

## Article

# Testing of Natural Sorbents for the Assessment of Heavy Metal Ions' Adsorption

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**Abstract:** Nowadays, the sorption-oriented approach is on the agenda in the remediation practices of lands contaminated with heavy metals. The current growing quantity of research accounts for different sorbents. However, there is still a lack of studies utilizing the economic criteria. Therefore, to ensure a wide application of opportunities, one of the necessary requirements is their economic efficiency in use. By utilizing these criteria, this manuscript researches the generally accepted natural sorbents for the assessment of heavy metal ions' adsorption, such as peat, diatomite, vermiculite and their mixtures in different proportions and physical shapes. The methodological base of the study consists of the volumetric (titrimetric) method, X-ray fluorescence spectrometry and atomic absorption spectrometry. Experimental tests show a certain decline in the efficiency of heavy metal ions' adsorption from aqueous salt solutes as follows: granular peat–diatomite > large-fraction vermiculite > medium-fraction vermiculite > non-granular peat–diatomite > diatomite.

**Keywords:** natural sorbents; ameliorants; disturbed lands; heavy metals; adsorption; recultivation; environmental remediation; revitalization; renaturation; restoration; rehabilitation; reclamation



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## 1. Introduction

Modern intensive industrial production is accompanied by the formation of various man-made wastes. These wastes need to be neutralized and disposed. Wastes containing compounds of toxic chemical elements—heavy metals—are particularly dangerous. Heavy metals are pollutants which can be accumulated in the environment for a long time. Heavy metals are stable to biological and chemical degradation [1–5].

Nowadays, high research interest in the detection and sorption of heavy metal ions has been observed, including the development of novel sensors [6,7] because at relatively low concentrations, heavy metals are dangerous for soil, plants, living organisms and human health [8,9]. That is why technologies aimed at limiting the mobility of heavy metals are increasingly used [10]. Special functional substances—natural and synthetic sorbents—reduce the mobility of toxic elements by immobilizing heavy metal ions. Sorbents fix the mobile forms of heavy metals and significantly reduce their invasion into the biomass of plants, animals, fish and the human body.

Currently, the sorption-oriented approach is widely used. It acts as a tool for restoring disturbed land after any anthropogenic activity. This is due to the fact that natural soil remediation from heavy metals is very slow. For instance, the half-lives of lead, copper and cadmium are equal to 740–5900, 310–1500 and 13–110 years, respectively [11].

However, some of the traditional methods for the deactivation of heavy metals are extremely expensive. In this regard, they are used to isolate certain small contaminated

areas [12]. Therefore, researchers from different countries are currently studying the effectiveness of different sorbents. The core aim is the decontamination of heavy metals in mining and other industries. Natural sorbents are interesting due to their low cost, efficiency and availability of large reserves. They have the functional ability to act not only as sorbents, but also as ameliorants [13–15].

Organic raw materials of plant origin, such as peat, coal, sapropels, diatomite, vermiculite, industrial wood residue and agricultural waste present the greatest practical interest for the development of sorbent-ameliorants. The issue of bioremediation, using microorganisms in situ to decompose pollutants, is also relevant. In recent years, this technology has attracted significant attention from scientists and biotechnologists focused on practical research [16,17].

As a natural sorbent, diatomite modified with polyhydroxyl-aluminum was researched, particularly its increasing adsorption capacity to  $Pb^{2+}$  and  $Cd^{2+}$ . The results showed that diatomite modified with polyhydroxyl-aluminum significantly improved the adsorption of  $Pb^{2+}$  and  $Cd^{2+}$  by 23.79% and 27.36%, respectively [18].

There was research about peat's (from the Vale do Ribeira in Brazil) adsorption capacity of lead (Pb) and cadmium (Cd). The obtained results demonstrated that peat could improve the characteristics of soil contaminated with heavy metals. The researchers concluded that soil–peat mixtures were capable of minimizing the potentially toxic metal contamination. In addition, these are affordable and cheap materials [19].

Numerous studies confirm that adsorbents such as clay, coal, peat moss, zeolite and chitosan are affordable and effective for the remediation of land contaminated with heavy metals. However, despite the significant adsorption characteristics and low cost, there is a lack of a comprehensive studies of the sorption abilities of natural adsorbents [20,21], except for a few studies conducted a long time ago [22–25]. This article is an attempt to compare the sorption abilities of common natural substances, including peat, diatomite, vermiculite and their mixtures, in different proportions and physical shapes.

## 2. Materials and Methods

### 2.1. Materials

The cost of sorbents is one of the necessary requirements for sorbents to ensure the possibility of wide application. In this regard, it is rational to use primarily inexpensive materials as sorbents [26]. Based on these economic criteria, this paper researches the generally accepted natural sorbents for the assessment of heavy metal ions' adsorption, such as peat, diatomite, vermiculite and their mixtures in different proportions and physical shapes.

The following materials have been employed in the study (Table 1).

**Table 1.** Characteristics of the natural sorbents discussed in the study.

Sorbent Name	Ratio (%)	pH	Moisture (%)	Ash Content (%)	Apparent Density (kg/m <sup>3</sup> )	Specific Surface Area of Grains (m <sup>2</sup> /kg)	Temperature (K)
1. Granular peat-diatomite	50%	6.5–7.5	15	Less than 5	215	1.94	295
2. Non-granular peat-diatomite	50%	6.5–7.5	25	Less than 5	272	0.05	295
3. Diatomite	100%	8.5–9.5	2	Less than 1	465	0.15	295
4. Large-fraction vermiculite	100%	5.5–6.0	8	Less than 1	134	3.24	295
5. Medium-fraction vermiculite	100%	5.5–6.0	8	Less than 1	145	2.17	295

The first material was neutralized high-moor fractionated peat (fraction 0–10), with a peat moisture content from 50% to 60%, pH in the range of 5.5–6.0 and ash content of less than 5%. The main inorganic peat compounds were nitrogen (up to 1.5%), phosphorus, potassium and calcium (in total) up to 0.6%. The content of humic substances was 7.4–7.9%.

Peat was mixed with diatomite in the mass ratio of 2/1. Diatomite is a soft, lightweight, thin-pored massive material consisting of the mass of the smallest (0.01–0.04 mm) opal shells of bacillariophytes. Their density is usually nearly 0.5–0.7 g/cm<sup>3</sup>, and its porosity reaches 70–75% [27].

The apparent density of the peat and diatomite mixture was  $272 \text{ kg/m}^3$ . Parts of this mixture were formed in granules in the screw pelletizer with further drying in the drum-type drier at a temperature of  $80 \text{ }^\circ\text{C}$ . The heat treatment of the pellets was completed when the humidity reached 25%. The apparent density of the absorbent grains was  $242 \text{ kg/m}^3$ , taking into account that the specific surface area of the grains was  $1.94 \text{ m}^2/\text{kg}$ .

The second material was medium-fraction vermiculite (fraction 1–4 mm) with an apparent density of  $145 \text{ kg/m}^3$ , as well as large-fraction vermiculite (fraction 5–10 mm) with an apparent density of  $134 \text{ kg/m}^3$  and a specific surface area of  $3.24 \text{ m}^2/\text{kg}$ .

Vermiculite is a mineral from the hydromicas group which turns into a flowing laminal material during heat treatment [28]. Vermiculite improves the soil structure, absorbs the excess moisture, loosens the soil and increases the soil breathability.

The third material was model toxicants, which are the individual solutions of salts of heavy metals and arsenic related to them, including  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{NaAsO}_2$ . To prepare the solution, a sample of salt was dissolved in a measuring container. Solutions with lower concentrations were prepared from the resulting initial solution by dilution. As a result, solutions of salts with the following titers (content) of heavy metals were procured:  $T(\text{Cr}^{+3}) = 1.0 \text{ mg/L}$ ,  $T(\text{Cr}^{+6}) = 0.5 \text{ mg/L}$ ,  $T(\text{Pb}^{+2}) = 1400 \text{ mg/L}$ ,  $T(\text{Cu}^{+2}) = 635 \text{ mg/L}$ ,  $T(\text{Cd}^{2+}) = 10000 \text{ mg/L}$  and  $T(\text{As}^{3+}) = 5.0 \text{ mg/L}$ . The ionic strengths of the prepared solutions were as follows:  $\mu(\text{CuSO}_4) = 0.04 \text{ mol/L}$ ,  $\mu(\text{Pb}(\text{NO}_3)_2) = 0.02 \text{ mol/L}$ ,  $\mu(\text{Cd}(\text{NO}_3)_2) = 0.267 \text{ mol/L}$ ,  $\mu(\text{Cr}_2(\text{SO}_4)_3) = 0.0001 \text{ mol/L}$  and  $\mu(\text{NaAsO}_2) = 0.0001 \text{ mol/L}$ . The calculated value of the ionic strength of the prepared sodium bichromate solution was close to zero. Standard (calibration) salt solutions as measuring instruments were prepared from the initial solutions by dilution. During the tests of the sorption properties of the materials, the mixing of different salts did not occur. Therefore, the formation of any precipitation was not observed during sorption in the heavy metal solutions.

## 2.2. Methods

The sorption properties of the sorbents were studied in static conditions at room temperature ( $T = 295 \text{ K}$ ). The sorbent subsamples were placed in glass flasks. The subsamples were taken with a weighing accuracy of  $\pm 0.01 \text{ g}$ . A fixed volume of a heavy metal salt solute with the initial concentration was added to the flasks at  $\text{pH} = 4.5$ . The solutions' system of a sorbent and heavy metal salt solute obtained from flasks was filtered through a medium-density paper filter after a certain contact time of the components. To determine the concentrations of heavy metal ions in the solutions before and after adsorption, chemical methods and instrumental methods of quantitative analysis, such as the volumetric and titrimetric methods, X-ray fluorescence spectrometry and atomic absorption spectrometry, were used.

## 2.3. Volumetric and Titrimetric Methods of Quantitative Analysis

This method in the variant of complexometric titration was used to determine the quantitative content of  $\text{Cd}^{2+}$  ions with the indicator—eriochrome black T—in an ammonia buffer solution before the transition of the initial red color to blue. Trilon B was used as the standard solution. A blank (control) experiment was performed to determine the correction during titration. The blank experiment consisted of repeating the chemical analysis procedure under similar conditions, but with the previous addition of distilled water to the analyzed sorbent instead of the heavy metal salt solute. A relative determination error of the quantitative content of heavy metal ions by this titrimetric method was 0.3%.

## 2.4. X-ray Fluorescence Spectrometry

The X-ray spectrometry method was used to determine the quantitative content of  $\text{Pb}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  ions. The analysis was performed by using an X-ray fluorescence crystal diffraction scanning spectrometer called a SPECTROSCAN MAX G. Standard solutions of the corresponding salts were used as calibration samples during the analysis. Standard solutions were prepared according to the exact subsamples of the starting sub-

stance ( $\pm 0.0001$  g). The error of the X-ray fluorescence analysis, according to the passport of the device, varied in the range of 0.2–3%.

### 2.5. Atomic Absorption Spectrometry

This method of analysis was used to determine the quantitative content of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions. The analysis was performed by using a Spectr AA-240 FS spectrometer (Varian Optical Spectroscopy Instruments, Varian Inc., Australia; it has been sourced from Hooegeveen, The Netherlands). Standard samples with a known content of heavy metal ions were used as calibration samples.

The method of atomic absorption spectrometry was characterized by the relative determination error of at least  $\pm 2\%$ .

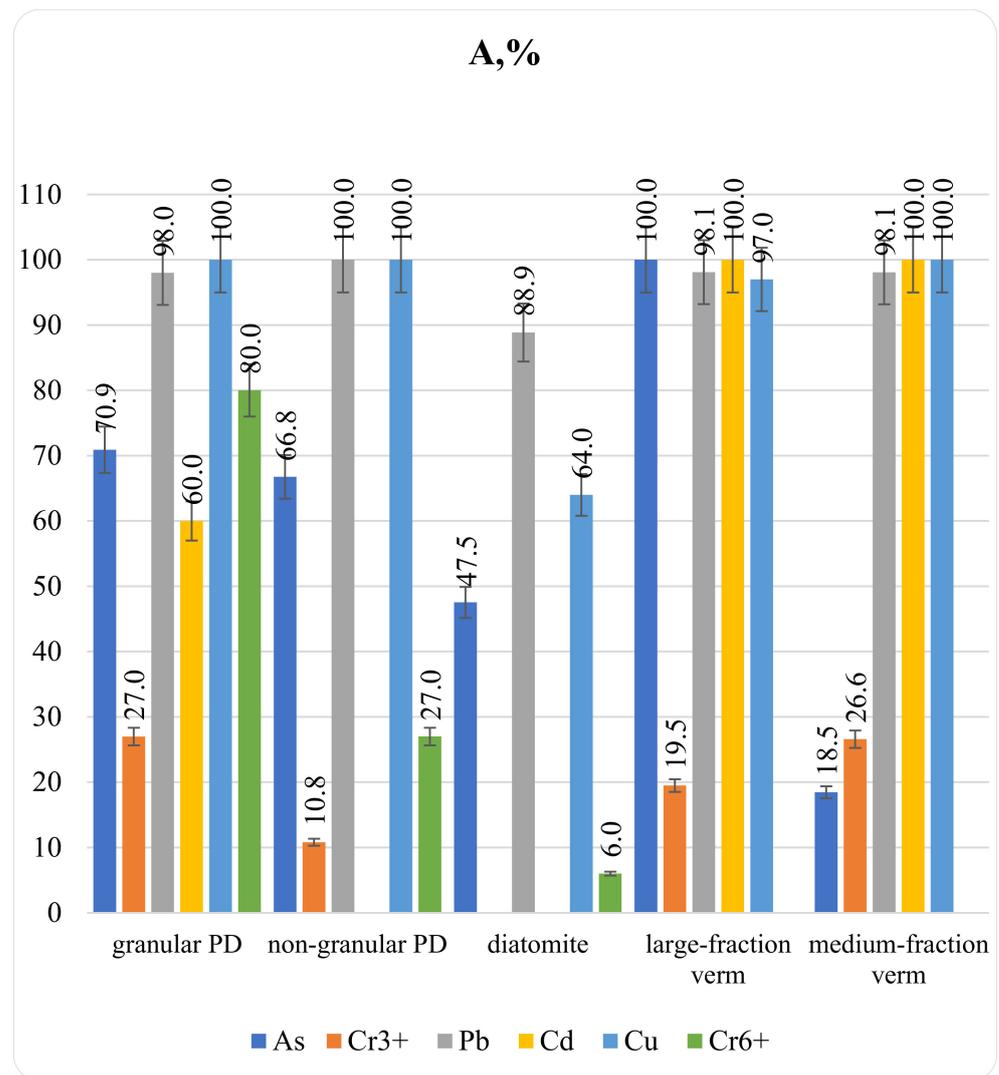
## 3. The Results of the Experimental Studies and Discussion

The results of testing the efficiency of the sorbents in relation to the heavy metal ions' adsorption are shown in Figure 1. The information in Figure 1 allowed for the evaluation of the efficiency of the studied sorbents in relation to the heavy metal ions' adsorption, which was shown during 70 h of the experiment. The maximum and close to the maximum possible heavy metal ion extraction from the solutions by sorbents of peat-diatomite and vermiculite of various fractions (medium and large) were noted. The granular sorbent peat-diatomite showed the greatest efficiency with respect to the ion binding of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ . In this case, the degree and quantity of extraction of these ions from aqueous solutes of salts were 100.0 and 98.0%. The granular sorbent peat-diatomite was less effective in relation to  $\text{Cr}^{6+}$  ions (in the composition of  $\text{Cr}_2\text{O}_7^{2-}$  ions),  $\text{As}^{3+}$  ions ( $\text{AsO}_2^-$ ) and  $\text{Cd}^{2+}$  ions. The degree of extraction of the listed ions by this sorbent was in a range from 60% to 80%. A fairly lower sorption efficiency of the granular sorbent peat-diatomite occurred with respect to the  $\text{Cr}^{3+}$  ions.

The non-granular sorbent peat-diatomite demonstrated nearly the same sorption efficiency as the granular sorbent peat-diatomite for the  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{As}^{3+}$  ions. This sorbent exhibited approximately half the capacity in relation to the chromium ions in a oxidation state +3, +6. For this sorbent, an anomalous decrease in the sorption capacity was observed in relation to the cadmium ions. The decrease occurred to a value which was comparable to the determination error of the quantitative content of the metal ions in the solution.

The high efficiency of adsorption in relation to the heavy metal ions in the experiments were noted for large- and medium-fraction vermiculite. Regardless of the fractional composition, vermiculite almost completely bound the ions of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ . At the same time, there was a five-fold difference in the sorption of  $\text{As}^{3+}$  ions. Large-fraction vermiculite sorbed almost all of the arsenic in the solution (medium-fraction vermiculite = only 18.5%). The probable reason for this discrepancy may be the use in the study of vermiculite from different manufacturers. They use various technological processing for natural source raw materials. Meanwhile, vermiculite of both fractions practically did not show the sorption properties in relation to the  $\text{Cr}^{6+}$  ions. The relevant experimental value of the adsorption was close to the value of the determination error.

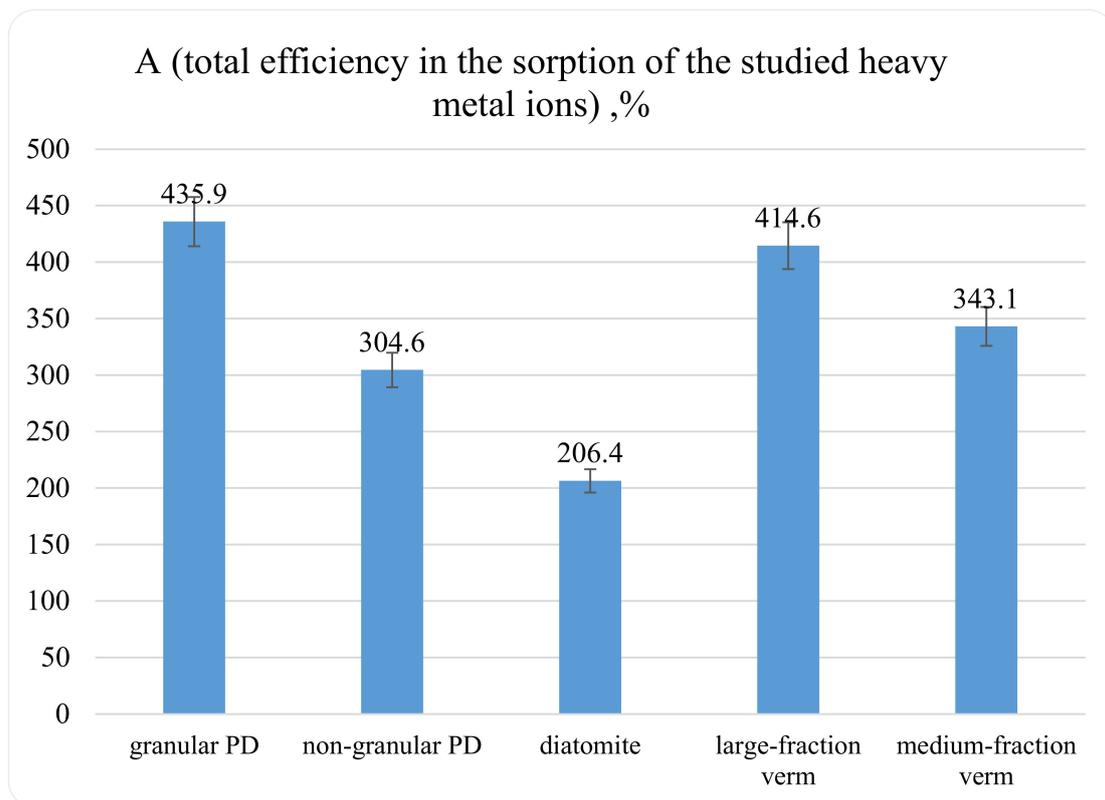
A relatively lower efficiency in the binding of heavy metal ions in the research was identified for diatomite. This material, when used as a sorbent, adsorbed 88.9% of  $\text{Tb}^{2+}$  ions and 64.0% of  $\text{Cu}^{2+}$  ions from the solution. These were the best results for this sorbent. Diatomite virtually did not bind cadmium. However, diatomite was 2.5 times higher than the medium-fraction vermiculite in terms of  $\text{As}^{3+}$  ion adsorption.



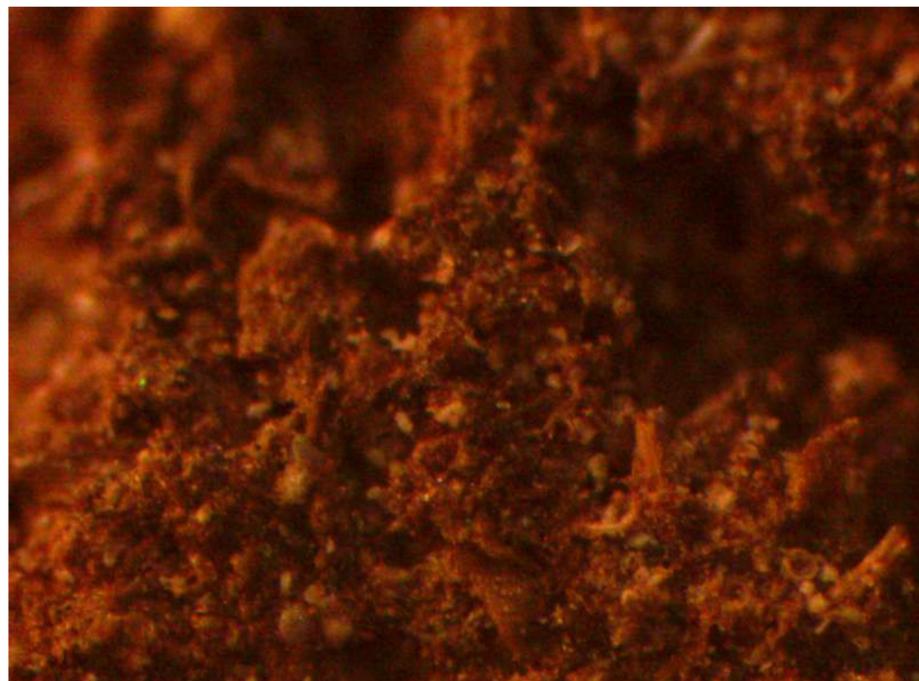
**Figure 1.** Efficiency of the sorbents (A) in relation to the grade of heavy metal ion extraction from the model solutions.

Figure 2 shows a general diagram for the studied sorbents and heavy metal salt solutions. Figure 2 demonstrates the total value of the adsorption of heavy metal ions. The granular sorbent peat–diatomite had the highest total efficiency in the sorption of the studied heavy metal ions. This was established based on the results of the sorbents’ testing. Large-fraction vermiculite was almost as good as the granular sorbent peat–diatomite in terms of the indicator under consideration. The lowest efficiency was shown by the sorbent consisting of diatomite, which did not contain peat additives. Medium-fraction vermiculite and non-granular sorbent peat–diatomite took the intermediate position in terms of sorption efficiency.

The difference in the sorption efficiency of the studied sorbents was linked to their chemical compositions and the structure of the adsorbing surface. To fix the structure of the sorbents, an Altami MET 1 digital microscope and an SNE4500M scanning electron microscope were used. The sorption properties of peat were due to the highly developed surface (Figure 3) and the presence in its composition of various functional groups, such as amine, amide, alcohol, aldehyde, carboxyl, ketone, phenolic, kinone and peptide groups. The adsorptive properties of peat were due to the presence of lignin, humic and fulvic acids [29,30].



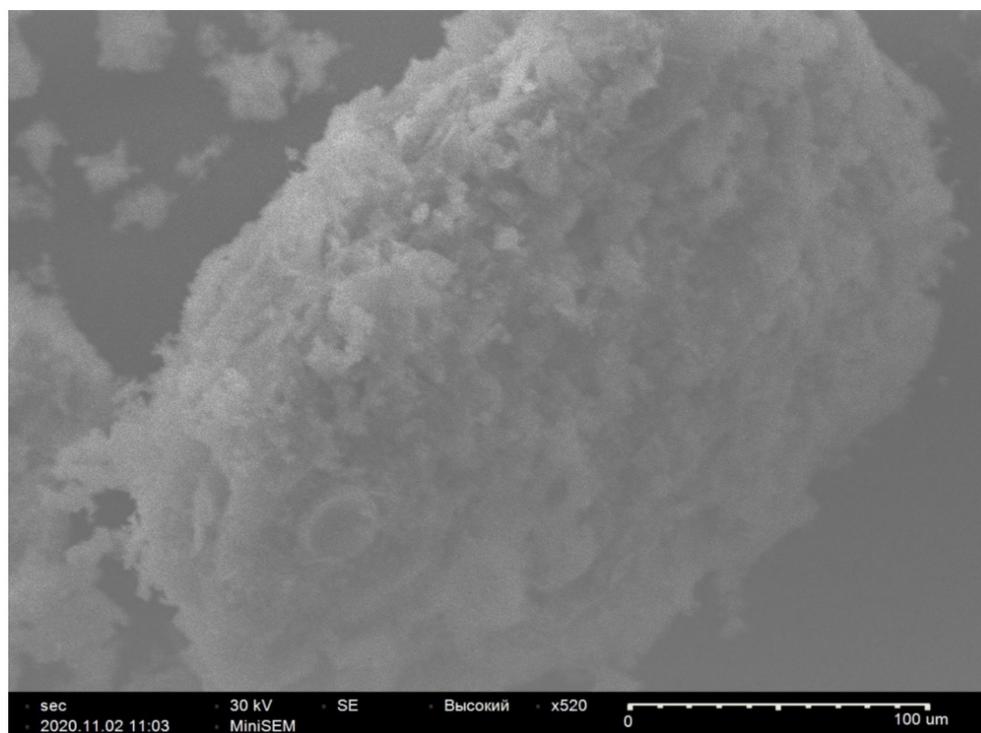
**Figure 2.** The total value of the degree of extraction of heavy metal ions (A) by various sorbents.



**Figure 3.** The surface of the peat–diatomite granular sorbent (Altami MET 1 optical microscope (Altami Ltd, Russia; it has been sourced from St. Petersburg, Russia); magnification  $\times 40$ ).

It should be noted that peat takes up a special place among the effective natural sorbents of heavy metals. Peat-based sorbents are good stabilizers of heavy metal ions. These sorbents have a higher sorption capacity than other single-component sorbents [31].

On the one hand, diatomite does not contain a larger number of different functional groups than peat. On the other hand, diatomite has a high porosity (Figure 4) and corresponding adsorption properties.



**Figure 4.** The surface of diatomite (SNE 4500M microscope).

Vermiculite is a mineral from the hydromica group. During heat treatment, vermiculite swells and multiplies in space, which also increases the area of the adsorbing surface (Figure 5). Exfoliated vermiculite has a variety of applications, including being a sorbent for gaseous and liquid industrial waste.

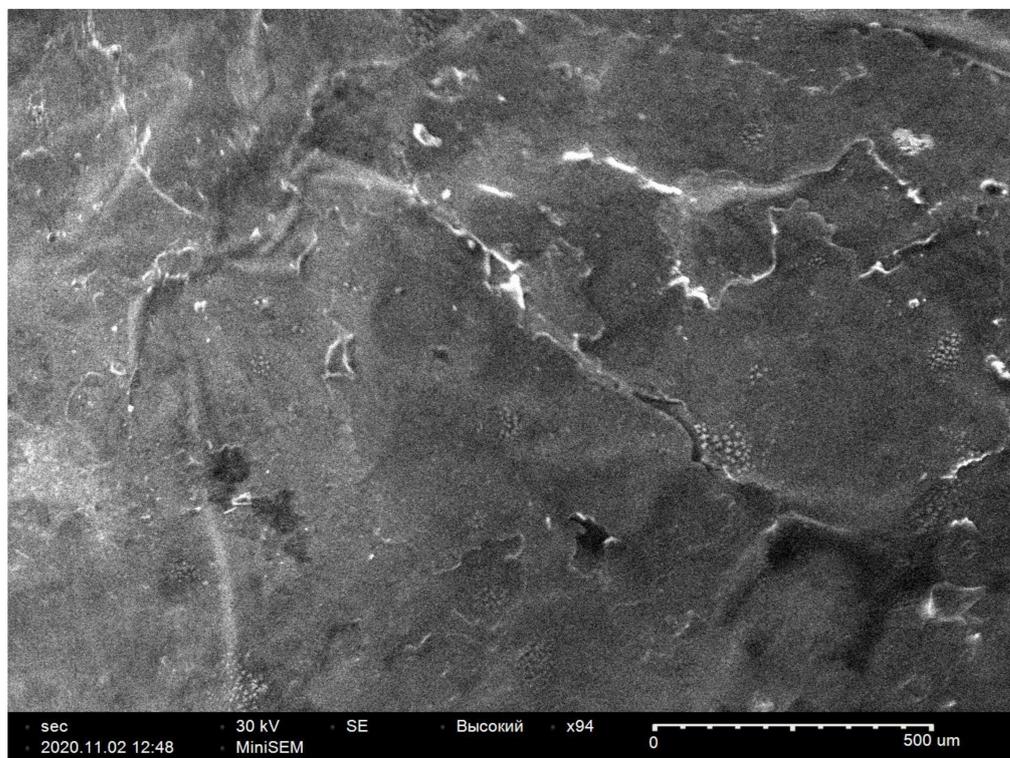
The study of the vermiculite's efficiency of heavy metal adsorption in comparison with other sorbents was also shown in [32], with the exception of peat–diatomite. In this research [32], Koptsik G.N. and Zakharenko A.I. used several types of ameliorants: vermiculite, zeolite, apatite superphosphate and lime. The residual copper content in the soils after the use of vermiculite on average did not exceed 9% of the initial concentration [32]. Their results are comparable to our study.

The use of peat and diatomite separately from each other was researched in [33,34]. In [34], filter modules were used to study the processes of sorption and desorption of emission components by materials of a vermiculite–sungulite composition, obtained through the enrichment of phlogopite mining waste. The study [34] concluded that pure peat had the greatest sorption capacity.

The study in [33] used diatomite rocks. The equilibrium state for the removal of heavy metals by diatomite clay was obtained by adding a constant mass of the absorbent (0.5, 1.0 and 2.0 g) to 100 mL of the initial concentrations of the prepared aqueous solution of heavy metals. The exposure time was 4 h. After that, the samples were filtered by using filter paper. The concentrations of various heavy metal ions were measured by using the ICP-MS method. It was concluded that the use of Egyptian diatomite demonstrated a significant efficiency of heavy metal adsorption [33,34].

The results of this study show a significant increase in the adsorption efficiency when two sorbents (peat–granular diatomite) are mixed in equal proportions (Figure 2). It is remarkable that the granular physical shape increases the heavy metal adsorption. Testing other proportions of different natural sorbents with various recipes of preparation, includ-

ing different physical shapes, is the direction of future studies. Due to the research results, a patent has been obtained: "Peat ameliorant for the remediation of lands contaminated with heavy metals" RU 2 745 456, dated 9 March 2020.



**Figure 5.** The surface of vermiculite (SNE 4500M microscope).

#### 4. Conclusions

The testing results demonstrate a certain sequence in terms of the gradual decline of the efficiency of heavy metal ion adsorption from aqueous salt solutes (peat–granular diatomite > large-fraction vermiculite > medium-fraction vermiculite > peat–non-granular diatomite > diatomite).

The high efficiency of peat-containing sorbents in relation to the adsorption of heavy metals and the widespread use of peat as a soil ameliorant can serve as the basis for the promising use of peat in the development of compositions of affordable complex ameliorants, stabilizers of heavy metals for the remediation of disturbed lands.

**Author Contributions:** Conceptualization, data curation and project administration have been done by V.Y. All authors—V.Y., R.A., A.U., M.L., A.M. and A.D.—took part in the investigation. While supervision was conducted by R.A. and V.Y., the validation was made by M.L., A.U. and A.M. The original draft was written by R.A., A.U. and M.L. Review and editing were done by V.Y. and A.D. All authors have read and agreed to the published version of the manuscript.

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