INVESTIGATION OF THE ABSORBING PROPERTIES OF MODIFIED SANDY SOIL TO CREATE A GEOCHEMICAL BARRIER FOR STORAGE LANDFILLS MUNICIPAL SOLID WASTE

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Abstract
The study of the absorption capacity of sandy soil modified with clay soil and organic binder (starch) in relation to lead under dynamic sorption conditions was carried out. The behavior of the pH and Eh of the filtrate during the absorption of lead by the soil has been studied. It was revealed that the absorption of lead ions by the soil leads to a change in the pH of the filtrate. The value of the CEC and pH_{ZPC} of the modified soil is investigated. It is shown that the maximum amount of lead absorbed by the soil at the initial concentration of lead in a solution of 1,25 g/l is 1,96 mg/g.

Key words
geochemical barriers, Pb, dynamic sorption, pH, technical soil reclamation

1 Introduction

Technical soil reclamation is a science that develops the theory and methods of artificial improvement of the condition and properties of soils. At the same time, methods of technical reclamation can be used both in engineering and construction activities and to eliminate the ingress of hazardous chemical elements into the geological environment from landfills for storing solid household waste by creating geochemical barriers capable of retaining pollutants. One of the most dangerous pollutants is lead. At the same time, it is known that clay soils and organic substances have the greatest absorption capacity in relation to heavy metals, in particular lead, while sandy soils have practically no absorption capacity. Thus, the creation of a geochemical barrier based on sandy soil modified with clay soil and organic binder (starch) is quite promising.

Therefore, the purpose of this work is to study the absorption capacity of modified sandy soil in relation to lead. To achieve this goal, tasks were solved in the work:
1. Study of the physico-chemical properties of the studied sandy soil, clay soil and organic binder (starch);
2. Experimental study of the absorbing properties of modified sandy soil under dynamic sorption conditions;
3. Determination of the pH and Eh of the filtrate solution as the filtration process proceeds;
4. Processing and interpretation of the obtained results.

2   Methods

2.1 Creation of model soil samples

To study the absorbing properties of the modified sandy soil, a model soil was created based on Lyubertsy sand J_3v_2, kilic clay and organic binder (starch) in a ratio of 10:1:1 (100 g of sand, 10 g of clay, 10 g of starch). This ratio was chosen in order to establish the optimal (relatively fast) filtration time through the model soil, since the filtration time through sandy soil is less than the filtration time through both dusty soil (the particle size of which corresponds to the size of starch particles) and clay soil.

2.2 Preparation of lead nitrate solution

A solution of $Pb(NO_3)_2$ lead nitrate with a concentration of 2 g/l was used for the study. The solution was prepared by adding a sample of lead (II) nitrate $Pb(NO_3)_2$ to the volume of distilled water. In the experiment, a solution with a lead concentration of 1.25 g/l and a normality of 0.01 N was passed through the model soil. Despite the fact that the amount of lead 1.25 g/l is much higher than the maximum permissible concentration (MPC) for soils, this concentration is convenient for use in order to accelerate the filtration experiment and observe more visual results.

2.3 Collecting a filtration column and conducting a filtration experiment

A filtration column was used to study the absorption capacity of the model soil under dynamic conditions (figure 1).
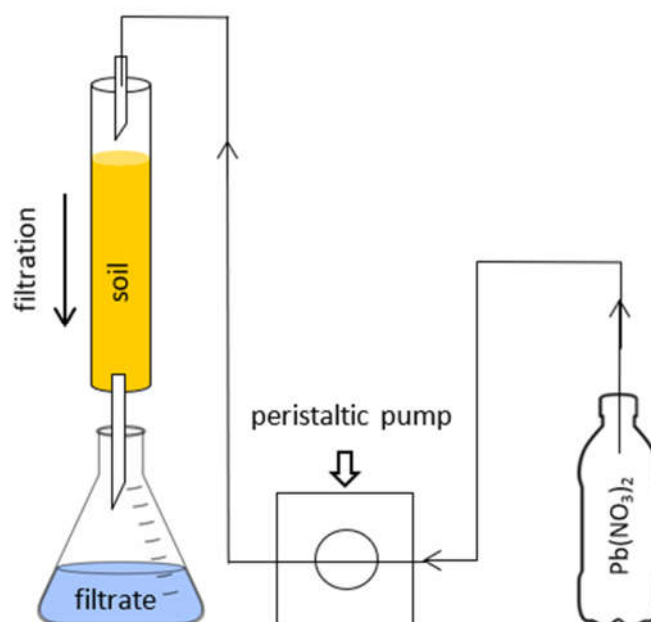

Figure 1. The general scheme of the filtration system.

The base area of column F was 7.07 cm^2, height – 13.5 cm, volume – 95.45 cm^3. A soil suspension was poured into each column to a height of 10 cm (the resulting volume of soil in the column is 70.7 cm^3) without compaction. On both sides, the column was closed with rubber stoppers with syringe nozzles. To prevent the particles from suffusing into the syringe nozzle, the soil was insulated with mesh filters and glass beads. The column with the sample was mounted on a tripod in an upright position. A peristaltic pump was used to filter the lead nitrate solution through the soil. A hose was connected to the

upper syringe nozzle, through which a $Pb(NO_3)_2$ solution was supplied using a pump. A receiving flask was supplied to the lower syringe nozzle, through which the solution filtered through the column (filtrate) was selected. The flow rate of solution Q during the experiment was estimated by measuring the volume of the solution passed through the soil per unit of time and was approximately 0.86 l/day (36 ml/hour), the filtration rate v was 1.22 m/day. The filtrate was selected as a volume of liquid equal to four pore volumes of the model soil accumulated in the flask. Steam volume refers to the maximum total volume of pores that can be filled with a solution. Thus, by selecting a filtrate whose volume is equal to the pore volume of the soil, taking into account numerous simplifications and assumptions, it is possible to accept the fact that the solution has passed through all the pores of the soil. Only sandy soil was used to assess porosity, since it was a large percentage of the total model soil compared to clay and starch. According to V.M. Shestakov, the porosity for sandy soil with a d60/d10 ratio equal to 2.4 (for Lyubertsy sand) is 35%. Therefore, for a soil volume of 70.7 cm^3, the pore volume is approximately 25 cm^3 or 25 ml. At a filtration rate of 1.22 m/day, a volume of 25 ml was selected in 42 minutes. Based on the first sampling attempts every 42 minutes and the subsequent pH values obtained, it was decided to select the filtrate by four pore volumes, that is, 100 ml every 2 hours and 48 minutes. Three parallel filtration experiments were carried out to ensure the accuracy of the obtained values.

2.4 Measurement of the pH and Eh of the solution by the potentiometric method

The determination of pH and Eh solutions was carried out potentiometrically on the pH-150 device in accordance with GOST R 51232-98: reference electrode EVP-1M4, measuring electrode ESL-45-11, the steepness of the electrode function 58.25.

2.5 Determination of the ground zero charge point

The zero charge point of the soil pH_{ZPC} – s the pH value at which the total charge of the surface of the soil particles is zero. By evaluating the difference between the pc and the pH of the solution, it can be concluded which ions (cations or anions) the soil will preferentially absorb. At pH > pH_{ZPC} the soil particles are negatively charged, therefore the soil will be capable of preferential absorption of cations. At pH < pH_{ZPC} the soil particles are positively charged, therefore the soil will preferentially absorb anions. In this work, pH_{ZPC} was determined for modified sandy soil both before and after the filtration process to compare the pH_{ZPC} values before and after lead ion sorption. To determine pH_{ZPC}, the method of acid-base titration of soil against the background of electrolyte solutions of different concentrations was used. HNO_3 acid and KOH alkali were used as titrants, and NaCl solutions with concentrations of 0.5 M, 0.1 M and 0.01 M were used as an electrolyte.

2.6 Determination of the soil cation exchange capacity

The cation exchange capacity (CEC) of a soil is a value that characterizes the ability of the soil to retain a certain amount of cations in an exchange form. Knowing the CEC of the soil, it is possible to estimate the total number of cations that can be displaced into solution from a unit mass of soil by a salt cation of a certain composition under standard conditions. In the work, the cation exchange capacity of the soil was determined for model soil (sand, clay, starch) and for sand modified only with kilic clay. The determination was carried out using a method based on saturation of the soil with sodium ion, followed by its determination by the gypsum method.

2.7 Determination of lead concentration in solutions

The concentration of lead in solutions was determined using the Quantum Z.ETA atomic absorption spectrometer, manufactured by NPO KORTEK, Moscow. The method of atomic absorption spectrometry (AAS) is based on the phenomenon of resonant absorption of light by free atoms (atomic vapor) of the element being determined.

3   Results

Based on the measurement results for three parallel filtration experiments, graphs of the dependence of pH and Eh on the number of selected filtrate pore volumes were constructed (figure 2 и 3, 1,2,3 – parallel experiments). The pH value of the initial solution was 5 units. In all parallel experiments, a dependence is observed: at first, the pH value fluctuates around 7-8 units, and then drops sharply to 5-6 units, which corresponds to the pH of the initial solution. Consequently, lead sorption was no longer carried out after the pH dropped to 5-6 units.

The Eh value in three parallel experiments ranges from 100-300 mV, and numerous areas of growth and decline of Eh are visible on the graph without a fixed pattern. The probable cause of such chaotic changes in the Eh value may be the activity of living organisms trapped in the solution or on the ground during the experiment.
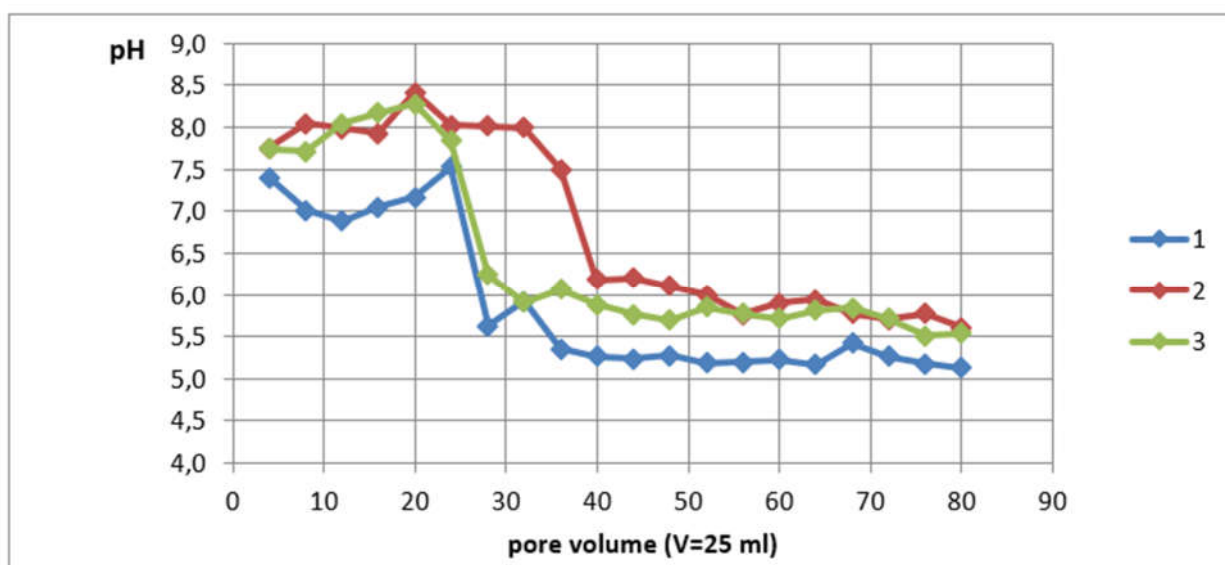

Figure 2. The dependence of pH on the selected volume of filtrate.
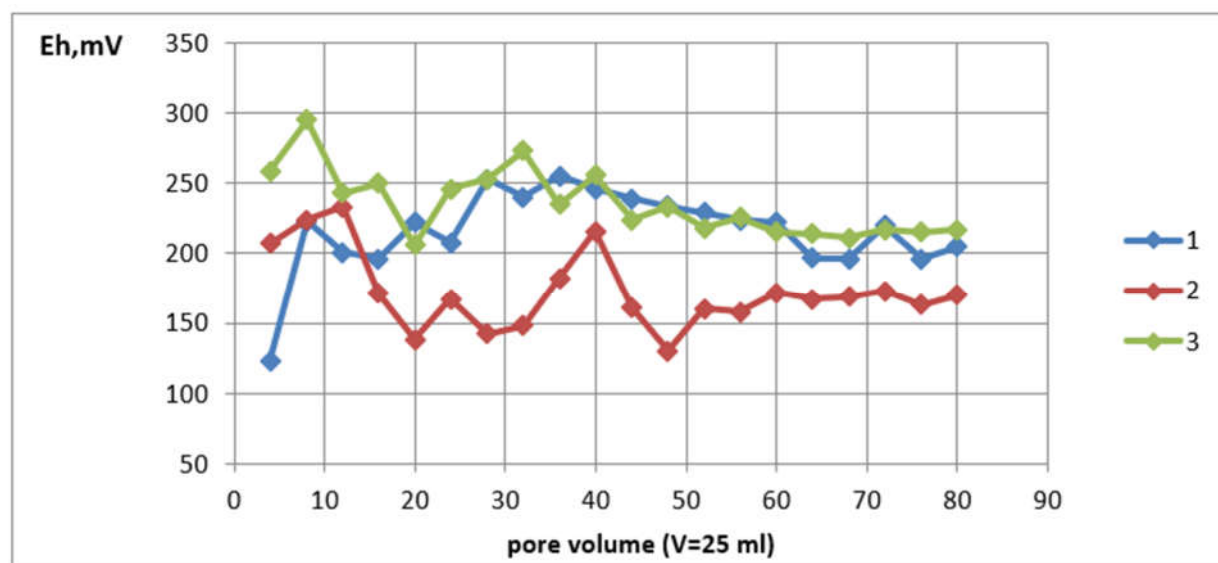

Figure 3. The dependence of Eh on the selected volume of filtrate.

The determination of the zero charge point of the soil showed that before the dynamic sorption process,

i.e. before the absorption of Pb ions by the soil, the pH_{ZPC} value was 8.5 units (figure 4). As the cations are absorbed by the soil, pH_{ZPC} shifts towards a more acidic medium and reaches a value of 6.25 after the dynamic sorption process (figure 5). Initially, the measured pH of the filtrate was 7-8 units, therefore, the pH of the surrounding solution was higher than pH_{ZPC} almost throughout the sorption process, that is, there was a predominant absorption of cations (namely Pb cations). After the filtrate reached pH 5-6 (less than 6.25 pH_{ZPC}), the predominant absorption of cations stopped, the sorption process was completed, which is confirmed by the final selected volumes of filtrate with pH 5-6.
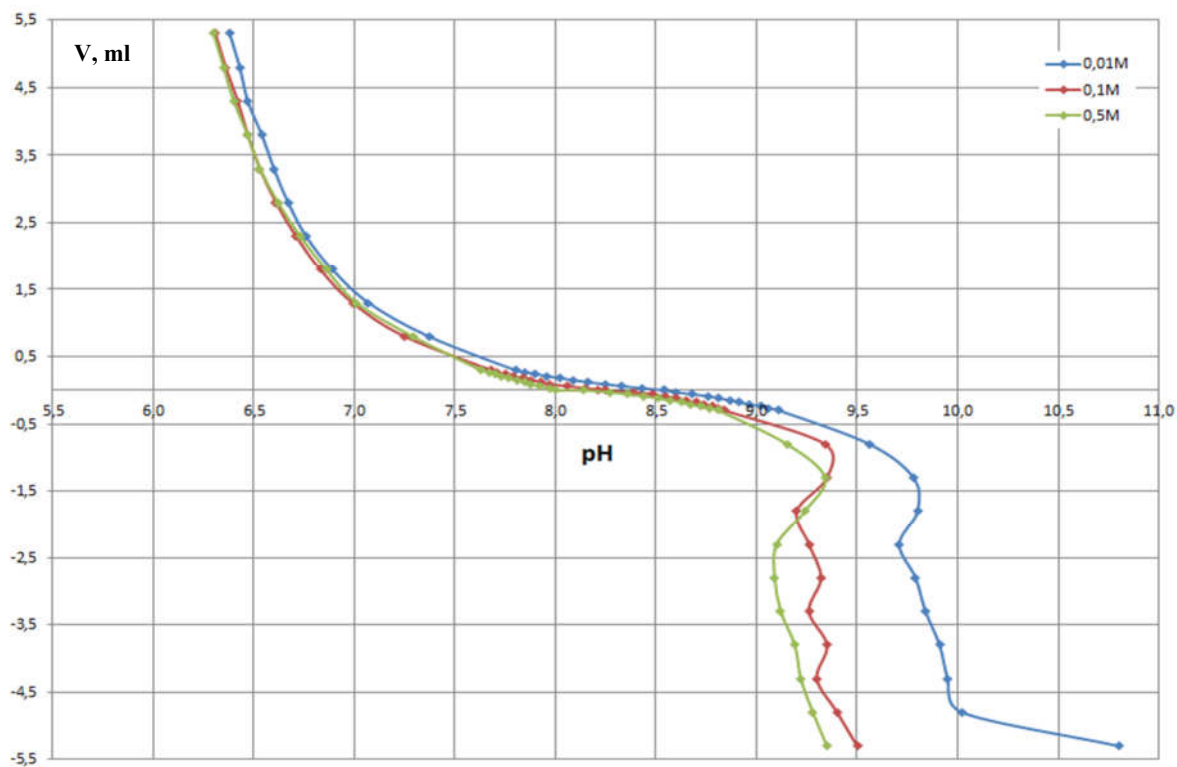

Figure 4. The dependence of the titrant volume V [ml] on the pH of the solution (starting soil, pH 8.5), 0.01 M, 0.1 M, 0.5 M is the concentration of NaCl.
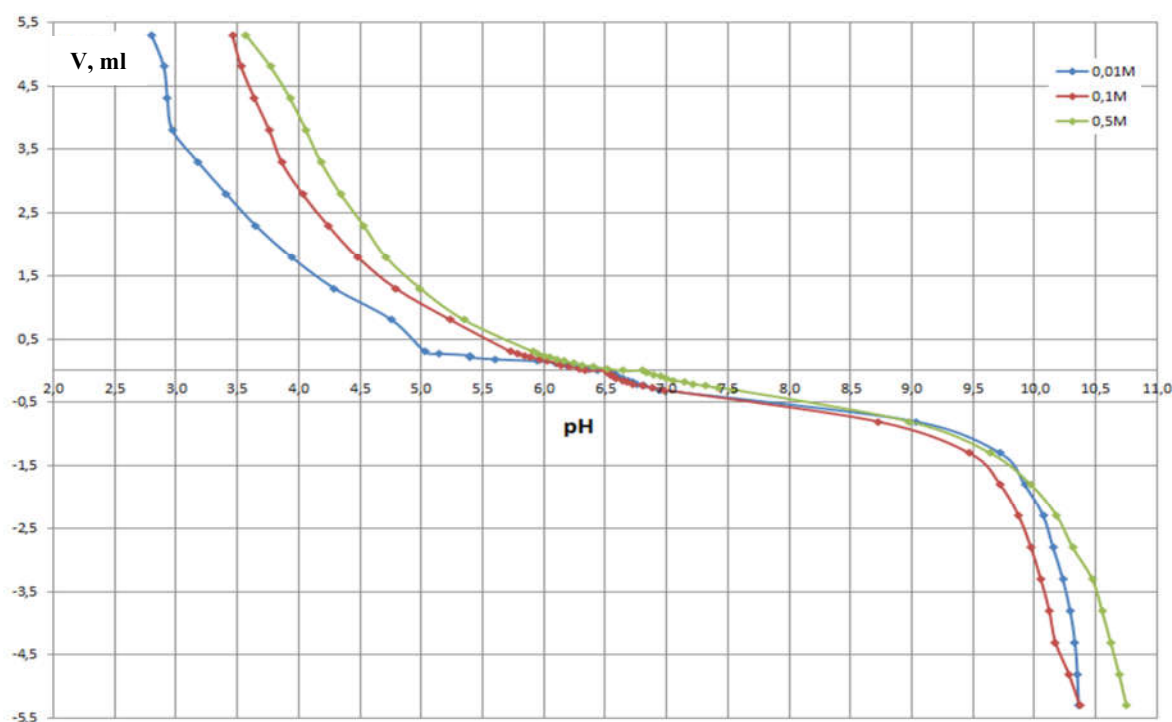
Figure 5. The dependence of the volume of the titrant V [ml] on the pH of the solution (soil after sorption Pb, pH 6.25), 0.01 M, 0.1 M, 0.5 M is the concentration of NaCl.

The obtained values of the cation exchange capacity of 0.072 mg-eq/100g for a mixture of sandy and clay soil and 0.069 mg-eq/100g for a mixture of sandy soil, clay soil and starch do not allow us to draw an unambiguous conclusion about the effect of CEC on the absorption of lead by soil within the limits of this study. According to A.I. Kovalevskaya's static sorption of lead with clay soil and clay soil modified with starch, it was found that at a concentration of $Pb(NO_3)_2$ in a solution of 2 g/l, lead sorption with montmorillonite is about 70 mg/g, sorption with montmorillonite with starch addition is about 50 mg/g. The obtained values vary quite a lot, while the obtained CEC values for the same soils are similar (about 0.07 mg-eq/100g). Thus, considering that sandy soils are practically incapable of cation exchange, it can be concluded that the absorption of lead cations does not depend on the CEC values. Consequently, lead, when absorbed by the soil, is sorbed not in the exchange complex of the soil, but in other more durable centers. It is likely that the absorption of lead by the soil occurs either in intra-atmospheric complexes on the soil surface with the formation of strong covalent bonds between the soil and Pb ions, or lead is embedded in the soil structure itself, in particular in the structure of clay soil and starch (the absorption process occurs).

Table 1 shows the results of an experiment to study the absorption capacity of modified sandy soil under dynamic conditions with respect to lead. Based on the obtained values for the model soil, absorption curves were constructed – the dependence of the amount of lead absorbed by the soil and the pH of the filtrate on the number of selected pore volumes (figure 6,7,8).

Table 1. The results of an experiment to study the absorption capacity of modified sandy soil under dynamic conditions with respect to lead

| V (25ml) | pH | | | Eh | | | C, mg/g | | | | | |
| | | | | | | | sand+clay+starch | | | clay+starch | | |
	1	2	3	1	2	3	1	2	3	1	2	3
4	7,40	7,75	7,74	123	207	259	0,25	0,26	0,26	1,48	1,55	1,54
8	7,01	8,05	7,71	223	224	295	0,74	0,50	0,50	4,44	3,01	2,98
12	6,88	7,99	8,05	201	233	243	1,21	0,75	0,73	7,29	4,48	4,39
16	7,05	7,93	8,17	196	171	250	1,70	0,99	0,96	10,20	5,94	5,75
20	7,17	8,42	8,28	222	138	206	2,19	1,23	1,13	13,13	7,35	6,79
24	7,53	8,03	7,84	208	167	246	2,43	1,45	1,28	14,56	8,71	7,65
28	5,63	8,02	6,24	253	142	253	2,43	1,66	1,41	14,59	9,95	8,48
32	5,92	8,00	5,91	240	148	273	2,43	1,75	1,49	14,60	10,50	8,93
36	5,35	7,50	6,06	255	182	235	2,43	1,82	1,56	14,60	10,93	9,34
40	5,26	6,18	5,88	246	216	256	2,43	1,84	1,57	14,60	11,05	9,43
44	5,24	6,20	5,76	239	161	224	2,43	1,85	1,58	14,60	11,10	9,48
48	5,27	6,10	5,69	234	130	233	2,43	1,86	1,59	14,60	11,15	9,53
52	5,19	6,00	5,85	229	160	218	2,43	1,86	1,59	14,60	11,15	9,53
56	5,20	5,76	5,77	224	158	226	2,44	1,86	1,59	14,61	11,15	9,53
60	5,23	5,90	5,71	222	172	215	2,44	1,86	1,59	14,61	11,15	9,53
64	5,17	5,94	5,81	197	167	214	2,44	1,86	1,59	14,61	11,15	9,53
68	5,42	5,77	5,84	196	169	211	2,44	1,86	1,59	14,61	11,15	9,53
72	5,26	5,70	5,71	220	173	217	2,44	1,86	1,59	14,61	11,15	9,53
76	5,18	5,77	5,51	196	163	215	2,44	1,86	1,59	14,61	11,15	9,53
80	5,13	5,61	5,54	205	170	217	2,44	1,86	1,59	14,61	11,15	9,53
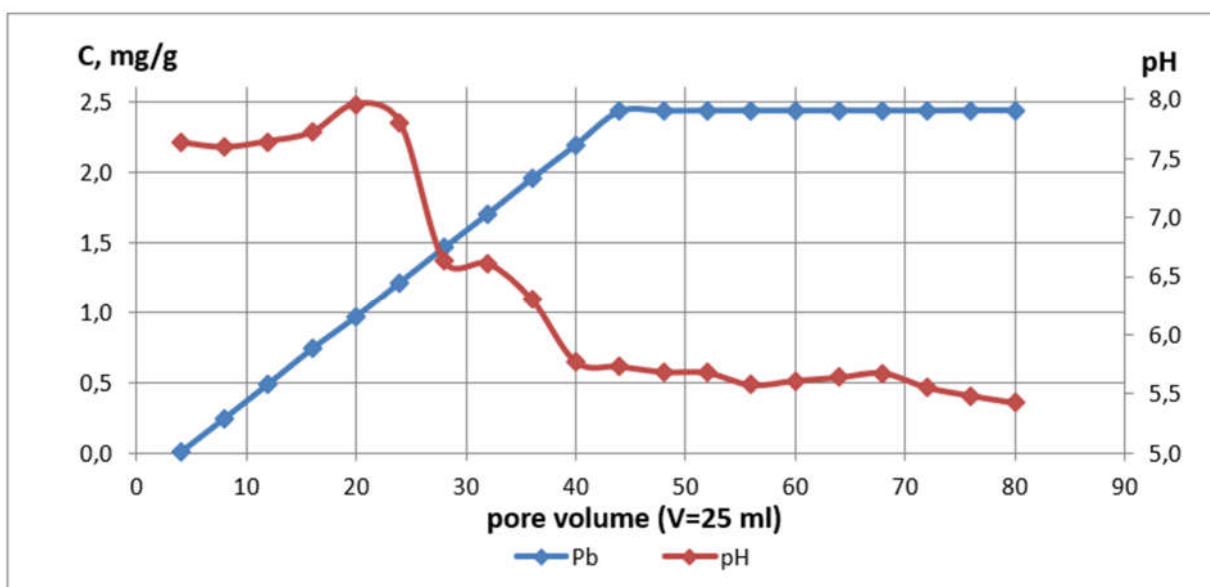
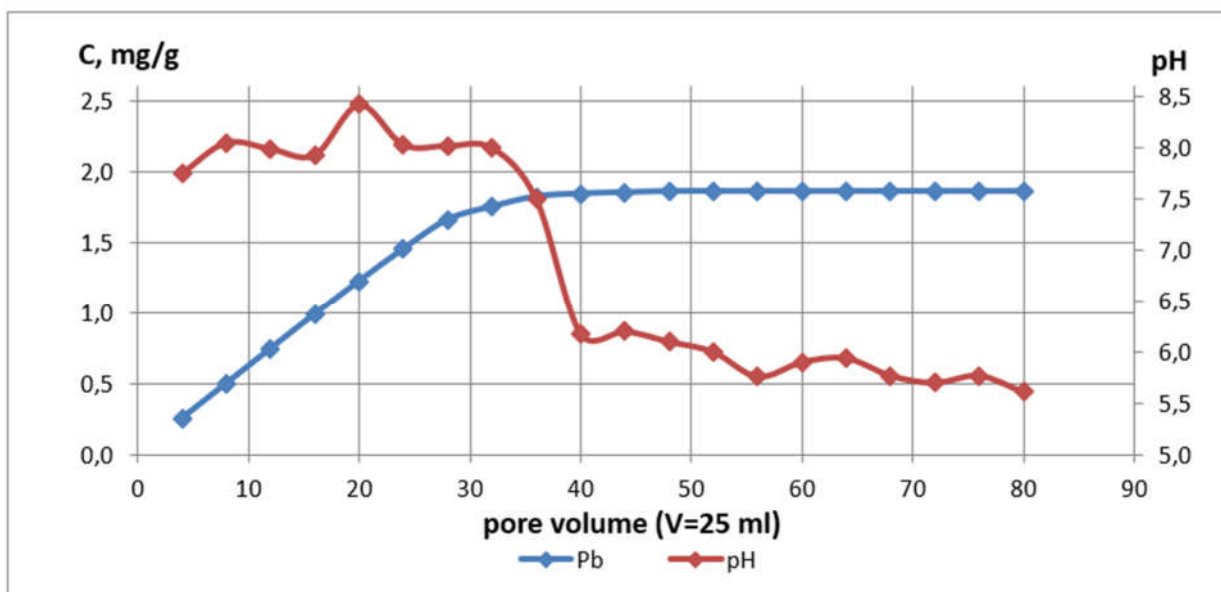**Figure 6.** Graph of lead absorption by modified soil (1 parallel experiment).

Figure 7. Graph of lead absorption by modified soil (2 parallel experiment).
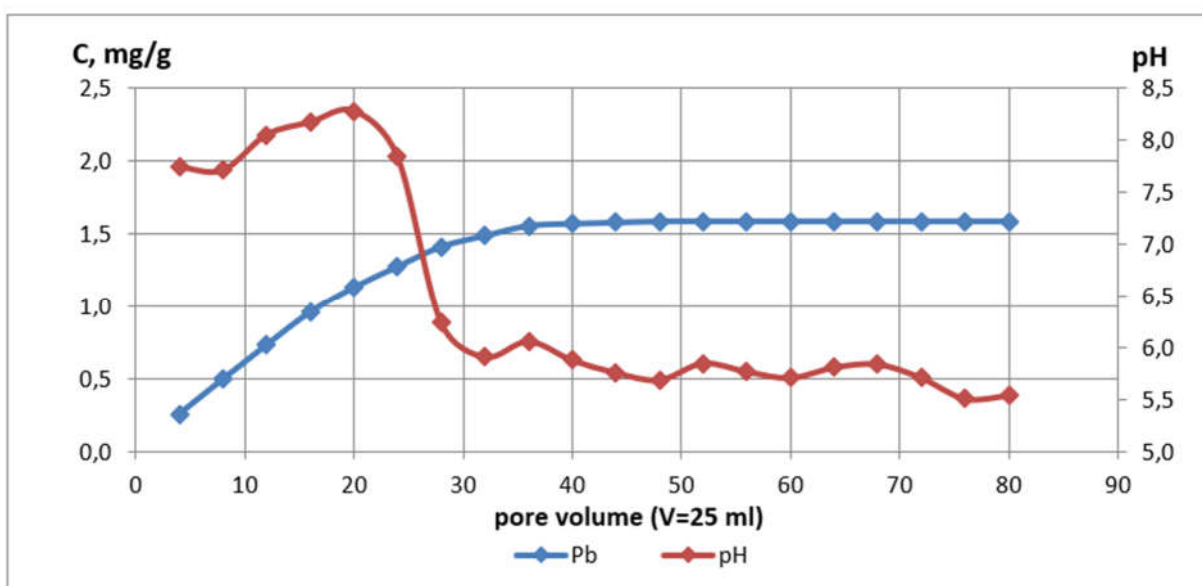

Figure 8. Graph of lead absorption by modified soil (3 parallel experiment).

As can be seen from the data obtained, the maximum possible value of lead absorbed by the model soil reaches 2.44 mg/g for the first, 1.86 mg/g for the second, 1.59 mg/g for the third parallel experiment. The average value of lead absorbed by the model soil for three experiments was 1.96 mg/g. The amount of lead absorbed by montmorillonite clay and starch (excluding sand) is 14.61 mg/g for the first, 11.15 mg/g for the second, 9.53 mg/g for the third parallel experiment. The average value of lead absorbed by clay and starch for three experiments was 11.76 mg/g. If we take into account the fact that the contribution of sandy soil to the Pb absorption process is quite low, then to assess the magnitude of the absorption capacity of clay and starch, we can rely on the research of A. I. Kovalevskaya on the absorption of Pb ions under static sorption conditions. Under static sorption conditions, at a concentration of Pb in the initial solution of 1.25 g/l, the absorption capacity of clay soil modified with starch was 48.24 mg /g, which is approximately 4 times higher than the values obtained by dynamic sorption. This difference may be related to the specifics of the present experiment:

1. Direct dynamic sorption with a fixed filtration rate, which means a shorter interaction time of the soil with the $Pb(NO_3)_2$ solution. The time of the dynamic sorption experiment was 56 hours, while for static sorption, sampling was carried out 3 weeks after the start of the experiment;

2. After carrying out the filtration processes, it was found that large aggregates were formed in the model soil by combining sandy and clay particles with starch, most pronounced after the second experiment. As a result, the absorption of lead ions took place over the surface area of the unit, including sand particles that are incapable of absorbing Pb, and not over the surface of clay particles and starch.

4   Conclusion

Thus, in this work, the absorption capacity of sandy soil modified with clay soil (montmorillonite) and organic binder (starch) in relation to lead was studied.

A relationship was revealed between the pH value of the solution and the amount of absorbed lead under dynamic sorption conditions (absorption of Pb ions by the soil leads to a change in the pH of the filtrate). Determination of the Eh values of the filtrate showed that the Eh value is probably influenced by living organisms.

The pH_{ZPC} value was obtained for the created model soil before (8.5) and after (6.25) lead absorption. At the same time, the obtained pH_{ZPC} values satisfy the general pattern of pH solution behavior.

According to the measurement of the cation exchange capacity, it was found that the absorption of lead cations does not depend on the value of the soil cation exchange capacity (0.072 mg-eq/100g for a mixture of sandy and clay soil and 0.069 mg-eq/100g for a mixture of sandy soil, clay soil and starch), therefore, the absorption of lead occurs with the formation of more durable complexes.

The maximum amount of lead absorbed by such a soil at an initial concentration of lead in a solution of 1.25 g/l is 1.96 mg/g. The maximum amount of absorbed lead without taking into account the mass of sand (absorption by clay and starch) is 11.76 mg/g, which is much less than the values obtained by studying the absorption capacity of similar soils under static sorption conditions (on average 48.24 mg/g according to A.I. Kovalevskaya). However, this study is significant because it has shown that a competent combination of sand, clay and starch can be used to create a model soil that plays the role of a protective barrier against Pb. Further research will allow us to find methods for creating protective barriers with greater absorption capacity.

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