC RPE "Burevestnik", St. Petersburg, Russian). Elemental analysis of the samples (liquid and solid phases) after the experiments was carried out using the X-ray fluorescence analyser Elvax Light SDD (Elvatech, Kiev, Ukraine). Limits of detection of impurities are not less than 10 ppm. pH was analyzed by pX-meter pX-150 (ionometer) (Gomel Plant of Measuring Instruments, Gomel, Belarus).

Moreover, chemical fractions were extracted using standard methods of metal speciation [Chernysh et al. 2017: 129-140; Chang Pan et al. 2018: 012113; Hentati 2018: 80-89].

Microscopic analysis of the samples was carried out using a Remm-102 raster electronic microscope microanalyzer (JSC "SELMA", Sumy, Ukraine) under SEM-EDX scanning electron microscopy [Chernysh 2018].

2.2. The characteristics of the biocomposite

The organomineral product is produced in the process of anaerobic stabilization of sewage sludge and phosphogypsum under conditions of sulfate-reduction [Chernysh et al. 2018: 1269], which, after separation from the liquid fraction and drying, has a gray-brown color and resembles aggregated soil particles in a consistency.

The main components of the biocomposite were determined by means of diffractometric analysis such as: quartz or amorphous silica – SiO_2; potassium

Table 1. Percentage content of oxides in the biocomposite

SiO_2	Al_2O_3	CaO	K_2O	MgO	Na_2O
37.65	8.4	31.3	3.2	1.7	3.4
SO_3	ZnO	Fe_2O_3	CuO	P_2O_5	NiO
9.5	0.01	0.45	0.003	0.5	0.0014

Source: Chernysh 2018.

hydroxide (potassium hydroxide) – KOH; brushite – $CaPO_3(OH)\cdot 2H_2O$; calcium – $CaCO_3$; ammonium sulfate (mascagnite), iron sulfides (marcasite), zinc (sphalerite), copper (kovelit) etc., which form a complex sulphide fraction. The content of the main elements in the organomineral composite is presented in the Table 1.

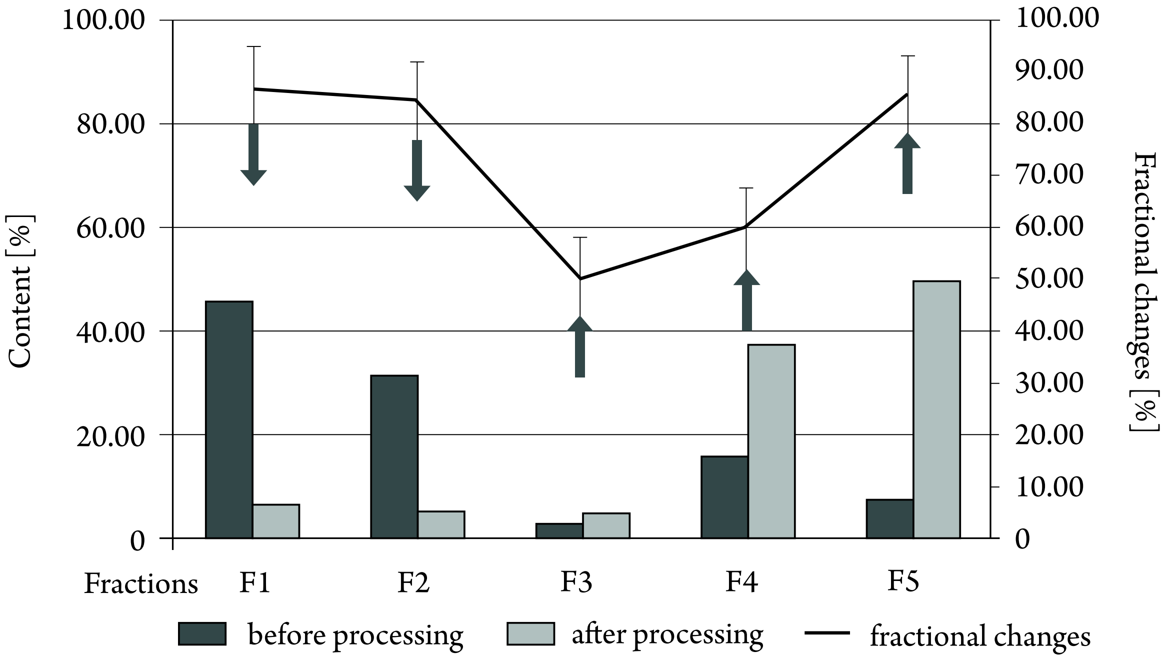
3. Results and discussion

3.1. Analysis of changes in the fraction composition of HM on the soil before and after the application of the biocomposite

Based on the analysis of the results, changes in the fractional metal composition is shown in the following diagram (Chart 1).

The largest portion of Pb and Cd (about 67%) before treatment was extracted as a portion of F1-Fe and F2-Fe, bound to amorphous oxides and hydroxide Fe: FeOMe, $(FeO)_nMe$, FeOMeOH, for example, $PbFe_2O_4$. The low portion of HM

Chart 1. Combined analysis of changes of fractional composition of metals in the soil before and after biocomposite introduction



F1 – oxides and oxyhydroxides of iron and manganese; F2 – exchange forms; F3 – carbonates, hydroxycarbonates; F4 – with organic substances; F5 – residue (silicates and sulphides).

Source: Chernysh 2018.

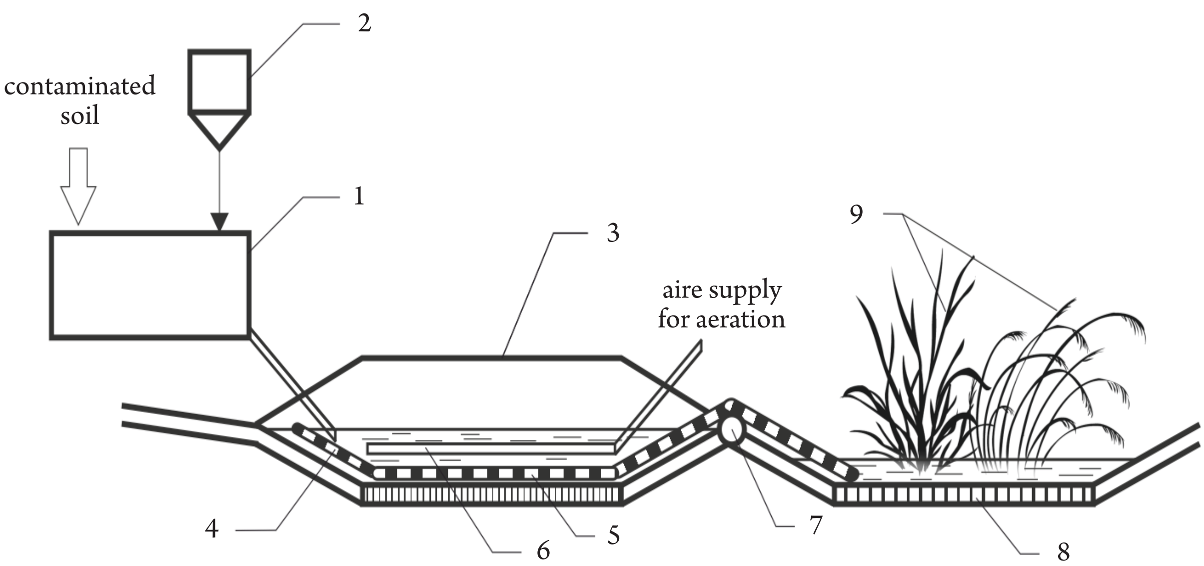
and Fe (i.e. <2% and <9.2% respectively) is extracted as bound to carbonate fraction. These results proved that Pb had main bonds with amorphous particles of iron oxide and ferrous hydroxide of soil, which is confirmed by diffractometry.

The diffractometric analysis showed traces of hematite, jarosite and scorodite, which are usual pyrite sedimentary products, which HM can generally bind to. The absence of residual mixed sulphide phases in soil may be connected with weathering of pyrite minerals.

During the extraction of $NH_2 OH \times HCl$, under these acidic conditions of pH (about 4), about 76% of total lead was extracted. The mechanism of lead desorption from the surface of oxyhydroxide Fe because of the competition with OH-ions can explain a rapid increase in lead extraction. The remediation of Fe remains very low (about 0.2% of total Fe). Fe remediation may be controlled by Fe hydroxyxide precipitation.

These results suggest that the biggest portion of Pb and Cd present in the soil is sorbed onto Fe oxyhydroxides. The remaining portion (about 22% out of total HM) can be considered as a portion coprecipitated with Fe and/or bound to resistant compounds (predominantly silicates).

After treatment, five major fractions of metals in the "soil complex – biocomposite" system were generally compatible (86%): 37% were found in stable organic compounds and 49% were found in residual fractions, which had firm



1 - hopper for mixing ground soil and biocomposite; 2 - dispenser for biocomposite supply; 3 - bioreactor; 4 - scraper conveyor; 5 - isolated bottom; 6 - aeration system; 7 - electric drive; 8 - playground; 9 – phytoremediation plants

Figure 3. Biotechnological concept of soil remediation

Source: Chernysh 2018.

bonds with the matrix of mineralized sediments (silicates and sulphides) (Fig. 3). There were only 12% of metals oxyhydroxides. The low portion of HM and Fe were extracted as exchangeable and bound with carbonate fraction. Thus, it was determined that at least 90% of lead was bound in inaccessible form to plants: primary and secondary silicate minerals, slightly soluble metal compounds (sulphides) and organomineral complexes. It should be noted that the carbonate fraction increased by 2% and, correspondingly, it accounted for 4% of the total, which is related to the substitution of calcium by lead in carbonate compounds contained in the composite, as lead ions are similar in size to calcium ions.

The results extraction of Pb and Cd from the contaminated soil using $NaCH_3COO$ solution after the introduction of the biocomposite are also shown in Fig. 3. It was found that the extraction with the help of this solution has no significant effect on the release of Fe and HM. However, it showed an increase in calcium solubility (approximately 500 times at pH of about 5) and at the same time was observed for phosphorus adsorption on Fe oxyhydroxides according to the results of diffractometric analysis.

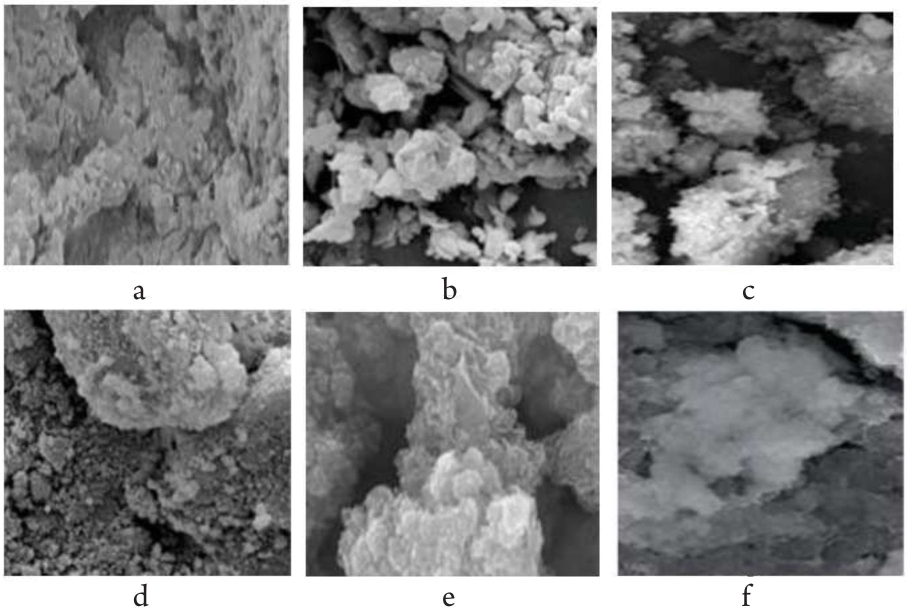
Thus, the accumulation of HM in soils and their distribution in fractions were also influenced by acid-base conditions. Thus, the restored soil had an acidity of 6.5 and the exchange fraction of lead decreased by 84%. The number of elements bound with hydroxides and oxides of Fe and Mn also decreased by 87%.

3.2. The technological concept of soil remediation

Technological processes that facilitate soil bioremediation will make it possible to reduce the processing time enabling the use of bioreactors, including fixed-bed reactors and slurry reactors with mixing [Barros et al. 2006: 1-10; Fulekar et al., 2012: 14-16; Napan 2014: 164]. The technological methods of intensifying the growth of microorganisms and improving the processes of soil bioremediation include: electro-kinetic activation, improvement of aeration conditions by blowing air through the soil etc.

The technological concept of an aerobic bioreactor for soil biodetoxification was developed (Fig. 3) based on the analysis of theoretical and experimental data.

The technological concept works as follows. The crushed soil contaminated with heavy metals is fed into the mixing hopper (1) together with the biocomposite from the dispenser (2). This mixture enters the bioreactor (3) through a pipeline, consisting of a trench with an insulated bottom (5) with a scraper conveyor (4), through which the soil moves. The aeration system (6) is arranged above the conveyor, which supplies air to the bioreactor in order to improve aeration conditions. The bioreactor is equipped with an electric drive (7). The previously



a – general view; elements: b – Fe; c – Pb; d – Ca; e – S; f – Si

Figure 4. SEM-EDX raster microanalysis map to 2 mm soil fraction (12X)

Source: Chernysh 2018.

cleaned soil is fed by the scraper conveyor (4) to a special platform (8) on which phytoremediation plants (9) are planted for further purification (phytoremediation), monitoring and control of pollutant content. Thus, the process of cleaning the soil from heavy metals and restoring its fertility, as a result of improving the development conditions of soil microbiota, is carried out in a two-stage process:

1. aerobic soil treatment with the biocomposite;
2. phytoremediation stage for additional treatment.

The map of the SEM-EDX raster microanalysis of 2-3 mm of the composite fraction was obtained by applying the biocomposite (Fig. 4).

In accordance with previous research [Chernysh et al. 2017: 129-140; Chernysh 2017: 131-133] the conceptual model of the influence of the proposed biocomposite on the protective function of the soil complex can be formulated. Contact of the organo-mineral biocomposite with the soil complex, aided by surface-sorption phenomena, can have protective properties and can lead to the formation of microaggregates consisting mainly of organic-mineral fine particles with the development of soil microorganisms on their surface. Subsequently, during the adaptation period a natural microbial association is formed in the aggregates, which develop into the system "biocomposite – soil – heavy metals" through the processes of microdiffusion and biosorption. Such a biotic component can play an important role in the conditioning and structuring of the environment, in particular, the mineral component (depositing of heavy metals) and influence the gradual release of biogenic matter from the biocomposite. The micro aggregates are depleted in readily available organic matter, because during the process of soil mineralization such compounds are used by microorganisms-destructors and, accordingly, are more resistant to degradation than the primary biocomposite applied into the soil.

Therefore, the biogenic composite based on sewage sludge and waste phosphogypsum in the process of anaerobic fermentation under the conditions of sulphate reduction can stimulate the development of necessary anaerobic groups of microorganisms in the intra-aggregate space. In this case, sulphatisation contributes to the formation of macromolecules of biogenic composites.

4. Conclusions

The mineral composition map of soil samples after processing by biocomposite based on sewage sludge and phosphogypsum was created. The results of analysing the microstructure and mineral composition of the biocomposite samples show evidence of the process of biochemical binding in the biocomposite structure of metal ions and particles aggregation with biosorption on the surface of its aggregate structures of organic substance and precipitation of complex metal compounds. When restoring soils contaminated with Pb and Cd, a significant increase in the relative portion of resistant metal compounds (silicates and sulphides) was observed at all levels of acidity (pH from 2 to 7) from 5.6-9.05% to 45.3-51.7%.

A biotechnological concept for soil remediation was developed, which consists of two stages: 1. aerobic soil treatment together with the application of the biocomposite; 2. phytoremediation stage for additional treatment and control of toxicant content in the soil. The development of the method for the remediation of contaminated soils using biocomposite material based on phosphogypsum and sewage sludge of treatment facilities is aimed at achieving agricultural and environmental effect, which includes the development of useful environmental and trophic groups of microorganisms that constitute the soil biomes; humification intensification of organic matter; long-term protective function.

Thus, soil management is important, directly and indirectly, to crop productivity, environmental sustainability, and human health both at the local and regional levels. The influence model of the proposed biocomposite on the natural regulation of the buffer properties of the soil complex was developed. The biochemical aspects of the impact of the biocomposite on the growth of natural soil microorganisms and formation of favorable biochemical conditions for the restoration of contaminated soil require further research.

The environmental and biochemical aspects of the influence of organomineral biocomposite on the development of natural soil microorganisms and formation of favorable biochemical conditions for the restoration of contaminated soil require further research.

References

Anderson N.P., Hart J.M., Sullivan D.M., Christensen N.W., Horneck D.A., Pirelli G.J., 2013, Applying Lime to Raise Soil pH for Crop Production (Western Oregon), *EM* 9057, 1-21, https://catalog.extension.oregonstate.edu/em9057 [access: 20.09.2018].

Barros A.J.M., Prasad S., Leite V.D., Souza A.G., 2006, The process of biosorption of heavy metals in bioreactors loaded with sanitary sewage sludge, *Brazilian Journal of Chemical Engineering*, 23(2), 153-162, http://dx.doi.org/10.1590/S0104-66322006000200001 [access: 11.08.2018].

Carmona D.M., Ángel Faz R.Z., Martínez-Martínez S., Jose A., 2011, Acosta reclamation of contaminated mine ponds using marble wastes, organic amendments, and phytoremediation, *Detoxification of Heavy Metals, Part of the Soil Biology book series* (SOILBIOL, 30), Berlin: Springer Berlin Heidelberg.

Chang Pan, Jun Chen, Ke Wu, Zhongkai Zhou, Tingting Cheng, 2018, Heavy Metal Contaminated Soil Imitation Biological Treatment Overview. *IOP Conference Series: Materials Science and Engineering*, 301, 012113, doi:10.1088/1757-899X/301/1/012113.

Chernysh Y., 2017, *The directions of natural regulation of the soil complex protective properties. Materials of IV International scientific and practical conference "Ecology and environmental in the optimizing system of relation between nature and society"*, Ternopil, 27-28 April 2017.

Chernysh Y., Plyatsuk L., 2017, Modeling the process of stimulating the protective functions of the soil complex using a biogenic composite based on technogenic waste, *Environmental Sciences*, 13, 129-140.

Chernysh Y., Balintova M., Plyatsuk L., Holub M., Demcak S., 2018, The Influence of Phosphogypsum Addition on Phosphorus Release in Biochemical Treatment of Sewage Sludge, *International Journal of Environmental Research and Public Health*, 15, 1269.

Chernysh Y., 2018, *The Environmental Friendly Solution for Stimulation of the Soil Protective Properties. Poster. Current challenges of local and regional development*, Poznan, 11–13 September 2018, www2.balticuniv.uu.se/bup-3/index.php/public/bup-events/current-events/current-challenges-of-local-and-regional-development/1439-yelizaveta-chernysh-the-environmnetal-friendly-solutions/file?download=1[access: 1.10.2018].

Dadenko E.V., Miasnikova M.A., Kazeev K.Sh., Kolesnikov S.I., 2013, Application of enzyme activity indicators while assessing the state of agricultural soils, *Proceedings of Samara scientific center*, 3(5), 1274-1277.

Derome J., 2000, Detoxification and amelioration of heavy-metal contaminated forest soils by means of liming and fertilization, *Environmental Pollution*, 107(1), 79-88.

Fulekar M.H., Sharma J., Tendulkar A., 2012, Bioremediation of heavy metals using biostimulation in laboratory bioreactor, *Environmental Monitoring and Assessment*, 184 (12), 7299-307, doi: 10.1007/s10661-011-2499-3.

Goulding K.W.T., 2016, Soil acidification and the importance of liming agricultural soils with particular reference to the United Kingdom, *Soil Use and Management*, 32(3), 390-399.

Hentati O., Abrantes N., Caetano A.L., Bouguerra S., Gonçalves F., Römbke J., Pereira R., 2015, Phosphogypsum as a soil fertilizer: Ecotoxicity of amended soil and elutriates to bacteria, invertebrates, algae and plants, *Journal Hazard Mater*, 294, 80-89.

Konhauser K., Riding R., 2012, Bacterial Biomineralization, in: *Fundamentals of Geobiology*, eds. A.H. Knoll, D.E. Canfield, K.O. Konhauser, Hoboken, NJ: Blackwell Publishing.

Napan K., 2014, *Distribution of Heavy Metals from Flue Gas in Algal Bioreactor*, https://digitalcommons.usu.edu/etd/4018 [access: 15.08.2018].

Yanyan Gong, Dongy Zhaob, Qilin Wang, 2018, An overview of field-scale studies on remediation of soil contaminated with heavy metals and metalloids: Technical progress over the last decade, *Water Research*, 147, 440-460.

Zachara J.M., Kukkadapu R.K., Fredrickson J.K., 2002, Biomineralization of Poorly Crystalline Fe(III) Oxides by Dissimilatory Metal Reducing Bacteria (DMRB), *Geomicrobiology Journal*, 19, 179-207.

Przyjazny dla środowiska sposób stymulacji właściwości ochronnych gleby

Streszczenie. Rozwój gospodarki glebowej na poziomie lokalnym i regionalnym napotyka wyzwania związane ze wzrostem poziomu zanieczyszczenia gleby w systemach zurbanizowanych. Tak więc intensywne użytkowanie gleby na Ukrainie w ostatnich latach spowodowało znaczną utratę próchnicy, czemu towarzyszą negatywne zmiany właściwości agrofizycznych, fizykochemicznych i biologicznych gleby. Celem badań było modelowanie procesu pobudzania naturalnych właściwości ochronnych kompleksu glebowego z uwagi na wpływ biokompozytu na osady ściekowe i fosfogips w warunkach siarczanowania. Przeprowadzono ekstrakcję frakcji chemicznych zanieczyszczonej gleby przed i po obróbce. Zastosowano dyfraktometrię rentgenowską i analizę mikroskopową do tworzenia obrazów powierzchniowych obrabianej gleby. Opracowano mapę składu mineralnego próbek gleby po przetworzeniu przez biokompozyt oparty na osadzie ściekowym i fosfogipsu. Opracowano model technologiczny procesu remediacji gleb, który obejmuje dwa etapy: uprawę aerobową z użyciem biokompozytu; etap fitoremediacji w celu dodatkowego leczenia.

Słowa kluczowe: właściwości ochronne, gleba, metale ciężkie, biokompozyty, fosfogips, osady ściekowe