

## PHYTOREMEDIATION OF TECHNOGENIC OBJECTS: PROCEDURE, SEQUENCE, MATHEMATICAL MODEL

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**Abstract.** The article is devoted to the biological reclamation of lands that have been disturbed as a result of industrial activities, in particular mining and thermal power plants. Various methods of reclamation are analyzed, including self-growth (natural phytoremediation), mining and biological reclamation. The disadvantages of traditional approaches to reclamation are identified, which do not ensure the full restoration of the ecological state of the soil cover and its detoxification. It is proved that for contaminated areas, the most effective is phytoremediation being an alternative and effective way of reclamation providing the removal or neutralization of toxic components in the soil due to the hyperaccumulating plants.

The sequence of works on the implementation of phytoremediation of contaminated soils in technogenic objects of mining enterprises and/or the surface of ash and slag heaps of thermal power plants is substantiated taking into account regulatory documents. The phytoremediation procedure is proposed to be divided into six main stages: search, preparatory, laboratory, office, field and final. The influence of the plant root system on the reduction of heavy metal concentration in soils is analyzed by mathematical modeling of the process of their extraction. The optimal selection of crops for different types of technogenic landscapes is proposed taking into account the toxicological characteristics of the soil. The analytical dependence of the residue of toxic trace elements in technogenic soil after the application of phytoremediation is established, which is represented by an inverse power dependence between the content of toxic components of heavy metals in the artificially created soil layer, the solubility of toxic trace elements in water, the number of plants, the period of growth and water consumption by plants. It was determined that the highest efficiency of heavy metal removal (in particular Cu, Cr, Zn, Ni, Pb, Cd) is demonstrated by *Melilotus officinalis*, which allows achieving permissible levels of pollution during three growing seasons. The results obtained can be applied in the implementation of measures for the revitalization of industrial territories of mining enterprises and thermal power plants, as well as adjacent residential areas.

**Keywords:** biological remediation, technogenic soils, phytoremediation, procedure, mathematical model, hyperaccumulating plants, heavy metals, removal.

### 1. Introduction

Mining activity is accompanied by an increase in technogenic environmental impact. Human intervention in natural ecosystems disrupts the balance of natural processes and negatively affects the health of the population. Mineral extraction, regardless of the method, almost always leads to soil degradation and destruction of natural landscapes. As a result, technogenic territories are formed consisting of quarries, dumps and other industrial facilities that change or destroy the structure of biogeocenoses.

The Land Code of Ukraine [1] defines *reclamation* as a set of organizational, technical and biotechnological measures for restoring the soil cover, improving the condition and productivity of disturbed lands. Article 166 [1] determines that lands that have undergone changes in the relief structure, ecological condition of soils and parent rocks, hydrological regime of territories as a result of mining operations, geological exploration, construction and other works are subject to reclamation. According to the classical scheme, soil previously removed and stored in a temporary dump is used for the reclamation of disturbed lands and the restoration of degraded lands,. But this does not solve the problem of cleaning technogenic objects and soil from



heavy metals and restoring the ecological component of the earth's surface to return ecologically clean lands to the community.

The modern alternative direction of the "biological stage of land reclamation" is phytoremediation. This can be achieved by phytomelioration, bioremediation or phytoremediation through the use of hyperaccumulating plants. This approach includes a complex of combined agrotechnical and phytoremediation measures specifically developed for restoring the fertility of disturbed lands. The use of the complex makes it possible to remove or, in critical conditions, to reduce the heavy metal concentration in the soil. Therefore, solving the problem of renovation of industrial enterprise territories and restoring soil cover at technogenic facilities is an urgent task to ensure the sustainable development of the country and the environmental safety of industrial regions.

Having summarized the own experience of working at technogenic facilities of mining enterprises and thermal power plants (TPPs), and having analyzed literary sources regarding the directions of reclamation of disturbed lands, innovations in the field of biological reclamation of soil cover, legislatively approved provisions and actually implemented reclamation projects, it was determined that in practice, the simplest methods of land restoration are used. The most common method is self-growth, while there are many other methods in project documentation and science. The main trends of reclamation in terms of their complexity can be summarized as follows:

1. *Self-growth (natural phytomelioration)*. Technogenic surfaces of dumps, sludge storage facilities and other objects are let to grow on their own with grassy, shrubby plants and trees (Fig. 1). This method does not involve dismantling of technogenic objects, restoring of disturbed relief and soil cover of disturbed lands, and is based on the development of plant cover without direct anthropogenic intervention.

The method of self-growth is attractive primarily for owners of mining enterprises, because it enables reducing the costs of reclamation of technogenic objects. While botanists, both domestic [2, 3] and foreign [4, 5] are interested in other aspects of the method. They study different plant species that are capable of acclimatization in an artificial technogenic environment, and justify the optimal conditions for their growth to enhance this process. However, unlike active reclamation methods, natural phytomelioration is long-term and may be limited in cases of extreme conditions or high toxicity of waste. Despite its economic attractiveness, this approach requires detailed monitoring to assess the dynamics of restoration and identify possible obstacles.

It should be noted, however, that the effects of natural plant succession frequently surpass those of traditionally conceived reclamation methods. On post-mining and post-industrial lands, where specific habitat conditions prevail, pioneer vegetation communities tend to develop [6–8]. In many cases, natural succession constitutes the only viable method of renaturalizing post-industrial wastelands. This is particularly true in areas where mineral raw materials were extracted from rock quarries, where the topographic complexity not only makes reclamation interventions difficult, but often renders them impossible due to health and safety risks.



a)



b)

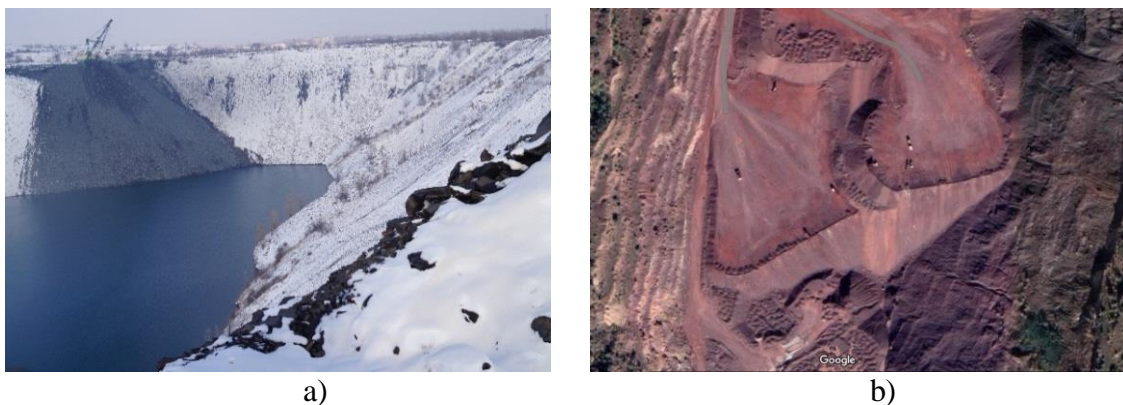
a) – Haniv dump; b) – sludge storage in Baburin gully

Figure 1 – Examples of self-overgrowth of technogenic objects (author's photo)

Long-term observations show that even 20 years after mining activities cease, valuable xerothermic grasslands can establish on quarry benches and slopes — not only in carbonate rock quarries, but also on igneous rock outcrops. As a result of weathering and erosion, rocky shelves give rise to scree formations that are rapidly colonized by spontaneous pioneer vegetation. Due to their unique biological value and high biodiversity, many former quarry sites in Poland have been designated as nature reserves [9].

There are numerous examples of spontaneous renaturalization of post-industrial sites, even in locations with seemingly unfavorable environmental conditions. One particularly notable case involves the so-called *galman grasslands*, plant communities that have developed on waste heaps from Zn-Pb ore processing [10]. Owing to their exceptional botanical value, these areas have been granted protected status as nature reserves, and some have even been included on the UNESCO World Heritage List and designated under the European Natura 2000 program.

2. *Mining reclamation* is performed in most cases for the storage of overburden in the excavated space of quarries (Fig. 2) or, in some cases, for leveling the surface of a technogenic object and applying a potentially productive layer from the soil, which was previously stored in a temporary dump [2,11,12]. However, this method is inefficient due to the soil quality characteristics degraded during temporary storage and mixing. The Institute of Geotechnical Mechanics of the NAS of Ukraine developed scientifically substantiated methods of mining reclamation with the restoration of the aquifer and the formation of microrelief [13–15].



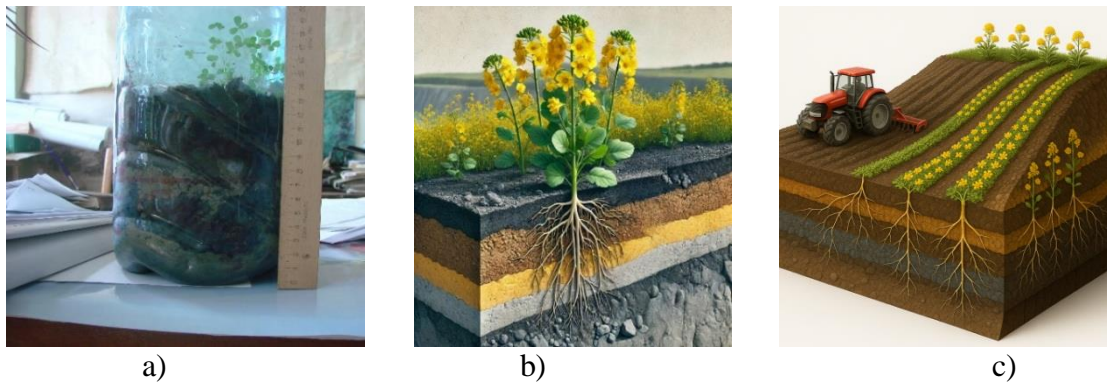
a) – quarry № 1 of PJSC “ArcelorMittal Kryvyi Rih” (author's photo); b) – Northern quarry (Google Map)

Figure 2 – Mining reclamation of the excavated quarry space

3. *Biological reclamation* is essentially a set of measures that are carried out after mining reclamation to restore the fertility of the reclaimed land, i.e. the final stage of land reclamation before agricultural or forestry activity [2,11]. Usually, biological reclamation is carried out according to land management projects that provide ecological and economic justification for crop rotation and land improvement, which are regulated by Article 52 [16]. That is, documentation should be developed for creating a favorable ecological environment, improving natural landscapes or restoring technogenic artificially created soil cover. These projects should justify the selection and (for) sowing of grasses, fertilizer application, and land reclamation. The prepared potentially fertile and non-phytotoxic rocks are selectively applied on the surface of the technogenic object.

The Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine developed a technology for layer-by-layer mining and biological reclamation [17,18]. The advantage of this technology is to improve the productive soil layer by creating artificial porosity by the root system of plants in the bulk soil layers (Fig. 3). However, all these methods of biological reclamation do not sufficiently address the main issue of reclamation of technogenic objects, namely, decontamination and reasonable extraction of trace elements of heavy metals and other toxic substances.

4. *Phytoremediation* is a modern direction of biological remediation, which enables “rehabilitation” of the soil through phytoextraction when a plant extracts pollutants from the soil with its root system and accumulates them. That is, when developing a *land management project that provides ecological and economic justification for crop rotation and land improvement*, it is necessary to research and justify the sowing of green manure crops that will absorb and neutralize toxic substances. This direction has gained significant resonance among leading scientific institutions, universities and botanical gardens of the world in recent years. Such great interest is due to a set of advantages, including environmental safety, relative economic efficiency and a proven ability to restore the natural balance of degraded ecosystems.



a) – plant germination according to laboratory studies (author's photo); b) and c) – root system distribution schemes in soil layers (AI generated)

Figure 3 – Elements of the scheme of layered mining and biological reclamation

Depending on the functional purpose, phytoremediation is divided into the following types: sanitary and hygienic, landscape and greening, melioration, anti-erosion, field protection and operational [1, 19]. Domestic and foreign scientists found that when using phytoremediation methods in combination with the phytoextraction method, interesting and positive results were obtained [19–24]. Namely, it is planned to cultivate hyperaccumulating plants that “extract” heavy metal (HM) residues from the soil with their root system. The work [25] presents the results of practical work that demonstrate a significant decrease of HM concentration in the soils of mining regions after forest technical reclamation, but the problem of the optimal choice of plant and tree species for such purposes remains open. Energy crops (*Miscanthus*, *Ricinus*, *Jatropha*, *Populus*) are considered promising [26]. Similar problems arise when considering the results of research on silver mining enterprises in Turkey [27].

There is positive experience in soil renovation with the participation of sewage sludge (SS) in the form of fermented sludge or activated sludge. It is proposed to use this mixture as a fertilizer, provided that the requirements for the HM content are met [28]. This process also immobilizes HM, converting them into compounds suitable for plants by way of absorbing sediments, which contributes to the remediation of HM-contaminated soils. According to [28,29], the remediation capacity of SS fertilizer can be increased by composting with biological products, lime, wood waste, manure, straw, as well as by increasing the proportion of organic components by preliminary dehydration to 35% of dry matter. For example, in experimental work [30], American scientists used compost as an immobilizer, which was obtained during the processing of sewage sludge and “green waste” and enriched it with minerals (clinoptilolite and bentonite) in different ratios.

Thus, the implementation of biological remediation with the latest method of phytoremediation is a necessary condition for the further effective use of the territories of technogenic objects for agricultural needs or for the creation of recreational zones.

Therefore, the purpose of the work is to establish an analytical dependence of the extraction of heavy metals by the root system of plants from artificially created soil

and to substantiate the sequence of actions and phytoremediation procedures within the framework of biological remediation of surfaces of technogenic objects.

## 2. Methods

To achieve the set goal, the work was carried out in three stages. The sequence of work, the methods used, and the results obtained are shown in the diagram (Fig. 4).

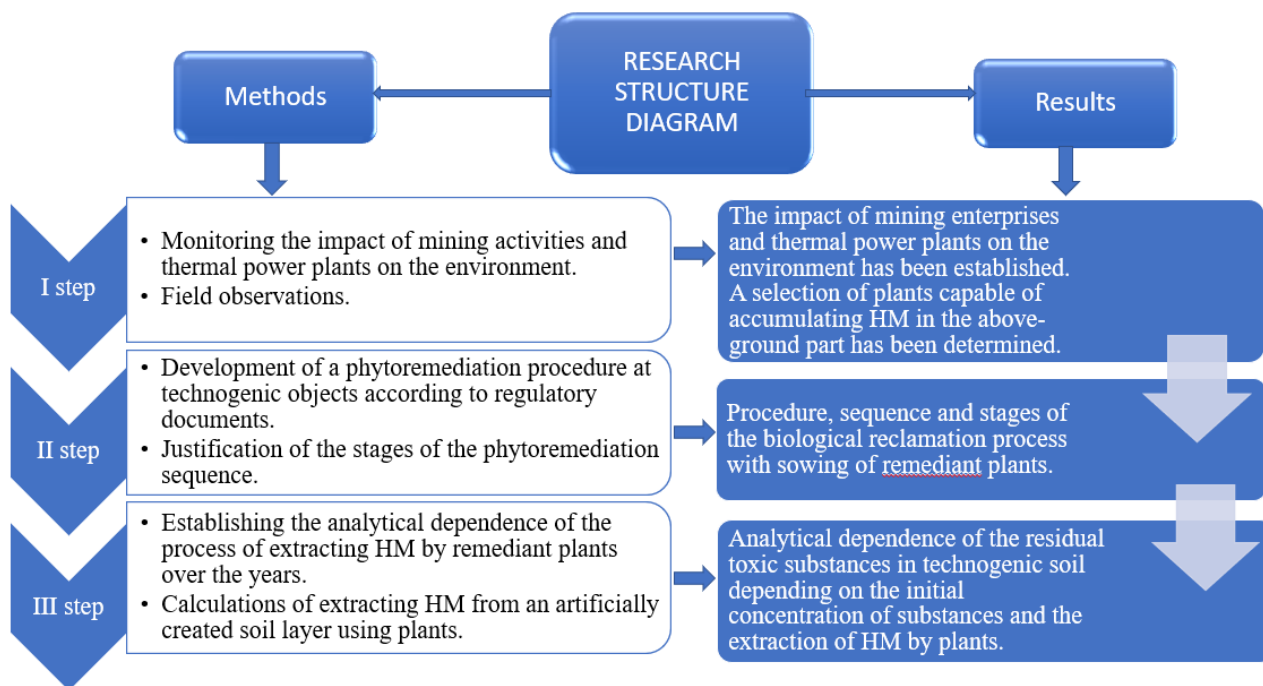


Figure 4 – Research scheme and results obtained

## 3. Results and Discussion

Further development of the technology of layer-by-layer mining and biological reclamation for the creation of productive soils in the territories of mining enterprises and thermal power plants is possible through the phytoremediation. But before the phytoremediation, feasibility of carrying out the work and monitoring should be justified. Therefore, it is proposed to divide the entire procedure - from justification to the planting/mowing hyperaccumulating plant - into six stages: search, preparatory, laboratory, office, field and final (Table 1).

Thus, the phytoremediation procedure is quite capacious. For its use, justifications are needed regarding the implementation of this method of remediation, the term and sequence of actions. Which in turn will allow developing a method of soil renovation for the frame of a technogenic object of mining enterprises or the surface of ash and slag heaps of TPPs.

For analytical substantiation of phytoremediation, a mathematical model of heavy metal removal from technogenic soil is proposed. Let us assume that harmful substances are uniformly distributed in the form of soluble salts in a unit volume of soil. And when the soil layer is filled with water during irrigation or natural precipitation, all harmful substances present in it dissolve in this water in proportion to their mass fractions.

Table 1 – Stages of the phytoremediation process of technogenically contaminated soils of technogenic objects of mining enterprises and/or surfaces of ash and slag heaps of TPPs

Stage name	Document	Type of analysis or methods of implementation
Search stage	DSTU 3575-97	Conducting patent searches and analyzing literature sources to identify innovative proposals
Preparatory stage	DSTU 4287:2004	1) drilling of single wells to the depth of the productive layer to the upper aquifer with the taking of cores in the underlying rocks; 2) establishing the real geological structure of the massif after mining reclamation; 3) taking surface soil samples according to the scheme, geochemical studies at the local and regional levels.
Laboratory stage	DSTU 4770.1:2007 4770.9:2007 GOST 30178-96	Determination of laboratory research and analysis of selected samples of soils, parent rocks, underlying layers, groundwater and plant material in order to confirm and clarify the results of field soil research, obtain objective data on their key characteristics, namely: 1) group composition of humus; 2) abbreviated gross analysis; 3) determination of the type and levels of contamination, substantiation of criteria for the level of content of mobile microelements of HM in technogenic soils (atomic absorption spectrophotometry method).
Office stage (card making)	DSTU 4287:2004 Pb, Cd, As, Hg, Cu, Zn, Ni, V, Mn, Cd - for DSTU 7850:2015	1) fulfillment of a thorough check, correction, critical review, and systematization of field observation data, records, official documents, collection samples, etc.; 2) creation and design of a soil map and development of relevant cartograms; 3) determination of the area of the contours of plots with different soil differences and soil cover structures; 4) calculation of cartometric coefficients and indicators reflecting the structure of the soil cover; 5) determination of the soil microelement composition based on the results of expert evaluation of current regulatory and reference documentation and calculation of the total contamination ( $C_{Me\ max}$ ).
Field stage	Methodology of the IGTM of the NASU	1) initial planting and growing of plants; 2) mowing the above-ground part; 3) taking soil samples, determining the content of chemical elements of toxic substances and comparing them with the MPC; 4) soil map correction; 5) if the content of chemical elements of toxic substances is exceeded, replanting of plants; 6) taking soil samples, determining the content of chemical elements of toxic substances and comparing them with the MPC; 7) preparation of updated soil maps.
Final stage	DSTU 4287:2004, DSTU [31], 7850:2015	1) statistical processing of the obtained data on the extraction of chemical elements of toxic substances by safety class, the completeness of their extraction and changes in the composition of nutrients; 2) transfer of land to the user.

Toxic soluble salt trace elements enter a plant along with water, the amount of which can be determined by the expression:

$$C_{Me} = C_{Memax} \cdot a \cdot k, \quad (1)$$

where  $C_{Me}$  – mass concentration of toxic microelements of HM in the plant, mg/kg;  $C_{Memax}$  – initial maximum mass concentration of toxic microelements of HM in the form of soluble salts in the volume of the artificially created soil layer, mg/kg;  $a$  – volume of water consumed by plants in 1 year, i.e. each vegetative cycle,  $m^3$ ;  $k$  – solubility coefficient,  $1/m^3$ .

Then the mass concentration of toxic microelements of the HM that will enter the plant during the first year of cultivation ( $C_{Me1}$ ) can be determined as:

$$C_{Me1} = C_{Memax} \cdot a \cdot k \cdot m, \quad (2)$$

where  $m$  is the number of plants growing on the surface of a unit volume of an artificially created soil layer, pcs.

As a result of the extraction of toxic soluble salt trace elements of HM by the root system of plants, the mass concentration of toxic trace elements of HM in technogenic soil decreases every year. Then, during the second year ( $C_{Me2}$ ), the third year ( $C_{Me3}$ ) and subsequent years ( $C_{Mei}$ ) as a result of plant cultivation, the mass concentration of toxic trace elements of HM decreases in the technogenic soil itself and, accordingly, in plants. It is determined by the following formulas:

$$C_{Me2} = C_{Memax} \cdot a \cdot k \cdot m \cdot (1 - a \cdot k \cdot m), \quad (3)$$

$$C_{Me3} = C_{Memax} \cdot a \cdot k \cdot m \cdot (1 - a \cdot k \cdot m)^2, \quad (4)$$

$$C_{Mei} = C_{Memax} \cdot a \cdot k \cdot m \cdot (1 - a \cdot k \cdot m)^{i-1}, \quad (5)$$

where  $i$  is the vegetative period of growing remedial plants, year.

Since  $k$ ,  $a$ ,  $m$  can be taken as constant values for a certain soil and plant, we denote them as  $H$ , that is:  $H = a \cdot k \cdot m$ . Then, taking into account mathematical transformations, formula (5) will take the form:

$$C_{Mei} = C_{Memax} \cdot H \cdot (1 - H)^{i-1}. \quad (6)$$

If the number of years is denoted as the time interval  $t$ , then the dependence between the mass concentration of toxic trace elements of the HM from the artificially created soil layer and time can be written in the following form:

$$C_{Me}(t) = C_{Me\max} \cdot H \cdot (1 - H)^{t-1}, \quad (7)$$

where  $t$  is the period of time during which the cultivation (growth) of remedial plants occurs, year.

The residual mass concentration of toxic trace elements of BM in the artificially created soil layer  $C_{Me\text{res}}$  is determined by the formula:

$$C_{Me\text{res}} = C_{Me\max} - \sum C_{Me}(t). \quad (8)$$

where  $\sum C_{Me}(t)$  is the total removed mass concentration of toxic microelements of the HM by remedial plants for the entire planned period of their cultivation, mg/kg.

In the classical sense, complete removal of HM is not possible, because, firstly, not all HM dissolve. Secondly, the main condition is to reduce the value of harmful substances to the maximum permissible concentration (MPC).

For the remediation of the surface of spent ash and slag heaps at thermal power plants using the phytoremediation method, a selection of remedial plants is recommended: the following plants belong to the family of cereals: spineless brome (Latin: *Brōmus inērmis*), the family of legumes: yellow sweet clover (Latin: *Melilotus officinalis*), and sandy sainfoin (Latin: *Onobrýchis arenária*).

Based on the results of research by the IGTМ scientists and the analysis of literature sources [31–36], data were collected on the content of toxic trace elements of heavy metals in ash-slag waste (ASW) of six thermal power plants of Ukraine: Cherkasy, Burshtyn, Trypilly, Zmiiv, Prydniprovskа, Darnytska TPP. These data were systematized with a division into hazard classes in relation to human health and published in Table 1 [37].

For the above-mentioned objects, calculations were made using mathematical expressions (5), (7), (8) of the residual mass concentration of toxic trace elements in the mixture of ash and slag waste from thermal power plants at maximum values exceeding the MPC.

Visualization of the analysis of calculations in the form of a diagram of the extraction of the mass concentration of toxic microelements of the HM by the remedial plants - yellow sweet clover (Latin: *Melilotus officinalis*) - and sand sainfoin (Latin: *Onobrýchis arenária*) from an artificially created soil layer over a planned period of time, namely three years, is shown in Figure 5.

The extraction analysis showed (see Fig. 5) that the artificially created soil layer of yellow sedge “cleans” with best effectiveness demonstrating the higher values for the extraction of harmful trace elements of cadmium, zinc, lead, copper, chromium and nickel. That is, in 3 years after planting yellow sedge, complete extraction of copper and chromium is possible. While when planting sainfoin, the above HM still remain in insignificant quantities. But in both cases, nickel and vanadium remain in a concentration higher than the MPC.

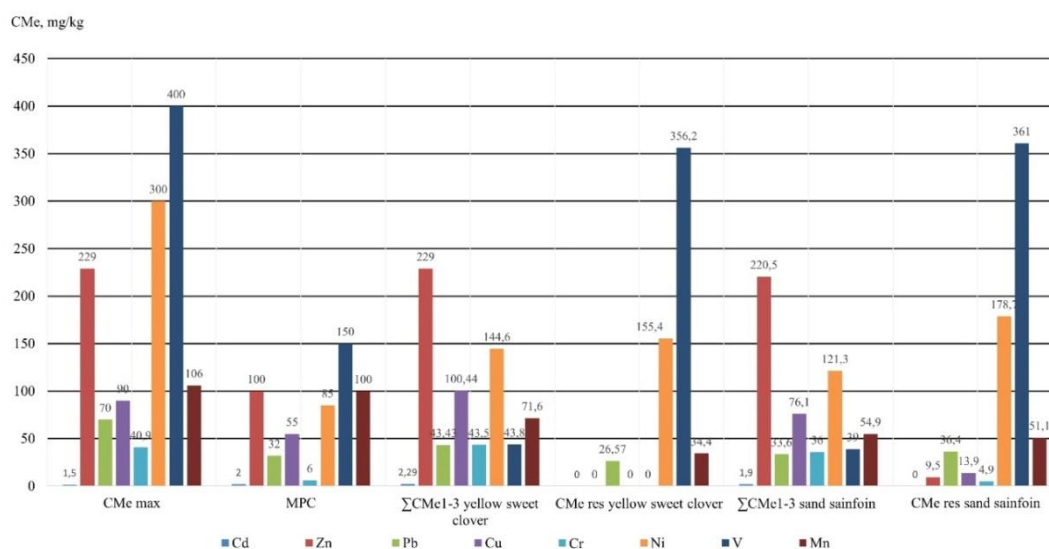


Figure 5 – Analysis of the extraction of mass concentrations of toxic microelements from HM by remedial plants: yellow sweet clover (Latin: *Melilotus officinalis*) and sand sainfoin (lat. *Onobrychis arenaria*)

#### 4. Conclusions

1. To improve the environmental safety and infrastructure of urban residential areas, it is recommended to implement measures to revitalize industrial zones of mining enterprises and thermal power plants and residential areas around them within the framework of regional environmental programs. It is proven that phytorecultivation is an effective way to restore land.

2. The amount of harmful substances removed by plants is represented by an inverse power dependence between the content of toxic components of BM in the artificially created soil layer, the solubility of toxic trace elements in water, the number of plants, the period of growth and water consumption by plants. The obtained pattern can be applied as long as the inequality  $C_{Me-res} \geq \sum C_{Me}(t)$  is satisfied.

3. The procedure, sequence, and main stages of implementing phytoremediation as a method of biological remediation of technogenic soils containing toxic substances are substantiated.

#### Conflict of interest

Authors state no conflict of interest.

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#### ФІТОРЕМЕДІАЦІЯ ТЕХНОГЕННИХ ОБ'ЄКТІВ: ПРОЦЕДУРА, ПОСЛІДОВНІСТЬ, МАТЕМАТИЧНА МОДЕЛЬ

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**Анотація.** Стаття присвячена біологічній рекультивациі земель, які були порушені внаслідок промислової діяльності, зокрема гірничодобувних та теплоенергетичних підприємств. Проаналізовано різні напрямки

рекультивациі, включаючи самостійне заростання (природну фітомеліорацію), гірничотехнічну та біологічну рекультивацию. Визначено недоліки традиційних підходів до рекультивациі, які не забезпечують повного відновлення екологічного стану ґрунтового покриву та його детоксикації. Доведено, що для забруднених територій найбільш ефективним є застосування фітореMediaції, як альтернативного і ефективного напрямку рекультивациі, що передбачає вилучення або знешкодження токсичних компонентів в ґрунті за допомогою рослин-гіперакумуляторів.

Обґрунтована послідовність робіт з впровадження фітореMediaції забруднених ґрунтів техногенних об'єктів гірничодобувних підприємств та/або поверхні золошлакових відвалів теплових електростанцій з урахуванням нормативних документів. Процедура фітореMediaції запропоновано поділити на шість основних етапів: пошуковий, підготовчий, лабораторний, камеральний, польовий та завершальний. Проведено аналіз впливу кореневої системи рослин на зниження концентрації важких металів у ґрунтах шляхом математичного моделювання процесу їх вилучення. Запропоновано оптимальний добір культур для різних типів техногенних ландшафтів із урахуванням токсикологічних характеристик ґрунту. Встановлено аналітичну залежність залишку токсичних мікроелементів в техногенному ґрунті після застосування фітореMediaції, яка представлена зворотною ступеневою залежністю між вмістом токсичних компонентів ВМ в штучно-створеному шарі ґрунту, розчинністю токсичних мікроелементів в воді, кількістю рослин, періодом зрощення і водоспоживанням рослинами. Визначено, що найвищу ефективність вилучення важких металів (зокрема Cu, Cr, Zn, Ni, Pb, Cd) демонструє буркун жовтий (*Melilotus officinalis*), що дозволяє досягти допустимих рівнів забруднення впродовж трьох вегетаційних періодів. Отримані результати можуть бути застосовані при впровадженні заходів з ревіталізації промислових територій гірничодобувних підприємств і теплоелектростанцій, а також прилеглих до них селітебних зон.

**Ключові слова:** біологічна рекультивация, техногенні ґрунти, фітореMediaція, процедура, математична модель, рослини-гіперакумулятори, важкі метали, вилучення.