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Assessment of performance and environmental friendliness of a sorbent-based remediation method for heavy metal and metalloid contaminated soils

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Abstract
The contamination of natural ecosystems with heavy metals and metalloids (HMMs) primarily results from anthropogenic activities. Consequently, ongoing efforts are dedicated to the development of technologies aimed at restraining the mobility of HMMs and expediting chemical reactions that convert pollutants from mobile to immobile states. Addressing the reclamation issue always necessitates the selection of the most promising and effective type of reclamation work, as well as justification of land prioritization for reclamation purposes. In terms of performance and future potential, the sorbent-oriented approach, grounded in the concept of "green" utilization of man-made waste as a raw material for creating novel composite sorbents, is gaining traction for land reclamation in disturbed areas. In international practice, diverse environmental risk assessment methods are employed to substantiate the necessity for and prioritize reclamation efforts.
The aim of the present study is to evaluate established conventional methods for assessing the risks associated with environmental harm. Additionally, this research aims to assess the efficacy and ecological compatibility of the composite sorbents developed by the author. This evaluation will be conducted by assessing and comparing the levels of potential environmental risks or risks of environmental damage subsequent to the application of these sorbents.
The objectives of this study are as follows: 1) to explore the theoretical aspects of HMMs: including the formulation of a definition, investigation onto the origins of HMMs, examination of HMMs' toxicity, and identification of prevalent methods for evaluating the environmental risks associated with HMMs; 2) to evaluate the effectiveness of established methods for assessing the environmental risks posed by HMMs; 3) to assess the efficacy and environmental sustainability of the composite sorbents developed by the author. This evaluation will involve an examination and comparison of the levels of potential environmental risks and the risks of environmental damage subsequent to the application of these sorbents.
The research subject: the mining allotment within the Levikhinskoye mine (classified as an environmental disaster site) is investigated as a disturbed land ecosystem, encompassing industrial waste dumps containing HMMs.
The research **hypothesis** aims to establish the viability of "green" waste utilization from industrial sources as a raw material for composite sorbents used in land reclamation, without escalating the environmental damage. The conducted experiments revealed that sorbents composed of peat/water treatment sludge (at a ratio of 20/80 wt. % with natural moisture content) and peat/diatomite/water treatment sludge (at a ratio of 5/15/80 wt. % with natural moisture content) exhibited the highest level of performance, surpassing an overall efficiency of 89%. A sorbent composed of peat/diatomite (at a ratio of 25/75 wt. % with natural moisture content) demonstrated an overall efficiency of 67.7%. The estimated environmental risks (*ER* and *ED*) after the application of the proprietary composite sorbents, which include water treatment sludge, exhibited an average reduction of 89.5% and 88%, respectively.

Keywords
sorbents, reclamation, disturbed lands, environmental risks, methods, assessment, "green" disposal, heavy metals and metalloids, biota, toxicity, environmental damage

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ТЕХНОЛОГИЧЕСКАЯ БЕЗОПАСНОСТЬ В МИНЕРАЛЬНО-СЫРЬЕВОМ КОМПЛЕКСЕ И ОХРАНА ОКРУЖАЮЩЕЙ СРЕДЫ

Научная статья

Оценка эффективности и экологичности сорбент-ориентированного метода восстановления загрязненных тяжелыми металлами и металлоидами почв

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Аннотация

Загрязнение природных экосистем тяжелыми металлами и металлоидами (НММ) – это главным образом результат антропогенной деятельности. Именно поэтому в настоящее время разрабатываются технологии, направленные на ограничение подвижности НММ и уменьшение сроков протекания химических реакций по переводу поллютантов из подвижной в неподвижную форму. Решение проблемы рекультивации всегда предполагает выбор наиболее перспективного и эффективного вида рекультивационных работ, а также обоснование приоритизации земель, подлежащих рекультивации. В части эффективности и перспективности популярность приобретает сорбент-ориентированный метод, основанный на принципе «зеленой» утилизации техногенных отходов в качестве сырья для создания композитных сорбентов нового типа в целях рекультивации нарушенных земель. Зарубежная практика в качестве обоснования необходимости и приоритизации рекультивационных работ использует различные методики оценки экологических рисков. **Цель** текущего исследования – апробировать имеющиеся распространенные методики оценки рисков причинения экологического ущерба и оценить эффективность и «экологичность» разрабатываемых авторских композитных сорбентов с позиции оценки и сравнения уровней возникновения потенциальных экологических рисков/рисков нанесения экологического ущерба после их (сорбентов) применения.

Задачи: 1) рассмотреть теоретические аспекты НММ: сформулировать определение, рассмотреть генезис НММ, исследовать вопрос токсичности НММ и выявить наиболее распространенные методики оценки экологических рисков НММ; 2) апробировать имеющиеся методики оценки экологических рисков НММ; 3) оценить эффективность и «экологичность» разрабатываемых авторских композитных сорбентов с позиции оценки и сравнения уровней возникновения потенциальных экологических рисков/рисков нанесения экологического ущерба после их (сорбентов) применения.

Объект исследования: горный отвод Левихинского рудника (зона экологического бедствия) как экосистема нарушенных земель, в составе которой присутствуют промышленные отвалы, содержащие НММ.

Гипотеза исследования: доказать возможность «зеленой утилизации» техногенных отходов в качестве сырья для композитных сорбентов, используемых для рекультивации нарушенных земель, без увеличения рисков причинения экологического ущерба природной среде. В результате проведённых экспериментов наибольшую эффективность продемонстрировали сорбенты торф/осадки водоподготовки (пропорция при естественной влажности: 20/80, %), торф/диатомит/осадки водоподготовки (пропорция при естественной влажности: 5/15/80, %), где суммарная эффективность превышала 89 %. У сорбента торф/диатомит (пропорция при естественной влажности: 25/75, %) наблюдается суммарная эффективность 67,7 %. Оцениваемые риски *ER* и *EH* после применения авторских композитных сорбентов, в состав которых входят осадки водоподготовки, снижались в среднем на 89,5 и 88 % соответственно.

Ключевые слова

сорбенты, рекультивация, нарушенные земли, экологические риски, методики, оценка, «зеленая» утилизация, тяжелые металлы и металлоиды, биота, токсичность, экологический ущерб

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Introduction

Human activity invariably exert an impact on the natural environment, leading to the depletion of natural resources, environmental pollution, and disturbances of the Earth's surface and subsoil. This anthropogenic pressure on nature intensifies each year, with over 30 million tons of pollutants entering the atmosphere annually, and approximately 19% of wastewater being discharged into bodies of water without prior treatment. Nearly all regions experience soil degradation due to factors such as water and wind erosion, excessive moisture, flooding, and waterlogging. Desertification has affected more than 100 million hectares of land, with an additional 18 million hectares comprising ecological zones contaminated by industrial complexes. About 4 billion tons of production and consumption waste are generated annually, while authorized waste disposal facilities occupy around 4 million hectares of land. More than 30 million tons have already been accumulated, including over 400 thousand tons of highly toxic substances. The volume of non-recycled waste is also on the rise. According to expert assessment, the annual loss of Russia's GDP due to environmental degradation (excluding health-damage) falls within the range of 4% to 6%[1]. The mining industry in Russia plays an important role in exacerbating environmental hazards. Although it may not rank highest in terms of industrial damage intensity, it impacts all components of the biosphere and facilitate the extraction and displacement of vast amount of rock material. As indicated by a study [1], the quantity of waste rock extracted from subsoil exceeds that of minerals extracted by a factor ranging from 1.1 to 6.7 times. This waste rock is deposited on the Earth's surface, resulting in the expansion of disturbed land areas. In these areas, waste rock dumps (WRDs) and tailing storage facilities (TSFs) account for the largest portion of land allocation, ranging from 62% to 75% at iron ore mining operations and even more at copper ore producing enterprises [1].

According to data from the Federal State Statistics Service, the regions characterized by a substantional degree of land degradation encompass the Urals, Siberia, and the Far East, which are home to key mineral resource hubs in the Russian Federation. Consequently, disturbances stemming from mineral deposit development activities account for approximately 80% of the total extent of disturbed land in these areas [2]. The open-pit mining method dominates the landscape, holding the largest share of disturbed land in Russia, and is widely prevalent. Disturbances extend to the subsoil as well, manifesting as the creation of man-made voids, both with and without surface access. In the former case, these voids pertain to open-pit excavations within active and exhosted mining pits and the collapse zones of operational and abandoned underground mines. In the latter case, they refer to underground man-made voids. Given that the rate of environmental change resulting from anthropogenic activities impacts significantly outpaces the natural restoration of the ecological balance, it becomes imperative to promptly address the aftermath of subsoil resource extraction. Consequently, reclamation work acquires primary importance and urgency.

Effectively resolving the reclamation challenge entails the selection of the most promising and efficient reclamation method, as well as substantiating the prioritization of lands slated for reclmation.

Regarding the selection of a promising and effective reclamation approach, it is important to note that studies [3–5] have identified two strategies for reclaiming disturbed lands: 1) a traditional approach, which involves a series of sequential reclamation, remediation, and recultivation measures. It encompasses a range of activities, starting from the cleaning and leveling of the reclaimed area, the application of an appropriate thickness of fertile soil, and concluding with the use of fertilizers and ameliorants, as well as the sowing or planting of vegetation; 2) an innovative approach, which is focused on methods and techniques that stimulate natural processes for the restoration and reclamation of disturbed ecosystems, particularly the process of soil formation. It achieves this through physical, chemical, and biological interventions on man-made substrates. Within the innovative approach, the author classifies four primary methods: algal, washing, bioremediation, and sorbent-oriented [6]. Of these, bioremediation and sorbent-oriented technologies, aimed at enhancing soil microflora, have garnered the most attention. Economic feasibility comparisons show that the sorbent-oriented method is the most promising when compared to bioremediation [7, 8]. A more detailed study of the sorbent-oriented method reveals that composite organo-|mineral sorbents of natural origin are currently in focus due to their cost-effectiveness, performance, abundant reserves, and their capacity to function not only as sorbents but also as soil ameliorants [9–11]. Furthermore, a contemporary scientific trend involves the "green" disposal of waste materials from

[1] Project "Environmental Safety Strategy of the Russian Federation for the period up to 2025", 2017; The Strategy of Environmental Safety of the Russian Federation for the Period up to 2025, approved by the Russian Federation. Decree of the President of the Russian Federation dated 19.04.2017 No. 176.

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sectors such as woodworking, agriculture, housing and communal services, and other areas of economy. These waste materials are used as components in innovative composite sorbents-ameliorants [12–15].

When it comes to prioritization, for example, as of 2020, as stated by the Deputy Chief Prosecutor: "Over 350 sites of accumulated environmental damage in the Urals require reclamation"[2]. In this scenario, the question arise of how to establish the order in which these sites should be reclaimed – first, second, and so forth (see Table 1). In foreign practice under similar circumstances, it is customary to employ legislative-level methods for assessing the risks associating with causing harm to the ecosystem [16–19].

Hence, the objective of the present study is to evaluate established methods for assessing the risks of environmental damage and to appraise the effectiveness and "environmental friendliness" of the author's developed composite sorbents. This evaluation is framed within the context of assessing and comparing potential environmental risks and the risks of environmental damage following the application of these sorbents.

The specific objectives are as follows: 1) to consider the theoretical aspects of HMMs, which encompasses the formulation of a precise definition, an exploration of the origins of HMMs, an investigation into HMMs' toxicity, and an identification of the most prevalent methods for evaluating the environmental risks linked to HMMs; 2) to condact practical assessment of established methods for gauging environmental risks associated with HMMs; 3) to assess the effectiveness and "environmental friendliness" of the author's developed composite sorbents. This assessment involves an analysis and comparison of potential environmental risks and the risks of environmental damage following the application of these sorbents.

The research focuses on the mining area within the Levikhinskoye mine, an area designated as environmental disaster site. This mining allotment functions as a disturbed land ecosystem, encompassing industrial dumps containing HMMs.

The research hypothesis seeks to validate the feasibility of "green utilization" of man-made waste as a fundamental ingredient for composite sorbents used in the reclamation of disturbed lands. This approach is designed to minimize the potential for environmental damage.

On the nature of heavy metals: definition, origin, toxicity, and environmental risk assessment

The term "heavy metals" is currently a subject of complexity and controversy [21]. It is frequently used to refer to metals and metalloids that act as pollutants within biogeocenoses and are toxic to biota. This term has been defined in various ways, often based on the criteria of density in relation to atomic mass and atomic number. Such a variety of definitions has led to debates regarding the definitive list of heavy metals and metalloids – namely, which elements should be included in this category and which should not. For example, there is ongoing scientific discourse on whether to include the metalloid As and, indeed, the non-metal Se in the list of heavy metals and metalloids. Some even argue that this term has lost its meaning and should be abandoned altogether [21]. However, within the scope of

[2] More than 350 objects of accumulated environmental damage in the Urals require reclamation. ITAR-TASS. October 28, 2020. URL: https://news.rambler.ru/ecology/45113183-bolee-350-obektov-nakoplennogo-ekologicheskogo-vreda-na-urale-trebuyut-rekultivatsii/?utm_source=copysharing&utm_medium=social

Table 1

Characteristics of mining allotments of deposits in the Sverdlovsk Region [20]

No.	Mining allotment (deposit)	Built-up area, km²	Mining allotment area, km²	Degree of disturbance	Characteristics
1	Levikhinskoye deposit	10.2	21	Highly disturbed	Environmental disaster area
2	Degtyarskoye deposit	19	2.2	Highly disturbed	Environmental disaster area
3	Berezovskoye deposit	33	15.1	Moderately disturbed	Densely built-up area
4	Bulanashskoye deposit	16.8	3.3	Highly disturbed	Zone of dangerous collapse and flooding
5	Pyshminsko-Klyuchevskoye deposit	20	Data not available	Moderately disturbed	Densely built-up area

the current study, we propose adopting a comprehensive interpretation of this term, one that is substantiated by numerous scientific studies by both domestic [22–24] and foreign researchers [25–26]. In this understanding, heavy metals and metalloids (HMM) are viewed as pollutants that resist biological and chemical degradation, possess the capacity to accumulate for a long time in the natural environment, and exhibit toxic properties affecting the biodiversity of ecosystems. According to a study [27, 28], the most commonly encountered HMMs in the natural environment include copper, zinc, chromium, nickel, lead, manganese, cadmium, and arsenic. The release of HMMs into the environment is primarily the result of rock weathering and anthropogenic activities, with the latter being a significant contributor to environmental challenges. Consequently, a defining characteristic of HMMs is their toxicity. Even at relatively low concentrations, HMMs pose risks to soil, plants, living organisms, and, as a result, human health. The most highly toxic HMMs include chromium, cadmium, lead, zinc, copper, mercury, and arsenic [29, 30] (see Table 2). Table 2 presents values of HMMs' Maximum Permissible Concentrations (MPC), including both mobile water-soluble and non-mobile forms.

Table 2 illustrates the variations in maximum permissible concentration values for HMMs, and it is noteworthy that not every country or consortium of nations has adopted legislatively defined maximum permissible concentrations. For example, this omission is observed in the case of the European

Table 2

HMMs toxicity: MPC of HMMs, including mobile water-soluble and immobile forms

Country/ Organization	Land Category/Soil Type, UoM	Cr (VI)	Cd	Pb	Zn	Cu	Hg	As	S
United Nations [31]	Agricultural lands, ppm	0.1	0.003	0.1	n/a	n/a	0.08	n/a	n/a
China [31]	Agricultural lands, ppm	150–300	0.3–0.6	80	n/a	n/a	0.3–1.0	n/a	n/a
USA[1]	Agricultural lands, ppm	11	0.43	200	n/a	n/a	1.0	n/a	n/a
Italy[2]	Residential area, mg/kg	2	2	100	150	120	1	20	n/a
	Industrial land, mg/kg	15	15	1,000	1,500	600	5	50	n/a
Finland[3] [32]	Threshold value, mg/kg	100	1	60	60	100	0.5	5	n/a
	Minimum value, mg/kg	200	10	200	200	150	2	50	n/a
	Maximum value, mg/kg	300	20	750	400	250	5	100	n/a
Canada[4]	Agricultural land, mg/kg	250	3	200	n/a	n/a	0.8	n/a	n/a
Germany [33, 34]	Agricultural land, mg/kg	500	5	1,000	10–300	2–100	5	1-50	n/a
Spain[5]	Acidic soils, mg/kg	100	1	50	150	1.000	1	5	n/a
	Alkaline soils, mg/kg	150	3	300	450	1,700	1.5	55	n/a
Russian Federation[6]	Sandy and sandy loam, mg/kg	0.05	0.5	32.0	55.0	33.0	2.1	2.0	n/a
	Acidic (loamy and clayey), exchange soil acidity $pH_{KCl} < 5.5$, mg/kg	0.05	1.0	65.0	110.0	66.0	2.1	5.0	n/a
	Near-neutral, neutral (loamy and clayey) $pH_{KCl} > 5.5$, mg/kg	0.05	2.0	130.0	220.0	132.0	2.1	10.0	160

Note: N/A indicates that data is not available.

Source: The table was compiled by the authors using reference [28].

[1] New York state brownfield cleanup program. Development of soil cleanup objectives. Technical support document. Albany, NY, USA: New York State Department of Environmental Conservation and New York State Department of Health; 2006.

[2] Decreto Legislativo n. 152 del 3 aprile 2006 "Norme in materia ambientale", Supplemento Ordinario alla "Gazzetta Ufficiale" n. 88 del 14 aprile 2006. URL: https://www.camera.it/parlam/leggi/deleghe/06152dl.htm

[3] Government Decree on the Assessment of Soil Contamination and Remediation Needs 214/2007, 1 March 2007; Ministry of Environment: Helsinki, Finland, 2007 (the legally binding document is In Finnish or Swedish)

[4] Soil, Ground Water and Sediment Standards for Use under Part XV.1 of the Environmental Protection Act. Toronto, ON, Canada: Canadian Ministry of the Environment (CME); 15 April 2011.

[5] Real Decreto 1310/1990, de 29 de octubre, por el que se regula la utilización de los lodos de depuración en el sector agrario. URL: https://www.boe.es/buscar/doc.php?id=BOE-A-1990-26490

[6] SanPiN 1.2.3685-21 "Hygienic Standards and Requirements for Ensuring the Safety and (or) Harmlessness of Environmental Factors for Humans".

Union as a whole [28]. However, it is crucial to acknowledge that elevated concentrations of HMMs pose environmental risks to human health and overall quality of life (as depicted in Fig. 1). Concerning these risks, research practice offers methods for assessing environmental risks based on the level of soil and subsoil contamination with HMMs [16–19], with two widely recognized methods being:

1. HMMs' potential environmental risk (*ER*) assessment methodology:

$$ER = I_t \times Z = I_t \times \frac{Z_m}{Z_a}, \quad (1)$$

where I_t is the toxicity level of HMMs and the biota's sensitivity to these elements. This indicator is empirically determined and is treated as a specific constant for each elements: Cr, Ni, Cu, As, Cd, Pb, Zn, and S, with values of 2, 6, 5, 10, 30, 5, 5, 15, respectively. *Z* represents a microelement contamination coefficient, determined by the ratio of the measured concentration of an element in a subject(Z_m) to the background concentration (Z_a).

The *ER* calculation results categorize the soil or subsoil under investigation as follows: if $ER < 150$, the environmental risk from HMMs is considered low; if $150 \le ER < 300$, it is categorized as medium; if $300 \le ER < 600$, it is considered high; if $ER \ge 600$, it is classified as very high.

One limitation of this methodology is its reliance on the availability of data for the I_t indicator.

Chromium
Persistent forms that are toxic to humans: Cr(III) and Cr(VI). Cr(VI) is the most dangerous since it can more easily enter the human body through inhalation, ingestion, and skin contact. The human organs adversely affected include the liver, kidneys, spleen, and skeletal system. Diseases and manifestations caused by this heavy metal include ulcers, dermatitis, perforation of the nasal septum, and respiratory system cancers. When chromium enters a pedosphere, it can alter the structure of microbial communities and inpede their growth.

Copper
Copper plays a crucial role in various biological processes, including oxidation, photosynthesis, and the metabolism of carbohydrates, proteins, and cell walls. High concentrations of copper can lead to cellular-level damage in human organs. The effects and symptoms associated with this heavy metal include nausea, vomiting, and abdominal pain. Prolonged exposure to cooper can result in damage to the liver and kidneys. In the plant kingdom, copper tends to accumulate in the roots, leading to reduce growth and impaired absorption of other trace elements that are vital for healthy plant development.

Zinc
This element plays a significant role in the metabolism of nucleic acids and proteins, as well as in the growth, division, and overall functioning of cells. However, when present in high concentrations, zinc can induce symptoms such as vomiting, muscle cramps, and kidney damage in humans. In plants, elevated levels of zinc leads to a decrease in both growth and development, causing symptoms such as chlorosis and disruptions in metabolic processes.

Cadmium
Cadmium inhibits cell proliferation, differentiation, apoptosis, and DNA repair mechanism. Diseases and manifestations caused by this heavy metal include skeletal demineralization and issues with kidneys and liver function. In plants, excessive Cd accumulation can disrupt critical functions, including photosynthesis and respiration. This, in turn, hinders the transport and absorption of mineral nutrients, adversely affecting plant growth and development.

Lead
This microelement is swiftly absorbed into the bloodstream, resulting in damage to various systems, particularly the nervous and lymphatic systems. It has a detrimental impact on kidney function and the overall development of the human body.

Mercury
It is a highly toxic element capable of accumulating in various human body, tissues. It damages the brain, thyroid, pectoral muscle, myocardium, muscles, liver, kidneys, skin, and pancreas. Among these, the nervous system is the most severely affected. by mercury exposure.

Arsenic
This metalloid is known to cause a range of severe health issues. These include skin lesions as well as cancers affecting the lungs, bladder, liver, and kidneys. Arsenic exposure is also linked to coronary heart disease and can lead to impaired cognitive abilities, motor functions, and hormonal regulation.

Sulfur
Exposure to sulfur can lead to a range of adverse effects, including irritation of the mucous membranes of the eyes, excessive tearing, difficulty breathing, nausea and vomiting, headaches, increased fatigue, weakening of muscle strength, memory loss, slower cognitive perception, reduced heart function, changes in the bactericidal properties of the skin.

Fig. 1. Toxic effects of HMMs on biota

2. The second methodology aims to assess the risks of environmental damage (*ED*):

$$EH = \frac{Z_m}{Z_l}, \qquad (2)$$

where Z_m similar to the formula (1), represents the measured concentration of an element in a subject, while Z_l, distinct from Z_a, denotes the maximum permissible concentration of an element established by current legislation.

The results of the environmental damage (*ED*) risk calculation indicate a low likelihood of adverse consequences if $ED < 1$. Conversely, if $ED > 1$, the probability of adverse events and environmental damage is high. This underscores the need for soil/subsoil remediation and reclamation.

Therefore, in both the first method for evaluating potential environmental risk from HMMs and the second method for assessing the risks of environmental damage, when the final indicators exhibit high values, soil/subsoil reclamation becomed necessary.

Materials for the study

The study used the following materials:

1. A composite sorbent comprising peat/water treatment sludge in a weight ratio of 20/80 at natural moisture. This composition was determined through numerous experiments and the construction of adsorption isotherms [35].

2. Another composite sorbent (peat/diatomite/water treatment sludge) containing peat, diatomite, and water treatment sludge in a weight ratio of 5/15/80 at natural moisture.

3. A composite peat/diatomite sorbent, consisting of peat and diatomite in a weight ratio of 25/75 at natural moisture.

Neutralized and fractionated high-moor peat (fraction 0–10). This peat had a moisture content ranging from 50 to 60%, a pH of the water extract between 5.5 to 6.0, and an ash content of less than 5 %. The main inorganic components of the peat included nitrogen up to 1.5% (wt.), and phosphorus, potassium, calcium (in total) up to 0.6%. The peat also contained 7.4–7.9% humic substances.

Diatomite from the Kamyshlovskoye deposit. This material is employed in the creation of silicate binder-fillers containing silicon, activated sorbents, construction and refractory materials, as well as for modifying the agrochemical properties of soils, among other uses.

Water treatment sludge originating from the Western Filtration Station in Yekaterinburg city. X-ray phase analysis revealed that over 70% of the sludge consists of X-ray amorphous organic matter. The chemical composition of the sludge includes silicon, aluminum, and iron. The sludge's particle size distribution is polydisperse, with a wet sieve analysis indicating a dominance of particles smaller than 50 µm (21%) and particles larger than 100 µm (18%);

4. Man-made soil obtained from the waste rock dump of the Levikhinskoye group of copper-sulfide deposits (Levikha settlement, Sverdlovsk Region). This soil is comprised of loose terrigenous material consisting of angular grains. In the upper section of the dumps, it primarily includes psammite and psephite fractions (sand and crushed stone). In the lower section, there is a prevalence of the psephite fraction (blocks). The proportion of pelite fraction generally remains within the range of 5–10%. The waste rock comprises fragments of quartz-sericite and quartz-chlorite schists, sulphide ore, limonite, chalcedony, and quartz with vein and disseminated sulfides.

Methods and study algorithm

The samples gathered from the waste rock dumps of the Levikhinskoye group of copper-sulfide deposits (Levikha settlement, Sverdlovsk Region) were thoroughly blended in a single container. The rock mixture was not crushed to replicate the natural conditions of man-made areas. The grain-size distribution of the rock ranged from 12 cm to 1.5 mm.

Each container received 500 g (±5 g) of rock measured on floor scales, creating a 2 cm-high layer of rock in the containers. A rectangular container with an 880 cm^3 volume for each test was partitioned by a plastic divider. In the first part of the container, the rock was first placed, and various sorbents were poured on top in separate containers:

1. Composite sorbent peat/water treatment sludge (P/S) in the ratio of 20/80 by weight at natural moisture.

2. Peat/diatomite/water treatment sludge. This composite sorbent, composed of peat/diatomite/water treatment sludge (P/D/S), was in the ratio of 5/15/80 by weight at natural moisture. Each sorbent subsample weighted 50 g (± 0.5 g), and the height of the sorbent layer varied from 0.4 to 0.6 cm based on the type of sorbent and the soil's looseness.

3. Peat/diatomite. This composite peat/diatomite sorbent (P/D) had a ratio of 25/75 by weight at natural moisture. Each sorbent sub-sample weighted 50 g (± 0.5 g), and the height of the sorbent layer varied from 0.4 to 0.6 cm depending on the type of sorbent and the soil's looseness.

Next, 500 ml of distilled water was evenly poured into the first part of each container containing the rock and sorbents. This was done to establish a moist environment within the container to facilitate the free movement of HMMs ions in the aqueous solution with the immersed sorbent and rock, with the solution flowing into the second part of each container. Circulation of the solution between the two sections in the container occurred throughout the test, but the soil and sorbent did not migrate into the second part.

In order to minimize errors, prevent the entry of various dust particles, and reduce solution evaporation, the containers were sealed.

The testing solution was allowed to stand at room temperature for a minimum of 24 hours.

Subsequently, the solutions were filtered through medium-density paper filters to enable the quantitative and qualitative chemical composition of the solutions to be studied.

In order to analyze the quantitative chemical composition of the man-made soil and the author's sorbents and to determine the degree of heavy metal ions adsorption, atomic absorption and atomic emission spectrometry methods were employed. The corresponding analyses were carried out using an ICPE-9820 inductively coupled plasma parallel atomic emission spectrometer manufactured by Shimadzu (Japan) and a Kvant-2 flame atomization atomic absorption spectrometer. The tests were conducted in accordance with GOST ISO 22036–2014 Soil Quality. Determination of Microelements in Soil Extracts Using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), and Environmental Regulatory Document (PND) F 16.1:2:2.2:2.3.78-2013, titled "Quantitative Chemical Analysis of Soils". Methodology for Measuring the Mass Fraction of Mobile Forms of Metals: Copper, Zinc, Lead, Cadmium, Manganese, Nickel, Cobalt, Chromium in Soil, Subsoil, Bottom Sediments, Sewage Sludge Samples by Flame Atomic Adsorption Spectrometry.

Findings

Assessment of ER and ED of man-made soil

The analyses of samples collected from the waste rock dumps of the Levikhinskoye group of copper-sulfide deposits were carried out in the laboratory [36]. The results of the studies are presented in Table 3.

The results of the studies[3] have shown that the maximum concentrations of S, Cu, and Zn in the samples fall within the dangerous category of soil pollution according to the methodology proposed by the authors of the study. The primary source of pollution is sulfur, with copper and zinc playing a lesser role.

To determine the initial concentration of water-soluble HMMs ions in the man-made soil from the waste rock dumps of the Levikhinskoye group of copper-sulfide deposits, a similar test was conducted, but without the composite sorbent. As a result, HMMs ions were detected in the man-made soil, as presented in Table 4.

[3] SanPiN 1.2.3685-21 "Hygienic Standards and Requirements for Ensuring the Safety and (or) Harmlessness of Environmental Factors for Humans".

Table 3

Concentration (total) of HMMs ions in the waste rock dumps of the Levikhinskoye group of copper-sulfide deposits

Component	Grade, wt.% min/max	Content in sulphide sands, wt.%	MPC and APC*, wt.%	Factor Concentration min/max	Concentration factor in sulfide sands min/max
S	0.026/1.370	32.6	0.016	1.6/85.6	2037.5
Cu	0.005/0.1	0.16	0.0132	0.4/7.6	11.9
Zn	0.0097/0.0353	0.015	0.022	0.4/1.6	0.7

Note: * for the group of soils close to neutral and neutral (loamy and clayey), $pH_{KCl} > 5.5$.

Table 4

Concentration of water-soluble HMMs ions (mobile form) in the man-made soil from the waste rock dump of the Levikhinskoye group of copper-sulfide deposits and in a control sample

Sample	Cu, mg/l	Zn, mg/l	S, mg/l
Averaged (composite) sample from dumps (12 sampling points)	0.84427	0.61632	2.50000
Control sample (background contamination)	0.00500	0.00970	0.08900

The risk assessment, as per formulas (1) and (2), is provided in Table 5.

The *ER* values for all three HMMs are above 300, indicating that zinc and sulfur are ranked as high-risk, while copper is classified as very high-risk. However, the results for the *ED* indicator appear contradictory, as the risk of environmental damage for all three HMMs is below 1, signifying a low probability of negative consequences. This can be attributed to the fact that the sample was averaged (composited), and the long-term impact of surface precipitation on the environmental disaster area. Consequently, the concentrations of HHMs in the surface layer of soil are relatively low compared to the MPC but exceed background values. The arithmetic mean of the risk level indicators also reflects this pattern, with a high value for *ER* and a low value for *ED*.

Analysis of HMMs content in man-made soil after the application of the author's sorbents

The data from Table 4, showing the concentrations of HMMs ions in man-made soil samples from the waste rock dumps of the Levikhinskoye group of copper-sulfide deposits (Levikha settlement, Sverdlovsk Region) are presented in Fig. 2.

The tests showed that the application of the proprietary sorbents resulted in a decrease in HMMs' concentrations in the man-made soil. Fig. 3 presents the test results on the degree of water-soluble ions Cu (*a*), Zn (*b*), and S (*c*) extraction by the sorbents.

The sorbents, as depicted in Fig. 3, exhibit near-maximum performance in binding (adsorption) Cu, Zn, and S ions, with the exception of the

Table 5

Assessment of potential environmental risks from HMMs (ER) and risks of environmental damage (ED) based on the content of HMMs in man-made soil

HMM	Concentration, mg/l	Hazard Factor	Background, mg/l	MPC[1] (mobile form, acidic soils, neutral regarding sulphur), mg/kg	Concentration, mg/kg	*ER*	*EH*
Cu	0.84427	5.00000	0.00500	3.00000	1.68854	844.27000	0.56285
Zn	0.61632	5.00000	0.00970	23.00000	1.23264	317.69072	0.05359
S	2.50000	15.00000	0.08900	160.00000	5.00000	421.34831	0.03125
Arithmetic Mean of HMMs Risk Level						527.76968	0.21590

[1] SanPiN 1.2.3685-21 "Hygienic Standards and Requirements for Ensuring the Safety and (or) Harmlessness of Environmental Factors for Humans".

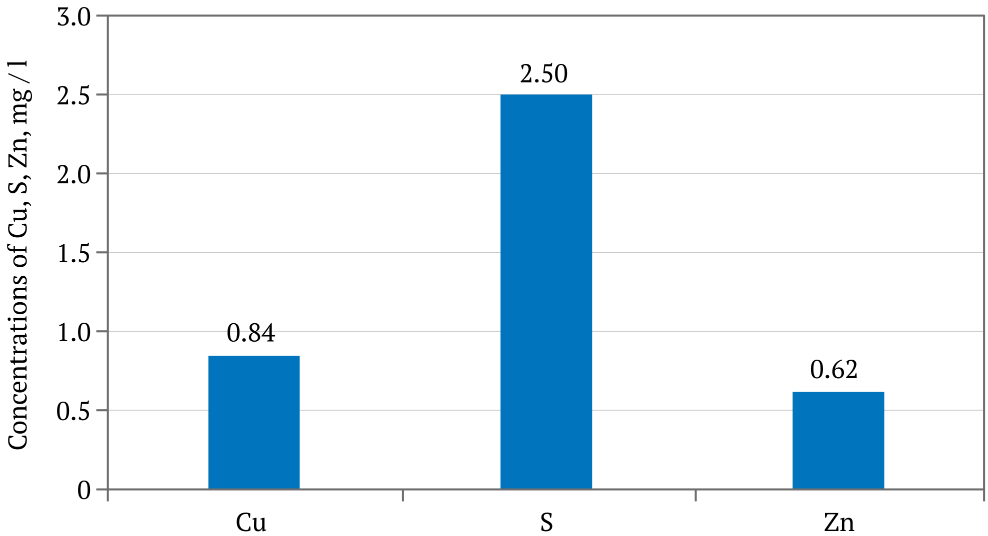

Fig. 2. Concentration of HMMs in the man-made soil from the waste rock dumps of the Levikhinskoye group of copper-sulfide deposits

peat/diatomite sorbent (at the ratio of 25/75, wt.%, at natural moisture), which shows moderate adsorption performance in relation to S.

The studies indicated that the adsorption of Cu ions was more efficient when the peat content in the sorbent exceeded 20 wt.% (at natural moisture). The addition of water treatment sludge significantly enhances the adsorption of Zn and S. It was not possible to evaluate the effect of the quantitative content of the water treatment sludge on adsorption performance, as only one content of this man-made component was tested (80 wt.% at natural moisture). An increase in the weight percentage of diatomite in the composite sorbent negatively affects the adsorption of Zn and S.

The best performance was achieved by the peat/water treatment sludge sorbent (at a ratio of 20/80 wt.% at natural moisture) and the peat/diatomite/water treatment sludge sorbent (at a ratio of 5/15/80 wt.% at natural moisture), both of which

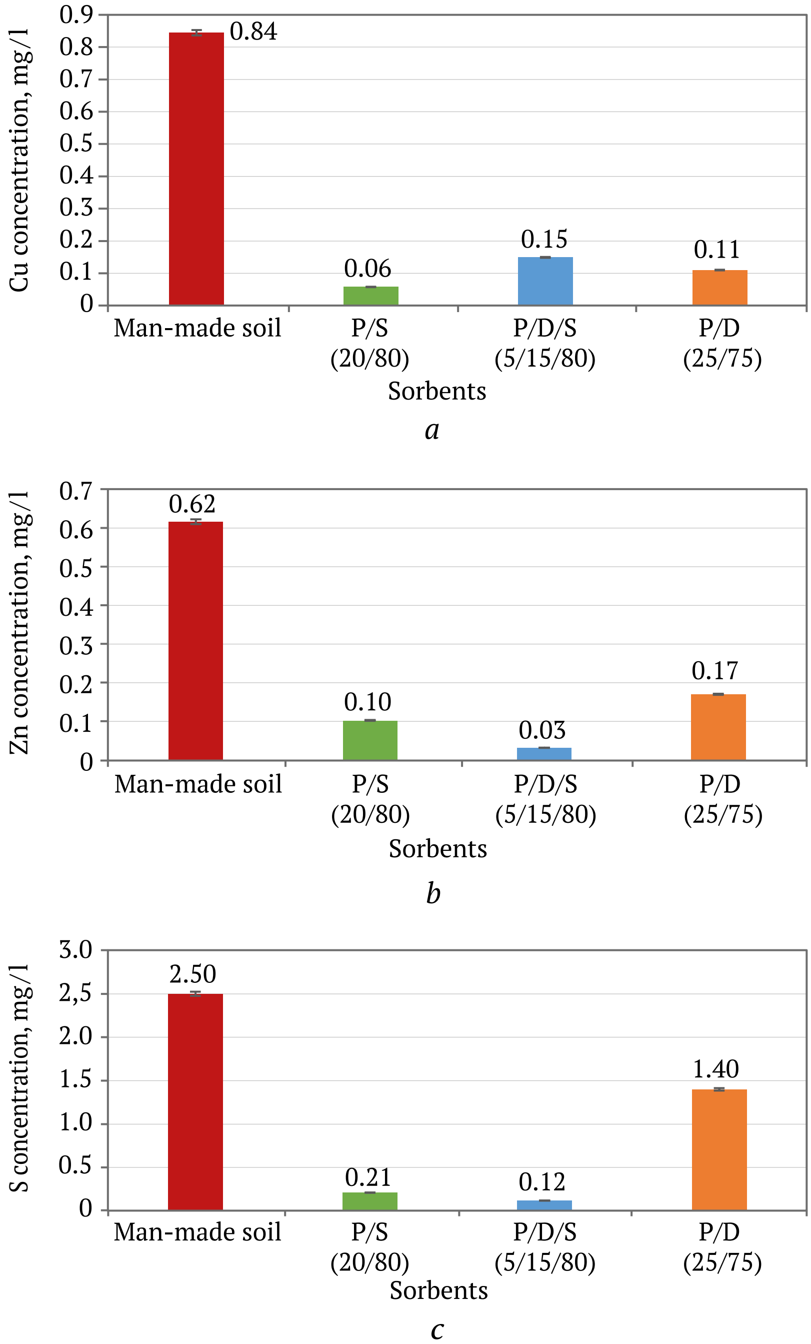

Fig. 3. Degree of Cu, Zn, S ions extraction by sorbents: peat/water treatment sludge (at the ratio of 20/80 wt.% at natural moisture), peat/diatomite/water treatment sludge (at the ratio of 5/15/80 wt.% at natural moisture) and peat/diatomite (at the ratio of 25/75 wt.% at natural moisture):
(*a*) degree of Cu ions extraction; (*b*) degree of Zn ions extraction; (*c*) degree of S ions extraction

exhibited an overall performance exceeding 89%. The peat/diatomite sorbent (at a ratio of 25/75 wt.% at natural moisture) demonstrated an overall performance of 67.7%.

Consequently, the results obtained after applying the authors' sorbents are presented in Tables 6–8.

After the application of the author's sorbents, the *ED* indicator decreased even further. The P/S (20/80) sorbent exhibited the highest performance in reducing the risks of environmental damage. Similarly, concerning the average value of the HMMs Potential Environmental Risk Index (*ER*), the P/S (20/80) sorbent proved to be the most effective. However, in terms of ER for selective sorption of zinc and sulfur, the P/D/S (5/15/80) sorbent demonstrated the highest performance. The P/D (25/75) sorbent showed the least favorable results. The calculated data obtained support the hypothesis regarding the possibility and, moreover, the effectiveness of "green utilization" of man-made wastes for the reclamation of disturbed lands. This is evident as all sorbents, whether they included water treatment sludge selectively or comprehensively, exhibited maximum sorption performance (Table 9).

Table 6

Assessment of potential environmental risks from HMMs (ER) and risks of environmental damage (ED) based on the content of HMMs in man-made soil after applying P/S (20/80) sorbent

HMM	Concentration after applying P/S (20/80) sorbent, mg/l	Hazard Factor	Background, mg/l	MPC (mobile form, acidic soils), mg/kg	Concentration after applying P/S (20/80) sorbent, mg/kg	*ER*	*EH*
Cu	0.06000	5.00000	0.00500	3.00000	0.12000	60.00000	0.04000
Zn	0.10000	5.00000	0.00970	23.00000	0.20000	51.54639	0.00870
S	0.21000	15.00000	0.08900	160.00000	0.42000	35.39326	0.00263
Arithmetic Mean of HMMs Risk Level						48.97988	0.01711

Table 7

Assessment of potential environmental risks from HMMs (ER) and risks of environmental damage (ED) based on the content of HMMs in man-made soil after applying P/D/S (5/15/80) sorbent

HMM	Concentration after applying P/D/S (5/15/80) sorbent, mg/l	Hazard Factor	Background, mg/l	MPC (mobile form, acidic soils), mg/kg	Concentration after applying P/D/S (5/15/80) sorbent, mg/kg	*ER*	*EH*
Cu	0.15000	5.00000	0.00500	3.00000	0.30000	150.00000	0.10000
Zn	0.03000	5.00000	0.00970	23.00000	0.06000	15.46392	0.00261
S	0.12000	15.00000	0.08900	160.00000	0.24000	20.22472	0.00150
Arithmetic Mean of HMMs Risk Level						61.89621	0.03470

Table 8

Assessment of potential environmental risks from HMMs (ER) and risks of environmental damage (ED) based on the content of HMMs in man-made soil after applying P/D (25/75) sorbent

HMM	Concentration after applying P/D (25/75) sorbent, mg/l	Hazard Factor	Background, mg/l	MPC (mobile form, acidic soils), mg/kg	Concentration after applying P/D (25/75) sorbent, mg/kg	*ER*	*EH*
Cu	0.11000	5.00000	0.00500	3.00000	0.22000	110.00000	0.07333
Zn	0.17000	5.00000	0.00970	23.00000	0.34000	87.62887	0.01478
S	1.40000	15.00000	0.08900	160.00000	2.80000	235.95506	0.01750
Arithmetic Mean of HMMs Risk Level						144.52797	0.03521

Table 9

Assessment of changes in the established risk levels after applying the author's sorbents

HMM Risk	Average for HMMs in man-made soil	Mean for HMMs after applying P/S (20/80) sorbent		HMMs average after applying P/D/S (5/15/80) sorbent		Mean for HMMs after applying P/D (25/75) sorbent		Mean changes after applying sorbents with Water Treatment Sludge (S), %
		Actual Performance	Changes as compared to mean value for HMMs in man-made soil, %	Actual Performance	Changes as compared to mean value for HMMs in man-made soil, %	Actual Performance	Changes as compared to mean value for HMMs in man-made soil, %	
ER	527.76968	48.97988	90.72	61.89621	88.27	144.52797	72.62	89.50
EH	0.21590	0.01711	92.08	0.03470	83.93	0.03521	83.69	88.00

Conclusions

The study successfully achieved its objective, which was to test the existing conventional methods for assessing environmental damage and to evaluate the effectiveness and "environmental friendliness" of the developed author's composite sorbents. This evaluation was done by assessing and comparing the levels of potential environmental risks and risks of environmental damage after the application of these sorbents. The results showed a significant reduction in estimated risks of *ER* and *ED* by an average of 89.5% and 88%, respectively, after applying the proprietary composite sorbents, which include water treatment sludge. This confirms the research hypothesis that "green utilization" of man-made waste as a raw material for composite sorbents used in land reclamation can be achieved without increasing the risks of environmental damage.

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