Study of the natural mineral sorbents' absorption properties of the Ural region (Russia)

Yu Baikin*, N Vashukevich, A Serebrennikova, A Gusev and A Belichev
Ural State Agrarian University, 42, Liebknecht str., Ekaterinburg, 620075, Russia

E-mail: ubaikin@rambler.ru

Abstract. The article is devoted to the study of the sorption properties of natural mineral sorbents from deposits located in the Ural (Sverdlovsk, Kurgan, Chelyabinsk regions). For the experiments, the following natural sorbents were used: bentonite clays with an admixture of carbonate inclusion; flasks - dense, slightly porous rocks consisting of the smallest particles of biogenic silica; diatomite; glauconites- layered low-temperature ferruginous micas; calcined vermiculite. The absorption capacity in relation to heavy metals: copper, zinc, lead, cadmium, nickel, chromium, arsenic has been investigated. The are no significant differences in the completeness of sorption between the studied sorbents, all of them can be successfully used under certain conditions for ecological and geochemical recultivation of soils contaminated with HMs. Separately, the influence of sorbents on the copper and chromium absorption as the largest soil pollutants in the Urals was considered. Experiments have shown that copper in the form of a bivalent cation is well sorbed by all sorbents, while chromium in the form of a complex anion (in a hexavalent form) is practically not sorbed. To ensure a proper chromium sorption effect, it was decided to preliminary transfer it into a trivalent cationic form by a reducing agent, which was ferrous ammonium sulfate - FeSO₄·(NH₄)₂·SO₄·6H₂O. The reduction of chromium to a trivalent cation increases the sorption completeness to 94-99%.

1. Introduction
Soil contamination with toxic heavy metals is a worldwide problem. Industrial and mining activities are among the most important anthropogenic sources of heavy metals; the excessive accumulation of heavy metals (HMs) in soils often threatens human health, food safety and soil eco-services [1,2]

One of the detoxification ways of soils contaminated with heavy metals is the introduction of natural sorbents into them, which ensure the sorption of the most toxic mobile forms of HMs and, thereby, significantly reduce their entry into vegetation [3,4,5]

The Ural region is the largest industrial center of the Russian Federation and is an ecologically unfavorable region, as well as due to technogenic pollution of soils with heavy metals. Monitoring of the soil cover of agricultural lands shows that in some areas adjacent to large industrial enterprises, the concentrations of certain toxic heavy metals exceed the established sanitary and hygienic standards. The largest cases' number of exceeding the maximum permissible concentration (MPC) was noted for such elements as: lead, arsenic, cadmium, copper. Almost all of these elements are classified as substances of the 1st hazard class, except for copper, which belongs to the 2nd hazard class [6].

The Sverdlovsk region and the adjacent territories have significant reserves of natural sorbents and other nonmetallic minerals used in reclamation, amelioration, detoxification of soils (limestone, dolomite). Diatomites, bergmeal, flasks, bentonites, glauconites, zeolite-containing deposits and...
zeolites, vermiculites, etc. are widespread here. Many dozens of deposits and occurrences of this raw material are known, but not all of them are in the exploitation stage [7].

With the practical use of natural sorbents for the reclamation of soils contaminated with HMs, two ways are possible: 1) the use of natural non-activated sorbents; 2) preliminary activation (modification) of sorbents with various salts, acids, alkalis, or their combinations.

The similarity of many physicochemical features and adsorption properties of various natural sorbents determines the similarity of the ways of their use and interchangeability. For this, a comparative analysis of physical and chemical properties is carried out and the adequacy degree of natural sorbents to various technological processes is determined.

This work examines the sorption properties of natural non-activated sorbents from individual deposits of the Ural region in relation to heavy metals.

2. Materials and Methods

For the experiments, the following natural sorbents were used, the deposits of which are located in the Sverdlovsk, Kurgan and Chelyabinsk regions.

1. Bentonite clays with an admixture of carbonate inclusions. Represented by greenish-gray, yellow-gray, light gray lumpy clays, consist mainly of alkaline earth (Ca-Mg) montmorillonite; in terms of chemical composition, they are characterized by an increased content of aluminum oxide (up to 20%), iron oxide (4.5% or more) and often silicon oxide (60-70%). They have good sorption capacity. The sum of their exchangeable cations is 64.4 mg/g. Zyryanovskoe deposit of alkaline earth bentonites, Kurgan region [8].

2. Flasks are dense, slightly porous rocks consisting of the smallest particles of silica of primary biogenic nature. The clay component of the rocks is usually represented by montmorillonite, beidellite, hydromica and kaolinite. Krasnogvardeysko-Kilachevskoe deposit, Artyomovsky district of Sverdlovsk region [9].

3. Diatomites, soft light fine porous rocks composed of opal shells (or their remains) of diatoms. Generally, diatomite consists of silicon dioxide with signs of its partial crystallization into cristobalite and α-quartz with a small presence of cristobalite and it is characterized by a high degree of homogeneity of chemical and mineralogical composition. Zaikovskoe (Irbitskoe) and Kamyshlovskoe deposits, Sverdlovsk region [10-11].

4. Glauconites. They consist of layered low-temperature ferruginous micas, have different shades of green color, formed mainly in the marine environment, occur in the form of microconcretionary aggregates (from 0.01 to 0.6 mm) with a composition from glauconite to glauconite-montmorillonite. Mugai site, 40 km north of the city of Alapaevsk, Sverdlovsk region [12].

5. Calcined vermiculite, iron-magnesium aqueous aluminosilicate is a secondary mineral formed from biotite. A remarkable feature of vermiculite is its high cation exchange capacity. Potaninskoye deposit located near Kasli town in Chelyabinsk region [13].

Limestone and dolomite from quarries in Pervouralsky district of Sverdlovsk region were also used. Loose carbonate rocks do not belong to natural sorbents but are widely used for soil reclamation (liming), reducing their acidity, reducing the mobility of aluminum, manganese and HM, improving the phosphate and nitrogen regime of soils, their physical properties, and microflora activity.

Analytical determinations were carried out according to the methods certified in Russia. Determination of heavy metal ions' concentrations in solutions before and after adsorption was carried out using atomic absorption spectrometry in the licensed laboratory "Ural Central Laboratory".

Laboratory experiment methodology

1. The study of the absorption capacity of natural mineral sorbents in relation to the following heavy metals has been carried out: copper, zinc, lead, cadmium, nickel, chromium, arsenic.

Experiment's algorithm. A standard solution was prepared containing: copper and zinc by 10 mg/l, nickel - 1 mg/l, chromium - 0.54 mg/l, arsenic - 0.5 mg/l, lead - 0.3 mg/l, cadmium - 0.01 mg/l. The ratio of the elements' concentrations in the solution approximately corresponded to their natural and technogenic distribution in the contaminated soils of the Ural region. 500 ml of a standard solution was
Placed in 1 l flasks, added with 2 g of crushed limestone (to bring the solution pH to 6) and by 50 g of the studied sorbents, previously crushed to a particle size of 0.06 mm or less. Solutions with sorbents were mixed on a rotator for 30–40 min, then filtered through a double dense filter. The residual amounts of the above elements were determined in the filtrate.

2. Further, given that the main contamination of soils in the Ural region is associated with copper and chromium, subsequent experiments concerned these two elements. The previously described scheme was used to study the absorption of chromium (VI) by natural sorbents in the presence of copper (II). The concentration of chromium in the form of potassium dichromate in the solution was 10 mg/l, copper in the form of chloride - 50 mg/l. The experiment was carried out under different conditions: a) at pH of 5-6 (to reduce the acidity of the solution, 1 g of limestone was added) and a sorption time of 30-40 minutes; b) at pH 7 (10 g of limestone was added) and a sorption time of 90 min.

3. The experiment on the reduction of chromium (VI) to chromium (III) in solution was carried out using ferrous ammonium sulfate - FeSO₄(NH₄)₂SO₄6H₂O. About 0.1 g of ferrous ammonium sulfate was added to 500 ml of the same standard solution (until the color of the solution changed from yellow-orange, due to CrO₄²⁻ and Cr₂O₇²⁻ ions, to green, due to Cr³⁺ ions). The solution pH was adjusted to 7. Further, as in item 1.

4. To study the bond strength of absorbed HMs with sorbents, experiments were carried out on desorption of HMs from sorbents by exposing them to distilled water and a 0.01n HCl solution. In both cases, 25 g of sorbents were taken and mixed with 1 l of the extractant in a 2 l flask for 30 min. The suspension was filtered through a double dense filter. In the filtrate, the concentrations of the extracted elements were determined.

5. The absorption capacity of sorbents in relation to heavy metals (for example, copper) was determined during the following experiment. Standard solutions were prepared with a copper concentration of 50 and 200 mg/l having pH of 5.0 and 6.3-6.9. 500 ml of solutions was added with a certain sample of sorbent (20-50 g) and stirred on a rotator for one hour (on average). Then the suspension was filtered off and the residual copper concentration was determined in the filtrate. The specified volume of the initial solution was again poured into the filtered sorbent sample. The experiment was repeated until the residual metal concentration in the filtrate reached approximately 50% of the initial one.

3. The Results of the Experimental Studies and Discussion

At the first stage, the study of the absorption capacity of various natural mineral sorbents in relation to the following heavy metals was carried out: copper, zinc, lead, cadmium, nickel, chromium, arsenic. The results of the experiments are presented in table 1.

It follows from the data presented that various element are sorbed by natural sorbents with different completeness. Being a typical representative of HM, copper is sorbed best. Lead, zinc, nickel, arsenic, and partly cadmium show similar results on the sorption completeness. Chromium has a relatively worse sorption (no higher than 73-85%), probably due to its partial presence in the solution in the form of a complex anion of hexavalent chromium.

The lowest sorption capacity among the studied samples under the conditions of the experiment was found in vermiculite, which did not practically sorb cadmium and very poorly sorbed nickel, zinc, and arsenic. In this regard, this sorbent was excluded from further research.

| Natural sorbents | Concentration | Cu  | Zn  | Ni  | As  | Pb  | Cd  | Cr  |
|-----------------|---------------|-----|-----|-----|-----|-----|-----|-----|
| Flask           | source solution, mg/l | 10  | 10  | 1   | 0.5 | 0.3 | 0.01| 0.34|
|                 | filtrate, mg/l   | 99.4| 93  | 61  | 98.2| >98.3| 48  | 85.3|
Considering the specifics of the Pervouralsko-Revinsky industrial hub, near which the soils are most contaminated with copper and chromium [6], further experiments concerned these two elements.

In particular, the problem was solved to determine the sorbents' absorption completeness of copper and chromium (Cr+6) from more concentrated solutions. The results of the experiment are presented in Table 2.

**Table 2. Sorption results of copper and chromium (hexavalent) by natural sorbents (solution pH 5-6).**

| Natural sorbents       | Copper                                      | Chromium (Cr+6) |
|------------------------|---------------------------------------------|-----------------|
|                        | initial solution, mg/l                      | filtrate, mg/l  | sorption completeness, % | initial solution, mg/l | filtrate, mg/l  | sorption completeness, % |
| Diatomite              | 10                                          | 0.06            | <0.05                     | 10                        | >99                      | 99.4                       |
|                        | 10                                          | 0.25            | <0.05                     | 0.5                       | 98.2                     | >95                       |
|                        | 10                                          | 0.009           | <0.005                    | 0.3                       | 98.3                     | >95                       |
|                        | 10                                          | <0.005          | >99                       | 0.01                      | 83                       | 73.5                      |
|                        | 10                                          | 0.09            | >99                       | 0.34                      |                          |                           |
| Bentonite              | 10                                          | <0.05           | >99                       | 10                        | >99                      | 96.1                       |
|                        | 10                                          | 0.39            | >99                       | 10                        | 99.6                     | >95                       |
|                        | 10                                          | 0.002           | >99                       | 0.01                      | 99.6                     | >95                       |
|                        | 10                                          | 0.009           | >99                       | 0.07                      | 99.6                     | >95                       |
|                        | 10                                          | >99.5           | >99                       | 0.07                      | 99.6                     | >95                       |
| Glauconite             | 10                                          | 0.07            | 0.14                      | 0.5                       | <0.005                   | 9.1                       |
|                        | 10                                          | 0.28            | 0.14                      | 0.3                       | 86                       | >98.3                     |
|                        | 10                                          | 0.032           | 0.14                      | 0.4                       | 86                       | >98.3                     |
|                        | 10                                          | <0.005          | 0.14                      | 0.34                      | 86                       | >98.3                     |
| Vermiculite (calcined) | 10                                          | 1               | 0.91                      | 0.5                       | 66                       | >98.3                     |
|                        | 10                                          | 7.7             | 0.91                      | 0.3                       | 66                       | >98.3                     |
|                        | 10                                          | 0.91            | 0.91                      | 0.01                      | 66                       | >98.3                     |
|                        | 10                                          | 0.01            | 0.91                      | 0.34                      | 66                       | >98.3                     |
|                        | 10                                          | >98.3           | >98.3                     | 0                         | 66                       | >98.3                     |

Similar results were obtained by repeating experiments with 10 g of limestone (to create pH = 7) and increasing the sorption time to 90 min.

Experiments have shown that copper in the form of a bivalent cation is well sorbed by all sorbents, while chromium in the form of a complex anion (in a hexavalent form) is practically not sorbed.

To ensure a proper chromium sorption effect, it was decided to preliminary transfer it into a trivalent cationic form by a reducing agent, which was ferrous ammonium sulfate - FeSO₄ · (NH₄)₂ · SO₄ · 6H₂O. The experimental results are shown in Table 3.
Table 3. Sorption completeness of chromium (trivalent) by natural sorbents, %.

| Element   | Initial solution concentration, mg/l | Aliquot part of the solution, ml | Flask | Diatomite | Bentonite | Glauconite |
|-----------|-------------------------------------|----------------------------------|-------|-----------|-----------|------------|
| Chromium  | 10                                  | 50                               | 97    | 96.9      | 94        | 99         |
| Chromium  | 10                                  | 10                               | 97.1  | 96.8      | 94        | 99         |

Considering the results obtained, from which it follows that the reduction of chromium to a trivalent cation increases the sorption completeness to 94-99%, an experiment was set up to assess the sorption completeness of copper and chromium from the same standard solutions by natural sorbents under the following conditions: a) neutralization of a solution of 5 g crushed limestone, sorption time - 30 minutes; b) neutralization of a solution of 10 g of crushed limestone, sorption time - 40-60 minutes.

The results are presented in Table 4.

Table 4. Sorption completeness of copper and chromium (trivalent) by natural sorbents, %.

| Element   | Experimental conditions | Flask | Diatomite | Bentonite | Glauconite |
|-----------|-------------------------|-------|-----------|-----------|------------|
| Copper    | a                       | 64    | 48        | 98.4      | 97.1       |
| Copper    | b                       | >98.8 | >99       | >99       | >99        |
| Chromium  | a                       | >99   | >99       | >99       | >99        |
| Chromium  | b                       | >99   | >99       | >99       | >99        |

a - neutralization of a solution of 5 g of crushed limestone, sorption time - 30 minutes; b - neutralization of a solution of 10 g of crushed limestone, sorption time - 40-60 minutes.

From the data in Table 4 it follows that to ensure the completeness of copper sorption, the solution medium should be close to neutral, which is provided by 7-10 g of limestone and the sorption time should be at least 40-60 minutes.

To study the bonds' strength of copper and chromium with various sorbents, experiments were carried out on desorption of these heavy metals under the following conditions: a) exposure of sorbents containing absorbed copper and chromium (after the last experiment) with distilled water with stirring for 30 min; b) exposure to the same sorbents with a solution of 0.01 N hydrochloric acid (pH ≈ 3-4) for 30 minutes.

In both cases, 25 g of sorbents were taken, mixed in a 2 l flask with 1 l of distilled water (experiment "a") or with 1 l of a weak solution of hydrochloric acid (experiment "b"); those were stirred on a rotator (30 min), filtered through a double filter "blue ribbon", copper and chromium were determined in the filtrate. The results are shown in Table 5.

Table 5. Desorption degree of copper and chromium from natural sorbents, % rel. of the original quantities.

| Element   | Experimental conditions | Flask | Diatomite | Bentonite | Glauconite |
|-----------|-------------------------|-------|-----------|-----------|------------|
| Copper    | a                       | 0.14  | 0.3       | <0.1      | 0.52       |
| Copper    | b                       | 1.11  | 0.52      | 0.82      | 0.14       |
| Chromium  | a                       | <0.5  | <0.5      | <0.5      | <0.5       |
| Chromium  | b                       | <0.5  | <0.5      | <0.5      | <0.5       |

a - distilled water; b - 0.01 n HCl

As can be seen from the data in Table 5, more than 99% of copper and chromium are firmly bound in sorbents and are not leached either with distilled water or with a weak solution of hydrochloric acid.
4. Conclusions

Thus, the conditions have been determined to ensure sufficient sorption completeness of HMs including chromium by various natural sorbents of the Ural region.

It can be assumed that similar conditions should be maintained for other elements that form complex anions in higher valences (tungsten, molybdenum, arsenic, antimony, etc.). Their conversion into a low-valent cationic form by interaction of solutions with various reducing agents is a prerequisite for ensuring a sufficient absorption completeness by natural sorbents.

At the same time, no significant differences were found in the sorption completeness between the studied sorbents and all of them can be successfully used under certain conditions for ecological and geochemical recultivation of soils contaminated with HMs.

The determining factor is likely to be the composition and properties of the contaminated soils. So, for sandy loamy soils, the use of bentonite is likely to give the best results, for heavy clay soils - diatomite, flask, glauconite.

References

[1] Damao X, Rong-Bing F, Jun-Xian W, Yu-Xiang S and Xiao-Pin G 2021 Chemical stabilization remediation for heavy metals in contaminated soils on the latest decade: Available stabilizing materials and associated evaluation methods — A critical review Journal of Cleaner Production 321 128730

[2] Sana K, Muhammad S, Nabeel Khan N, Behzad M, Irshad B and Camille D 2017 A comparison of technologies for remediation of heavy metal contaminated soils Journal of Geochemical Exploration 182 (part B) 247-268

[3] Yurak V, Apakashev R, Dushin A, Usmanov A, Lebzin M and Malyshev A 2021 Testing of Natural Sorbents for the Assessment of Heavy Metal Ions' Adsorption. Appl. Sci. 11, 3723.

[4] Efremova S Y 2012 Detoxication Receptions Chemically polluted soils Izvestiya Penza State pedagogical university named after V. G. Belinsky 29 379–382

[5] Koptskik G N 2014 Modern approaches to remediation of heavy metal polluted soils: A review. Eurasian Soil Sci. 47 707–722

[6] Gusev A S, Baykin Y L, Vashukevich N V and Belichev A A 2020 Zone of technogenic pollution of the Pervouralsk-Revda industrial hub: soil assessment and land use issues Journal of Environmental Management and Tourism 11(5) 1054-1059

[7] Distanov U G and Konyukhova T P 2005 Natural adsorbents of Russia: resources, strategy and usage Exploration and protection of mineral resources 8 28-35

[8] Belousov P E and Krupskaya V V 2019 Bentonite clays of Russia and neighboring countries. Georesources 21(3) 79-90

[9] Ivanov M G, Likhareva O B, Matern A I and Yaroshevskaya H M 2014 Modification of opal-cristobalite - flask of the Krasnogvardeisky deposit of the Sverdlovsk region Bulletin of the Kazan Technological University 17(7) 54-59

[10] Smirnov P V 2016 Results of comprehensive studies of diatomite material composition from Irbit deposit Bulletin of the Tomsk Polytechnic University. Geo Assets Engineering 327(6) 93–104

[11] Smirnov P V and Konstantinov A O 2016 Comparative studies of eocene and paleocene diatomite from Transurals (on the example of Kamyshtov deposit and section Brusyana), Bulletin of the Tomsk Polytechnic University. Geo Assets Engineering 327(11) 96–104

[12] Slobodechikova E E 2016 Stratigraphy and lithology of the Cretaceous-Paleogene Sea sands of Transurals News of the Ural State Mining University 2 (42) 13-18

[13] Akhtyanov R Y 2012 On the industrial classification of vermiculite minerals. Refractories and industrial ceramics 1-2 73-77