

AGNIESZKA BOŻĘCKA*, STANISŁAWA SANAK-RYDLEWSKA*

SORPTION OF Pb²⁺ IONS FROM AQUEOUS SOLUTIONS ON ORGANIC WASTES (PART I)**SORPCJA JONÓW Pb²⁺ Z ROZTWORÓW WODNYCH NA ODPADACH ORGANICZNYCH (CZĘŚĆ I)**

This article presents the results of the research on the Pb²⁺ ions sorption from model aqueous solutions on walnut shells, plum stones and sunflower hulls. The effect of various factors, such as the concentration of natural sorbent, the pH, and the temperature was studied. The process of Pb²⁺ ions sorption on studied sorbents was described by the Langmuir model. The best sorption capacity has been revealed for sunflower hulls. The maximum sorption capacity for this material was 36.9 mg/g.

Keywords: sorption, lead ions, organic wastes

W artykule przedstawiono wyniki badań, które dotyczyły usuwania jonów Pb²⁺ z modelowych roztworów wodnych za pomocą odpadów organicznych, takich jak: łuski słonecznika, łupiny orzecha włoskiego i pestki śliwek. Dla badanego zakresu stężeń od 6,0-110 mg/dm³ i warunków procesu największą wydajność sorpcji, będącą w zakresie (89,4-96,3)% uzyskano dla łusek słonecznika. W przypadku łupin orzecha włoskiego i pestek śliwek sorpcja jonów Pb²⁺ jest znacznie niższa a jej wydajność wynosi odpowiednio (60,8-78,7)% i (62,3-81,3)%.

Zbadano także wpływ stężenia sorbentu, pH roztworu i temperatury na badany proces sorpcji. Dla wszystkich materiałów optymalne stężenie sorbentu wyniosło 5 g/dm³. Powyżej tej wartości nie obserwowano istotnych zmian w stopniu redukcji jonów Pb²⁺ (rys.2).

We wszystkich przypadkach maksima sorpcji osiągnięto przy pH równym 4,0±0,1 co obrazuje rysunek 3. Obniżenie sorpcji, występujące przy pH poniżej i powyżej wartości 4,0 prawdopodobnie związane jest to z ładunkiem gromadzącym się na powierzchni sorbentu (elektrostatyczne odpychanie i przyciąganie badanych jonów). Wartość pH roztworu determinuje także formę oraz stężenie badanego jonu w roztworze. W roztworach silnie kwaśnych ołów występuje głównie w postaci kationów. Stopniowy wzrost pH prowadzi do tworzenia jonów kompleksowych i strącania go w postaci wodorotlenku.

Wykazano również, że ze wzrostem temperatury w zakresie (293-313)K następuje stopniowy spadek sorpcji, co prawdopodobnie może być związane z niszczeniem miejsc aktywnych obecnych na powierzchni sorbentu lub przesunięciem równowagi procesu na korzyść desorpcji (rys. 4). Wyniki uzyskane potwierdzają również egzotermiczną naturę badanego procesu sorpcji.

Adsorpcję jonów Pb²⁺ na użytych sorbentach opisano za pomocą modelu Langmuira. Założenia tego modelu podano w rozdziale 4.1. Najlepsze właściwości sorpcyjne w stosunku do jonów Pb²⁺ wykazały

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF MINING AND GEOENGINEERING, AL. A. MICKIEWICZA 30, 30-059 KRAKOW, POLAND. Corresponding Author: e-mail: ssanak@agh.edu.pl

łuski słonecznika. Maksymalna pojemność sorpcyjna dla tego sorbentu wyniosła 36,9 mg/g (tabela 1, rysunek 5). W przypadku łupin orzecha i pestek śliwek stała q_{\max} izotermi Langmuira przyjmuje wartości równe 23,1 mg/g i 21,2 mg/g.

Słowa kluczowe: sorpcja, jony ołowiu, odpady organiczne

1. Introduction

Among pollutants present in natural waters, a particularly dangerous group of substances are heavy metals such as lead, cadmium, mercury, etc. These are extremely toxic substances which have ability to accumulate in living organisms. Because of this, reducing of their emissions and their removal from the environment is very important issue.

Amount of heavy metals in the aqueous environment is formed under the influence of anthropogenic factors. The largest water pollutions usually occur near the factories which emit untreated wastewaters. Smelting operations of zinc-lead ores as well as solid and liquid products derived during production of non-ferrous metals (e.g. copper, zinc and lead) by metallurgical methods are significant sources of heavy metals pollution in the environment (Dojlido, 1995; Baran at al., 2013).

The research shows that closed mines of Zn-Pb ores are serious threat to the quality of natural waters. Concentrations of metals (mainly zinc, lead and cadmium) in water, sediments and plants near the mines are still high. For example, in the region of the closed Zn-Pb ores mine called Matylda near Chrzanów (the Małopolska province), the average concentrations of these metals in river water samples from April 2009 to March 2010 were Zn: 0.112-1.341 mg/L; Pb: 0.0038-0.0316 mg/L; Cd: 0.0003-0.0035 mg/L (Aleksander-Kwaterczak at al., 2010). According to the Ministry of Environment Regulation dated 9 November 2011, for the classification of bodies of surface water and environmental quality standards for priority substances, the maximum concentrations of Zn, Cd and Pb in the studied river waters are higher than the limit values (Dz.U.11.257.1545).

Nowadays, biosorption process is important in the purification of water and wastewater from toxic metals. Biosorption is the process of binding substances (metal ions, chemical compounds, etc.) to the surface of the sorbent. This term includes all the processes in the cell wall, which in contrast to bioaccumulate, are not controlled by the metabolism of the cell. This process mainly refers to dead biomass. The use of dead biomass is more attractive in comparison to the alive biomass. The main reason being lack of toxic effect of metals on living organisms and no need to use nutrients or to maintain sterile conditions during tests (Chojnacka, 2010; Farooq at al., 2010).

The biosorption of metal ions from aqueous solutions is carried out in two phases, as it is illustrated in scheme in Fig. 1. During the contact phase, metal ions in the solution are bonding with biological material. In the desorption (second) phase metal is released from biosorbent. Regeneration of used material is a very important advantage of the biosorption process. It allows the re-use of biomass and recovery of metals from concentrated solutions after sorption (usually by precipitation or electrolysis or ion flotation). For the regeneration process, hydrochloric acid or nitric acid solutions are usually used.

Various materials can act as biosorbents. Also organic waste from the food and wood industry, and residues from agriculture can be used as biosorbents. This group include organic waste such as fruit and vegetable peelings, nut shells, fruit stones, straw and bark (Low at al., 2000;

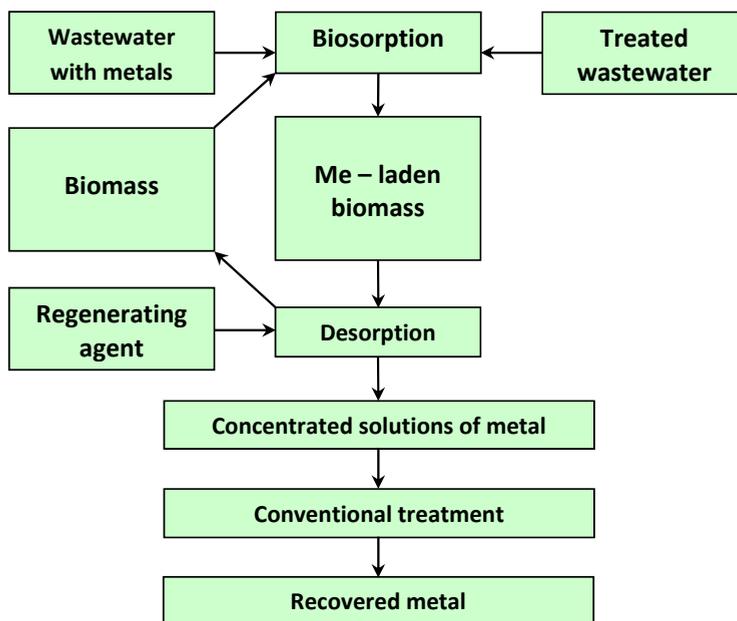


Fig. 1. The removing and recovery of metals from water and wastewater using biosorbents (Chojnacka, 2010)

Han at al., 2005; Pino at al., 2006; Meena at al., 2008; Gupta at al., 2009; Mohamad Ibrahim at al., 2010). Algae, seaweeds and mushrooms are also efficient sorbents (Sari & Tuzen, 2008; Uluozlu at al., 2008).

The sorption process of heavy metals from aqueous solutions on organic wastes has many advantages. For e.g.: low cost, the possibility of using unnecessary waste in landfills and biodegradation of used biomass. Furthermore, the used sorbents can be regenerated and thus it allows the recovery of adsorbed metals (Qi & Aldrich, 2008).

2. Aim of the study

The aim of this study was to compare the sorption properties of ground walnut shells (*Juglans regia*), plum stones (*Prunus domestica L*) and sunflower hulls (*Helianthus L.*) toward Pb^{2+} ions and the optimization of the studied sorption processes. The results obtained for sunflower hulls were compared to that of plum stones and walnut shells which were published before (Gala & Rydlewska, 2010, 2011a, 2011b).

3. Methods of the study

3.1. Preparation of sorbents

Walnut shells (*Juglans regia*), plum stones (*Prunus domestica L*) without the kernels and sunflower hulls (*Helianthus L.*) were used for the study as natural sorbents. The sorption process was carried out on the fraction with a particle size below 0.5 mm. Before the sorption, samples were purified (treatment with 0.001 mol/L nitric acid, washing with reverse osmosis water until the pH about 5.90), and then dried in temperatures up to 323 K.

3.2. The study of the equilibrium of the sorption process

The study of the sorption process was based on placing a known mass of sorbent (sample weight of 0.3 g to 1.5 g) in the beakers with 100 mL solutions of lead(II). The range of the studied initial concentration of the Pb^{2+} ions was from 6.0 to 110 mg/L. Metal was introduced into the solution in the form of salt $\text{Pb}(\text{NO}_3)_2$. All experiments were performed at a fixed pH value and at a ionic strength equal to 0.02 mol/L. The pH was studied in the range from 2.0 to 5.0. The pH was controlled with a 0.02 mol/L solution of nitric acid, while the ionic strength was controlled with a 0.04 mol/L solution of potassium nitrate(V).

The solutions with the sorbent were continuously stirred with a mechanical stirrer at 120 rpm at the constant temperature equal to 298 ± 0.5 K. The optimization studies of temperature were performed for a range of 293 to 313 ± 0.5 K. In all experiments, the samples for analysis were taken after one hour (the own studies has shown that in this time the system reached equilibrium).

3.3. Used instrumental methods

After adsorption, the lead(II) content in the solutions was determined by flow-through coulometry using EcaFlow 150 GLP apparatus manufactured by POL-EKO. Before measurements, the solutions were filtered to remove solid particles. Three measurements were performed for each sample.

The sorption capacity was determined as the amount of metal ions contained in the dry weight of sorbent according to the concentration in the aqueous solution. It was calculated from formula presented below:

$$Q = \frac{V(c_0 - c_{eq})}{m} \quad (1)$$

where:

- Q — amount of the Pb^{2+} ions per gram of the sorbent, mg/g;
- V — is the volume of the solution, L;
- c_0 and c_{eq} — are the initial and final concentrations of Pb^{2+} ions, mg/L;
- m — is the quantity of dry mass of the adsorbent, g.

4. Discussion of the results

4.1. The mathematical description of the sorption process

Sorption of Pb^{2+} ions on the studied sorbents was described using the most common adsorption models – the Langmuir isotherm.

Langmuir theory assumes that on the adsorbent surface there are specified quantity of adsorption centers, and each of them is able to adsorb only one molecule. The localized adsorption takes place, which means that particles cannot move freely on the surface. The adsorbed molecules do not interact with each other. This is the monolayer adsorption on the homogeneous surface. The obtained layer reduces the forces of adsorption interaction preventing formation of subsequent layers. This model is described by the following equation:

$$Q = \frac{q_{\max} b \cdot c_{eq}}{(1 + b \cdot c_{eq})} \quad (2)$$

where: q_{\max} is the maximum sorption capacity of the sorbent i.e. the maximum amount of metal ions needed to form a complete monolayer (Han at al., 2005), and b represents the energy of adsorption (Meena at al., 2008).

The values of coefficients q_{\max} and b in the Langmuir equation were determined based on the linear form of this isotherm:

$$\frac{1}{Q} = \frac{1}{q_{\max} b} \cdot \left(\frac{1}{c_{eq}} + b \right) \quad (3)$$

4.2. The effect of the sorbent concentration on the sorption of Pb^{2+} ions from aqueous solutions

The study of the sorbent's adsorption as a function of its concentration is shown in Fig. 2. The curves show that the highest sorption capacity of Pb^{2+} ions was obtained for sunflower hulls. The lowest sorption was observed for plum stones. For the studied concentration range, for sunflower hulls the reduction of Pb^{2+} in the solution was (72.4-92.5)%, for walnut shells (77.1-81.9)% and for the plum stones (53.7-70.0)%.

For all sorbents, the effectiveness of Pb^{2+} removal from the solution increases with sorbent concentration until it reaches a maximum at a sorbent concentration of 5g/L. Further increasing of sorbent concentration does not significantly modify the reduction degree of Pb^{2+} ions. This is most likely due to the phenomenon of aggregation of sorbent's particles in the solution, which can block the access of metal ions to functional groups on the sorbent surface. Consequently, further study was continued at a sorbent concentration of 5 g/L.

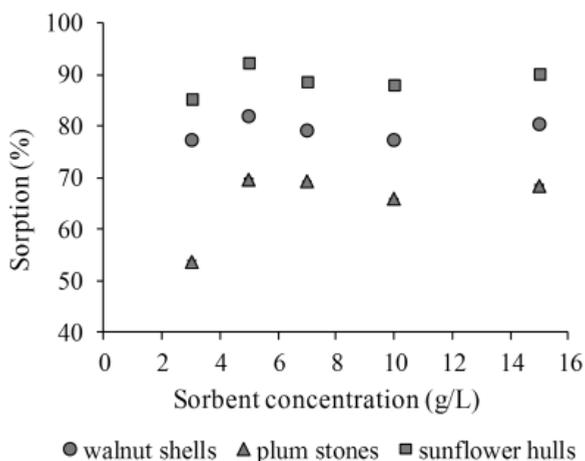


Fig. 2. The influence of the sorbent concentration on the sorption of Pb^{2+} ions on walnut shells, plum stones and sunflower hulls (initial Pb^{2+} concentration 15.6 mg/L; pH of 4.0 ± 0.1 ; sorbent's particle size class < 0.5 mm; ionic strength 0.02 mol/L; temperature (298 ± 0.5) K; time of adsorption 1 h; mixing speed 120 rpm.)

4.3. The effect of pH on the sorption of Pb^{2+} ions from aqueous solutions

The dependence of the sorption of Pb^{2+} ions efficiency as a function of pH, obtained for the sunflower hulls, walnut shells and plums stones is shown in Fig. 3. The presented figure shows that the sorption efficiency increases in pH range from 2.0 to 4.0 for all studied materials. Moreover, it can be observed that the maximal values of sorption was reached at $\text{pH } 4.0 \pm 0.1$. While, for

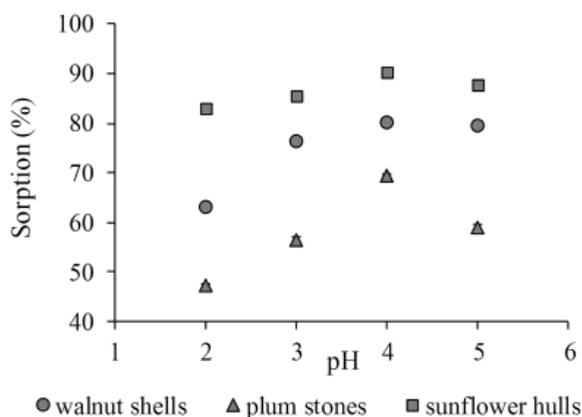


Fig. 3. The effect of pH on the sorption of Pb^{2+} ions on walnut shells, plum stones and sunflower hulls (initial Pb^{2+} concentration 15.6 mg/L; sorbent concentration 5 g/L; sorbent's particle size class < 0.5 mm; ionic strength 0.02 mol/L; temperature (298 ± 0.5) K; time of adsorption 1 h; mixing speed 120 rpm.)

plum stones and for solution with a pH of 5.0 ± 0.1 , the sorption was lower. For other materials, this dependence requires further study and it is not possible to interpret yet.

The obtained results, shown in Fig. 3, confirm that for very acidic solutions, the sorption is lower. Probably, it is connected to the different charge on the sorbent surface. The pH of the solution and the functional groups present on the sorbent surface (e.g., carboxyl, phenyl, hydroxyl and amide groups) determine the type and the volume of this surface charge (Bansal & Goyal, 2009).

The pH for which the maximum sorption capacity was noted (in this case at a pH of 4.0 ± 0.1) is the so-called pH_{pzc} (*point of zero charge*) (Meena at al., 2008). In solutions with pH below pH_{pzc} , the sorbent surface is positively charged, and above pH_{pzc} , charged negatively (Meena at al., 2008; Bansal & Goyal 2009).

In more acidic solutions the sorbent surface is positively charged e.g. due to the increased competition between hydrogen ions (numerous in this conditions) and lead ions for the sorbent's active sites. The positive charge sorbents surface in more acidic solutions can be attributed, among other things, to excessive protonation of the surface. Another cause of the positive charge of sorbent surface is that the excessive protonation of the functional groups is at low pH. Therefore, the studied metal cations have limited access to the surface of the sorbent and this leads to the reduction of the Pb^{2+} ions sorption as a result of electrostatic repulsion forces.

The gradual increase in the pH values causes the deprotonation of groups and thus the increasing of the sorption efficiency. When the sorbent surface is negatively charged due to the ionization of acidic groups (mainly carboxyl, phenyl and hydroxyl groups), the electrostatic attraction between metal ions and the sorbent surface occurs, which increases sorption. Also, with an increase of pH, the solution contains less hydrogen ions which compete with Pb^{2+} for sorption, thus increasing the efficiency of Pb^{2+} sorption.

The pH value also determines the type and concentration of the studied ion in the solution. In highly acidic solutions, metals are present mainly in the form of cations. A gradual increase in pH leads to the formation of complex ions and precipitation of metals in the form of hydroxides. The reduction in sorption, which in this case occurs at $pH 5.0 \pm 0.1$, is probably caused by the fact that lead hydroxyl ions are already forming (Meena at al., 2008). Considering that the exponent of the $Pb(OH)_2$ solubility product is 20, it was calculated that in a solution with a lead concentration of 15.6 mg/L, lead hydroxide will begin to precipitate at about pH 6.0 (Mizerski, 2008). The reduction of the sorption for the plum stones and sunflower hulls presents at $pH 5.0 \pm 0.1$ is probably due to the formation of hydroxyl ions lead.

4.4. The effect of temperature on the sorption of Pb^{2+} ions from aqueous solution

In order to study the effect of temperature on Pb^{2+} sorption on studied materials, sorption experiments were performed in the range from 293 to 313K. Other conditions remained the same as in previous experiments.

For all sorbents, it was observed that as the temperature increased in the range from 293 to 313 K, sorption decreased (Fig. 4). Such a result confirms the exothermic nature of Pb^{2+} sorption on studied sorbents. The decrease of sorption properties in a temperature range of 293 to 313 K may result from damage of active sites on the sorbent surface or the shift of the process equilibrium towards desorption of metal ions from the surface to the solution (Uluozulu at al., 2008).

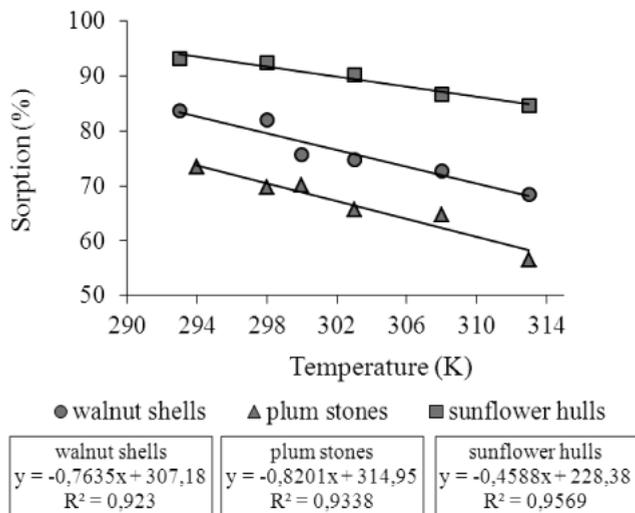


Fig. 4. The effect of temperature on the sorption of Pb^{2+} ions on walnut shells, plum stones and sunflower hulls (initial Pb^{2+} concentration 15.6 mg/L; sorbent concentration 5 g/L; sorbent's particle size class < 0.5 mm; ionic strength 0.02 mol/L; pH of $4.0 \pm 0,1$; time of adsorption 1 h; mixing speed 120 rpm.)

4.5. Isotherm of Pb^{2+} adsorption on walnut shells, plum stones and sunflower hulls

The results of the study described with the Langmuir equations were shown in Fig. 5. The initial concentration of Pb^{2+} ions in solutions changed from about 6.0 to 110 mg/L. For the studied

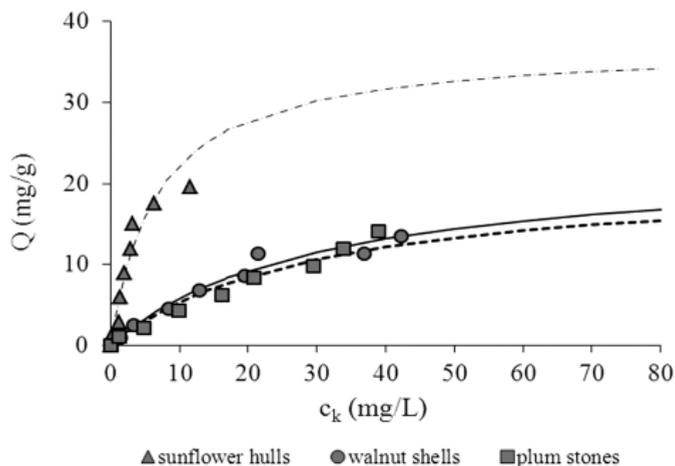


Fig. 5. Langmuir isotherms for Pb^{2+} adsorption on walnut shells, plum stones and sunflower hulls (sorbent concentration 5 g/L; sorbent's particle size class < 0.5 mm; ionic strength 0.02 mol/L; pH of $4.0 \pm 0,1$; temperature $(298 \pm 0,5)$ K; time of adsorption 1 h; mixing speed 120 rpm.)

concentration range, for sunflower hulls, the depletion of Pb^{2+} in the solution was (89.4-96.3)%, for walnut shells (60.8-78.7)% and for the plum stones (62.3-81.3)%.

The values of coefficients q_{\max} and b in the Langmuir equation were determined based on the linear form of these equations 3. All the parameters and their uncertainties were calculated using Microsoft EXCEL. The calculated values of adsorption isotherm coefficients and the correlation coefficients R are presented in table 1.

TABLE 1

Langmuir isotherms coefficients and their uncertainties

Studied material	q_{\max} (mg/g)	Δq_{\max} (mg/g)	b (L/mg)	Δb (L/mg)	R
Sunflowers hulls	36.9	0.76	0.15	0.0002	0.974
Walnut shells	23.1	0.53	0.03	0.00006	0.984
Plum stones	21.2	0.47	0.03	0.00005	0.940

Based on the calculated values of the correlation coefficients R (table 1), it can be concluded that Langmuir model very well describes Pb^{2+} sorption on the studied materials.

The sunflower hulls show the best sorption capacity toward Pb^{2+} ions. The maximum sorption capacity of this sorbent, estimated based on the parameter q_{\max} in the Langmuir isotherm, was 36,9 mg/g. For walnut shells and plum stones, the values of the constant q_{\max} are similar and were 23.1 mg/g and 21.2 mg/g, respectively.

5. Summary and conclusions

1. Studied organic sorbents can be used to remove Pb^{2+} ions from model aqueous solutions.
2. For the studied concentration range, for sunflower hulls the depletion of Pb^{2+} in the solution was (89.4-96.3)%, for walnut shells (60.8-78.7)% and for the plum stones (62.3-81.3)%.
3. The sunflower hulls show the best sorption capacity toward Pb^{2+} ions. The maximum sorption capacity of this sorbent was 36.9 mg/g. For walnut shells and plum stones, the values of the constant q_{\max} are lower and are 23.1 mg/g and 21.2 mg/g, respectively.
4. Sorption of Pb^{2+} on the studied organic sorbents depends on the sorbent concentration. For all materials, the optimum sorbent concentration was 5 g/L.
5. In all cases the best sorption was noted at pH 4.0 ± 0.1 .
6. The study also showed that as the temperature increases (from 293 to 313K) sorption gradually decreases.
7. In this paper the studies were carried out on the model aqueous solution. The study of the sorption process of Pb^{2+} ions in real samples is planned.

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