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CHEMICAL AND PHYSICO-CHEMICAL FEATURES OF MODIFIED BIOCARBON ECOSORBENT FOR BINDING HEAVY METAL IONS

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Abstract

The possibility of obtaining ecosorbents based on biologically and chemically modified carbon material from vegetable raw materials for the removal of Cd (II), Cu (II), Pb (II) and Zn (II) ions from aqueous solutions was studied. The peculiarities of obtaining an ecosorbent from sugar cane bagasse and rice husk are substantiated. Sulfur-containing biocarbon ecosorbent is obtained by one-stage pyrolysis of raw materials together with sulfur-containing reagents at a temperature of 350–400 °C. The temperature parameters and the duration of the pyrolysis process were determined experimentally from the conditions of the maximum content of biochar in the pyrolyzate. Sulfur-containing biochar has a high absorption capacity for heavy metal ions (more than 80–90 %) compared to the original biochar. Its specificity is due to the formation of insoluble metal sulfides on the surface and in the pores of the sorbent. Microbiological modification leads to the creation of biosorption material for strong binding of heavy metal ions. Sulfate-reducing bacteria immobilized on the surface of biochar are also able to convert sorbed heavy metals into insoluble sulfide forms. A comprehensive study of the structural-porous and sorption properties of the original and modified biochar was conducted. It was established that chemical and microbiological modification of biochar increases its sorption capacity due to the improvement of structural-porous and ion-exchange properties of the material. But the key property of ecosorbents from pyrolyzed and modified vegetable raw materials is the ability to form insoluble sulfide forms of metals on the surface and in the pores of the ecosorbent.

Keywords: adsorption; cadmium; lead; zinc; copper; bagasse; rice husk; pyrolysis; biochar; chemical modification; sulfate-reducing bacteria; sulfides.

ХІМІЧНІ ТА ФІЗИКО-ХІМІЧНІ ОСОБЛИВОСТІ МОДИФІКОВАНОГО БІОВУГЛЕЦЕВОГО ЕКОСОРБЕНТУ ДЛЯ ЗВ'ЯЗУВАННЯ ІОНІВ ВАЖКИХ МЕТАЛІВ

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Анотація

Вивчена можливість отримання екосорбентів на основі біологічно та хімічно модифікованого вуглецевого матеріалу з рослинної сировини для видалення іонів Cd (II), Cu (II), Pb (II) та Zn (II) з водних розчинів. Обґрунтовано особливості одержання екосорбенту з багаси цукрової тростини та рисового лушпиння. Сульфуровмісний біовуглецевий екосорбент отримують шляхом одностадійного піролізу сировини разом із сульфуровмісними реагентами за температури 350–400 °C. Температурні параметри та тривалість процесу піролізу визначали експериментально з умов максимального вмісту біовугілля в піролізаті. Сульфуровмісне біовугілля має високу поглинальну здатність щодо іонів важких металів (понад 80–90 %) порівняно з вихідним біовугіллям. Його специфіка зумовлена утворенням на поверхні та в порах сорбенту нерозчинних сульфідів металів. Мікробіологічна модифікація призводить до створення біосорбційного матеріалу для міцного зв'язування іонів важких металів. Сульфатвідновлюючі бактерії, іммобілізовані на поверхні біовугілля, також здатні перетворювати сорбовані важкі метали в нерозчинні сульфідні форми. Проведено комплексне дослідження структурно-пористих та сорбційних властивостей вихідного та модифікованого біовугілля. Встановлено, що хімічна та мікробіологічна модифікація біовугілля підвищує його сорбційну здатність за рахунок покращення структурно-пористих та іонообмінних властивостей матеріалу. Але ключовою властивістю екосорбентів з піролізованої та модифікованої рослинної сировини є здатність утворювати на поверхні та в порах екосорбенту нерозчинні сульфідні форми металів.

Ключові слова: адсорбція; кадмій; свинець; цинк; мідь; багаса; рисове лушпиння; піроліз; біовугілля; хімічне модифікування; сульфатредукуючі бактерії; сульфіди.

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Introduction

The biggest environmental problems are related to man-made pollution. The main sources of toxicant pollution are various industries. As a result of anthropogenic human activity, an excess amount of toxic metal ions enters the environment, namely water, air and soil. Sewage is the biggest source of pollution. With an insufficient degree of purification, they fall into water bodies, both surfaces and underground horizons on the surface of the soil. With flue gases, heavy metals enter the soil and are washed into water sources [1; 2]. Heavy metals such as Cd, Cu, Hg, Ni, Pb and Zn are toxic, non-biodegradable and accumulate in the environment [3–5]. Various methods have been proposed for cleaning water contaminated with metals, including chemical coagulation, oxidation, membrane filtration, extraction with various solvents, and ion exchange [6; 7]. These methods are expensive and limited by the high concentration of metal ions. The most accessible and economically beneficial are sorption methods of water purification using various types of adsorbents [8; 9]. Adsorption is a physicochemical process during which a pollutant (adsorbate) accumulates on the surface of a solid body (adsorbent). Carbon materials are used as adsorbents for water purification, as they have a porous structure and a large surface [10]. An urgent problem is the search for effective ecosorbents capable of reducing environmental pollution with toxic heavy metals and meeting the basic requirements – harmlessness and non-toxicity, high adsorption capacity, selective sorption of toxic compounds and complete absence of side effects.

One of the promising areas is the production of carbon sorption materials (biochar) from lignocellulosic waste [11]. The involvement of new types of renewable raw materials, in particular agricultural waste, in order to obtain sorbents for detoxification of heavy metals is relevant in both scientific and practical terms [12–14]. Plant waste is a priority natural renewable material for ecosorbents. The transformation of these wastes into sorption-active substances simultaneously allows obtaining vital materials, such as activated carbon, and solves the problem of environmental pollution with agricultural waste. Biochar is a stable carbon-rich product that is synthesized as a result of pyrolysis (carbonization) of plant biomass. The growing interest in the beneficial use of biochar has opened up new, unlimited possibilities. The main parameters that control its properties include pyrolysis temperature, time, and type of raw material. The effectiveness of biochar in neutralizing pollution depends on its surface area, pore size distribution, and ion exchange capacity [15; 16]. Pyrolysis temperature affects the properties of biochar and is a critical factor for evaluating the effectiveness of removing toxicants from the environment [17; 18]. In the process of carbon material formation during the pyrolysis of cellulose-containing material, reactive groups are formed on the coal surface, which determine the possibility of chemical and biological modification of the biochar surface to improve its sorption and detoxification properties. The modification of biochar with sulfur makes it possible to obtain sulfur-containing biochar. Sulfur-containing sorption materials, like low-molecular-weight organosulfur compounds, are capable of complex formation with heavy metal ions. Therefore, such sorbents can be used to clean wastewater and soils contaminated with heavy metals. Carbon disulfide materials are sorption-selective for a number of heavy metals due to the formation of insoluble metal sulfides on their surface. Known methods of obtaining sulfur-containing carbon sorbents involve the treatment of raw carbon materials with the most common sulphiding agents, such as concentrated sulfuric acid, oleum, gaseous sulfur dioxide [19–21]. As a result of such treatment, sulfocarbon materials are formed, which are multifunctional cation exchange resins and are sorptionally active in relation to heavy metals. The technology of obtaining such materials is complex and environmentally dangerous. Our proposed method of obtaining a sulfur-containing biocarbon ecosorbent is a one-stage pyrolysis of raw materials together with sulfur-containing reagents. Obtaining sulfur-containing carbon sorbent in this way has advantages over other methods. The priority is to obtain new types of ecosorbents from agricultural waste and to jointly solve two problems: ecological – waste disposal and technological – production of the necessary solid products to solve environmental problems.

Materials and methods

In this study, the possibility of obtaining an ecosorbent from rice husk and bagasse (plant waste from sugar cane production) was studied. Rice husk is a fibrous substance, which contains moisture, lignin, cellulose, pentosans, a small amount of protein and vitamins, as well as mineral ash, consisting of 92–97 % silicon dioxide. Composition of bagasse from sugar cane: cellulose

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47.59 wt. %, hemicellulose 26.92 wt. %, lignin 21.53 wt. %. The composition of lignocellulosic plant waste substantiates the possibility of obtaining carbon material (biochar) from them. In the process of heat treatment of plant waste, a laboratory reactor was used, which provided oxygen-free conditions for the process at temperatures from 250 °C to 600 °C. The pyrolysis process lasted from 10 to 60 minutes.

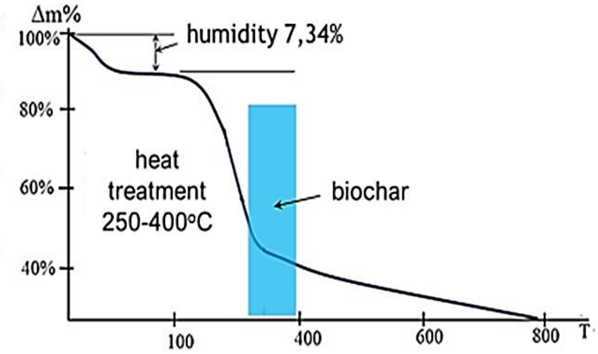

Fig. 1. Carbon release from plant material during pyrolysis at different temperature

The temperature parameters and the duration of the pyrolysis process were determined experimentally from the conditions of the maximum biochar content (Fig. 1) in the pyrolyzate. In the conditions of heat treatment at temperatures of 300–350 °C in the absence of oxygen, biomass undergoes exothermic processes and releases the maximum amount of carbon material. According to its structure, biochar belongs to the class of carbonized substances due to the commonality of their characteristic structural element. Carbon sorbents based on pyrolyzate of cellulose-containing raw materials are characterized by a polydisperse porous structure. The presence of micro- and mesopores in biochar determines its high internal specific surface, which plays an important role in chemical reactions occurring at relatively low temperatures. Macropores have a smaller contribution to the change in the specific surface area of biochar, but contribute to the access of biomolecules during bioactivation. According to its structure, such biochar belongs to the class of carbonized substances due to the commonality of their characteristic structural element. The structural element of the carbonized substance is an atomic mesh of polymerized carbon. The morphology of the surface of particles and whole flakes of the obtained rice husk pyrolyzate with a size of 500–1000 μm is presented in Fig. 2. It is shown that the size of the micro-cells of the cellular structure of the rice husk surface is approximately 20 μm.

Fig. 2. Morphology of pyrolyzed rice husk particles

With the help of chemical and biological modification of biochar, ecosorbents were obtained for absorption of complex compounds of heavy metal ions. One-stage pyrolysis of vegetable raw materials together with sulfur-containing reagents at a temperature of 350–400 °C produces sulfur-modified biochar. The sulfur-containing reagent sodium thiosulfate $Na_2S_2O_3$ was used as a modifier. at a certain raw material/reagent ratio. The resulting ecosorbent has heat resistance and

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mechanical strength. Ecosorbent does not contain components that can pass into water during its operation. The temperature treatment of the mixture of starting substances to determine the optimal sorption capacity of the obtained ecosorbents in relation to Cd (II), Cu (II), Pb (II) and Zn (II) ions was experimentally substantiated. Sulfur-containing sorption materials, similar to low-molecular organic sulfur compounds, are capable of complex formation with heavy metal ions. Sulfur-containing ecosorbents can be used to clean wastewater and soils contaminated with heavy metals. X-ray phase analysis of samples of sulfur-containing biochar showed the presence of 23–35 % bound sulfur on its surface, which determines the ability to firmly bind metal ions to the surface of the sorbent in an insoluble sulfide form and neutralize heavy metals in water and soil.

Microbiological modification of biochar was carried out. Microbiological modification leads to the creation of biosorption material for strong binding of heavy metal ions. Sulfate-reducing bacteria (SRB) immobilized on the surface of biochar are also capable of converting sorbed heavy metals into insoluble sulfide forms. CRP was isolated from galvanic effluents, oil wastewater and cultivated on an elective medium of the composition (g/cm^3): Na_2CO_3 – 0.1; $CaCl_2$ – 0.01; $MnSO_4$ – 0.02; NaCl - 3.0; Na_2HPO_4 – 1.5; KH_2PO_4 – 1.0; K_2HPO_4 – 1.0; nutrient agar for cultivation of CRP - 20.0 g; distilled water up to 1 dm^3. Sulfate-reducing bacteria (SRB) were identified and assigned to the genera Desulfotomaculum, Desulfosporomusa, Desulfosporosinus, Thermo-desulfobium, Desulfobacter, Desulfobacterium, Desulfobulbus, Desulfococcus, Desulfomicrobium. In the process of formation of carbon material in the process of pyrolysis of cellulosic material on the surface of coal. Reactive groups are created. The concentration of functional (carboxyl and phenolic) groups on the surface of the carbon material determines the ability to remain on the surface of the biomolecule due to a covalent bond or due to -COOH, COCl-, -NH_2-, -N_2 group. A sufficient number of immobilized cells on the surface of the sorbent is 120–200·10^4 cell/g.

The characteristics of the porous structure (specific surface area, total pore volume, pore diameter) were determined by the method of low-temperature nitrogen adsorption. The specific surface area of samples of carbonaceous material from plant waste obtained by pyrolysis was controlled by the amount of iodine adsorption. The specific surface area and pore volume are determined by nitrogen adsorption-desorption isotherm. The specific surface characterizes the surface area of the adsorbent on which adsorbates of a molecular nature can be absorbed. The characteristic is important for comparing different adsorbents with each other, as well as for evaluating the absorption capacity of the adsorbent. The pore volume characterizes the available pore volume in the adsorbent, in which adsorbates can be absorbed. Nitrogen adsorption-desorption isotherms were measured using an AUTOSORB-6B gas adsorption analyzer (Quantachrome, USA). The parameters of the porous structure were calculated using the AUTOSORB-1 program (Quantachrome, USA). The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method.

The method of determining the static exchange capacity consists in determining the number of ions absorbed from a constant volume of the working solution per unit mass of the sorbent.

Results and discussion

The structural-pore and ion exchange characteristics of raw materials, biochar, sulfur-containing biochar and biochar with immobilized sulfate-reducing bacteria were determined (Table 1). The specific surface is the average characteristic of the surface of the internal cavities (channels, pores) of the porous body or the total external surface of the particles of the fragmented phase of the dispersed system. It is defined as the total surface area of the material per unit mass (with units of m^2/kg or m^2/g). The specific surface area of carbonized plant material exceeds 500 m^2/g.

Values of static exchange capacity (SEC) indicate the ability of the material to bind ions of toxic substances. The SEC of biochar increases both in Cl^- and Na^+ cations, which creates prerequisites for increasing its sorption activity in ion exchange reactions of sorption of heavy metal cations Cd (II), Cu (II), Pb (II) and Zn (II). The specific surface area of biochar is higher than that of sulfur-containing biochar and biochar with SRB, which is explained by the immobilization of sulfur and SRB on the surface of biochar (Research results show that ecosorbents based on sulfur-containing biochar from agricultural waste and biochar with immobilized sulfate-reducing bacteria can strongly bind Cd (II), Cu (II), Pb (II) and Zn (II) ions and be used as effective ecosorbents for cleaning aqueous solutions. Their key property is the ability to form insoluble sulfide

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forms of metals on the surface and in the pores of the ecosorbent (Table 1).

Table 1

Structural-porous and ion-exchange characteristics of the raw stuff, biochar, sulfur-containing biochar

Indicator	The rice husk original	The original bagasse	Biochar from rice husk	Biochar from bagasse	Sulfur containing Biochar from rice husk	Sulfur-containing biochar from bagasse
Bulk density, g / cm^3	0.4	0.6	0.6	0.4	0.7	0.5
Specific surface area, m^2 /g	9	2	430–550	417	497–512	398
Total pore volume, cm^3 /g	0.11	0.14	0.42	0.35	0. 39	0. 31
Static exchange capacity for cations (Na^+), mg-eq / g	1.6	1.6	4.12	3.17	6.08	3.02
Static anion exchange capacity (Cl^-), mg-eq / g	0.22	0.28	0.58	0.52	0.38	0.46

The study of the process of sorption of toxic ions of heavy metals by native raw materials, biochar, sulfur-containing biochar and biochar with SRB was carried out under static conditions from aqueous solutions of salts: chlorides of lead, cadmium, zinc and copper. The kinetics of sorption was studied by the limited volume method: a series of flasks with portions of 0.2 g of sorbent were filled with 0.1 dm^3 of the model solution with the initial concentration, kept for 100 min at 20 °C. After certain time intervals, the solutions were filtered and the equilibrium concentration of metal ions was determined by atomic absorption spectroscopy. The amount of sorption was estimated by the decrease in the content of the test ion in the volume of the solution before and after sorption. Figure 3 shows isotherms of sorption of heavy metal ions by ecosorbent from native, pyrolyzed (biochar), sulfur-modified biochar and biochar with SRB.

It was established that sulfur-containing biochar and biochar with immobilized sulfate-reducing bacteria have a high absorption capacity (more than 80–90 %) in relation to Cd (II), Cu (II), Pb (II) and Zn (II) ions. The effect of the pH of the solution on the adsorption capacity of the ecosorbent was studied. Optimal sorption conditions were recorded at pH 5.0. Cd (II) ions are almost completely (70–90 %) extracted by a sulfur-containing ecosorbent from solutions with a pH of 5–6, Cu (II) ions at a pH of 4–5 (58–65 %). Decreased removal of Pb (II) and Zn (II) at pH greater than 6.0 may be associated with solvation and hydrolysis of metal ions. Hydrolysis of salts is the chemical interaction of salts with water, resulting in the formation of a weak electrolyte. The essence of hydrolysis is reduced to the chemical interaction of salt cations and anions with hydroxide ions OH- and H+ ions formed as a result of dissociation of water molecules. As a result of this interaction, a poorly dissociated substance (weak electrolyte) is formed. The processes of maintaining the pH value at a certain level are associated with the hydrolysis of salts. Hydrolysis products and pH of solutions of hydrolyzed salts are determined by the nature of cations and anions. The efficiency of sorption depends on the pH of the solution. The acidity of the environment affects the completeness of extraction of metal ions. Experimental data confirmed the influence of pH of solutions on sorption efficiency.

Research results show that ecosorbents based on sulfur-containing biochar from agricultural waste and biochar with immobilized sulfate-reducing bacteria can strongly bind Cd (II), Cu (II), Pb (II) and Zn (II) ions (Table 2.) and be used as effective ecosorbents for cleaning aqueous solutions.

Table 2.

Efficiency of sorption of heavy metal ions from aqueous solutions

The name of the sorbent	The amount of sorption.%			
	Cu	Zn	Cd	Pb
The original bagasse	13.1	17.0	19.1	17.2
Biochar from bagasse	37.1	39.1	32.3	37.4
Sulfur-containing biochar from bagasse	97.0	94.1	95.0	96.3
Biochar from bagasse with SRB.	92.0	90.0	92.0	94.6
The original rice husk	12.5	16.0	17.4	16.1
Biochar from rice husk	35.1	34.1	34.1	46,1
Sulfur-containing biochar from rice husk	93.0	78.2	92.6	88,2
Biochar from rice husk with SRB	91.7	91.0	90.1	85,!

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Their key property is the ability to form insoluble sulfide forms of metals on the surface and in the pores of the ecosorbent.

The chemical composition of the surface of particles of modified sulfur-containing biochar from a solution of cadmium salt was studied using the method of scanning electron microscopy. It is shown (Fig. 3) that in spectra 1–6, the presence of cadmium is in the range of 1.3–7.66 wt.% and sulfur is 0.98–10.84 wt.%. This indicates a possible chemical interaction in the Cd-S system. Thus, sulfur-containing biochar has the ability to absorb BM, compared to the original biochar, and its specificity is due to the formation of insoluble heavy metal sulfides on the surface and in the pores of the sorbent, which are non-toxic.

spectrum	C	O	Si	S	Ca	Cd	Cu
%							
1	57.15	30.16	5.53	0.98	2.32	1.99	1.87
2	66.20	24.31	2.70	1.50	1.80	2.39	1.10
3	81.58	11.94	0.96	1.38	2.15	1.30	0.71
4	70.04	21.06	2.75	2.1	0.15	2.65	1.25
5	10.22	41.94	11.32	10.84	14.62	7.66	2.90
6	32.00	39.55	21.93	1.42	1.72	2.00	1.38

Fig. 3. Chemical composition of sulfur-containing ecosorbent particles after sorption of Cd(II) ions

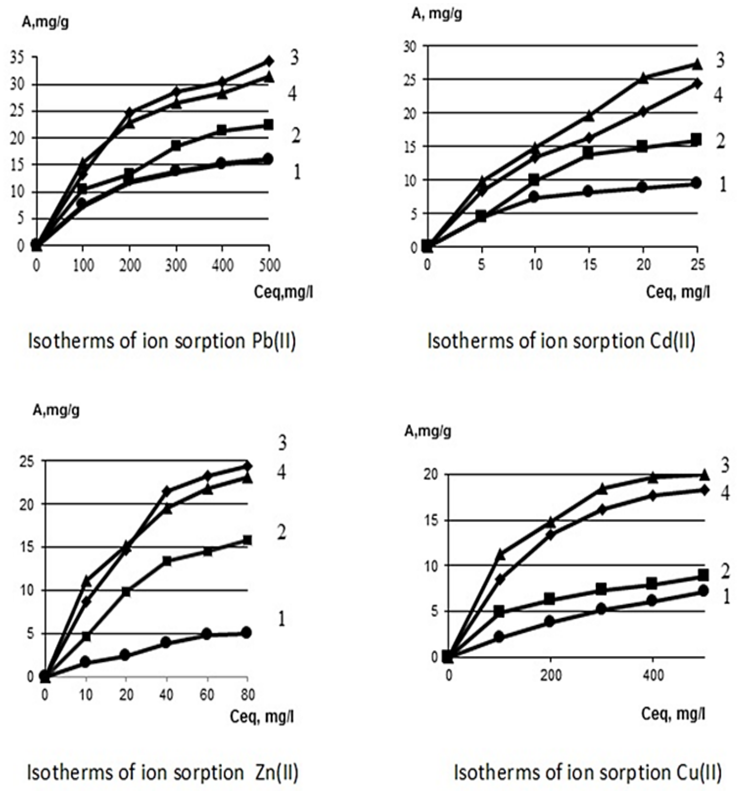

Fig. 4. Isotherms of sorption of heavy metal ions by ecosorbent: 1-native bagasse; 2 – biochar; 3 – sulfur-modified biochar; 4– biochar with SRB

The given isotherms of sorption of Cd(II), Cu(II), Pb(II) and Zn(II) ions by sugarcane ecosorbent show that the absorption capacity of the biosorption complex for heavy metal ions is almost at the same level as the absorption capacity of sulfur-containing biochar (Fig. 4). The study of the influence of the fractional composition of the ecosorbent on its binding capacity showed that shallow fractions are more effective. The conducted studies showed a correlation between the decrease in the concentration of the studied ions in the simulated solution and the increase in the content of metals in a bound state on the surface of the sorbent particles. The properties of ecosorbents are mainly determined by the chemical nature of the surface and to some extent depend on the features and methods of sorbent synthesis.

Conclusions

The conditions for obtaining effective ecosorbents for the removal of Cd(II), Cu(II), Pb(II) and Zn(II) ions from aqueous solutions based on biochar from agricultural waste were investigated. The conditions of biochar modification by sulfur- and sulfate-reducing bacteria were studied. A comparative analysis of structural-porous and sorption properties of various modifications of ecosorbents with biochar, sulfur-containing biochar – raw material, pyrolyzed raw material (biochar), sulfur-containing biochar and biochar with immobilized sulfate-reducing bacteria was performed. Sorptive binding of metals by sulfur-containing biochar and biochar with immobilized sulfate-reducing bacteria reaches 80–90 % due to the formation of insoluble sulfide forms of metals on the surface of the sorbent. It was established that the modification according to the proposed method allows to significantly improve the sorption properties of the material. Chemical and microbiological modification of biochar leads to the creation of an effective ecological sorption material for strong binding of heavy metal ions. The prospects of using lignocellulosic agricultural waste in the creation of active ecosorbents for the detoxification of toxic metals in the environment are shown. The obtained results, taking into account the cheapness and availability of raw materials, are promising for solving specific practical problems of man-made pollution.

References

[1] Chaffai, R., Koyama, H. (2011). Heavy metal tolerance in Arabidopsis thaliana, *Adv. Bot. Res,* 60, 1–49. doi: 10.1016/B978-0-12-385851-1.00001-9.

[2] Meyer, S.; Glaser, B., Quicker, P. (2011). Technical, economical, and climate-related aspects of biochar production technologies. A literature review, *Environ. Sci. Technol.*, 45, 9473–9483. doi: 10.1021/es201792c

[3] Reddy, D.H.K., Seshaia, K., Reddy, A.V.R., Rao, M.M. Wang, M.C. (2010). Biosorption of Pb^{2+} from Aqueous Solutions by Moringa oleifera Bark: Equilibrium and Kinetic Studies, *Journal of Hazardous Materials, 174*, 831–838.

[4] Ngah, W.S.W., Hanafiah, M.A.K.M. (2008). Removal of Heavy Metal Ions from Wastewater by Chemically Modi-fied Plant, Wastes as Adsorbents: A Review, *Bioresource Technology*, *99*, 3935–3948. http://dx.doi.org/10.1016/j.biortech.2007.06.011

[5] Tarnovsky, D.V., Tsyba, M.M., Kuznetsova, L.S., Khodakovska, T.A., Romanova, I.V. (2021). Physico-chemical properties of cerium and ferric doped titanium hydroxides synthesized by two methods, *Journal of Chemystry and Technologies*, *29*(2), 192–199. https://doi.org/10.15421/jchemtech.v29i2.232199.

[6] Atafar, Z., Mesdaghinia, A., Nouri, J., Homaee, M., Yunesian, M., Ahmadimoghaddam, M., Mahvi, A. H. (2010). Effect of fertilizer application on soil heavy metal concentration, *Environ. Monit, Asses.*, 160, 83–89. doi: 10.1007/s10661-008-0659-x

[7] Liu, X., Na, S., Lu, Z. D., Liu, Z. (2013). Adsorption, Concentration, and Recovery of Aqueous Heavy Metal Ions with the Root Powder of Eichhornia crassipes, *Ecological Engineering, 60*, 160–166. http://dx.doi.org/10.1016/j.ecoleng.2013.07.039

[8] Boonstra J., Dijman H., Lawrence R. And Buisman C.J.N. (2002). Water treatment and metals recycling using biogenic sulfide. Recycling and waste treatment in mineraland metal processing: technical and economic aspects, *Lulea, Sweden.*, l, 691-698.

[9] Xu, M., Yin, P., Liu, X., Tang, Q., Qu, R., Xu, Q. (2013). Utilization of Rice Husks Modified by Organomultipho-sphonic Acids as Low-Cost Biosorbents for Enhanced Adsorption of Heavy Metal Ions, *Bioresource Technology*, 149. 420–424. http://dx.doi.org/10.1016/j.biortech.2013.09.075

[10] Kwon, J.S., Yun, J.H., Kim, S.O., Jo, H.Y. (2010). Removal of Divalent Heavy Metals (Cd, Cu, Pb, and Zn) and Arsenic (III) from Aqueous Solutions Using Scoria: Kinetics and Equilibria of Sorption, *Journal of Hazardous Materials,* 174, 307–313. http://dx.doi.org/10.1016/j.jhazmat.2009.09.052

[11] M N Mohamad Ibrahim., W S Wan Ngah, M S Norliyana, W R Wan Daud, M Rafatullah, O Sulaiman, R Hashim (2010). A Novel Agricultural Waste Adsorbent for the Removal of Lead (II) Ions from Aqueous Solutions, *Journal of Hazardous Mate-rials,* 182, 377–385. http://dx.doi.org/10.1016/j.jhazmat.2010.06.044

[12] Ding, D., Zhou, L., Kang, F., Yang, S., Chen, R., Cai, T., Duan, X., Wang, S. (2020). Synergistic Adsorption and Oxidation of Ciprofloxacin by Biochar Derived from Metal-Enriched Phytoremediation Plants: Experimental and Computational Insights, *ACS Applied Materials & Interfaces*, 12, 48, 53788–53798.

[13] Demirbas, A. (2008). Heavy Metal Adsorption onto Agro-Based Waste Materials: A Review, *Journal of Hazardous Materials*, *157*, 220–229. http://dx.doi.org/10.1016/j.jhazmat.2008.01.024

[14] Kaur, R., Singh, J., Khare, R., Cameotra, S.S., Ali, A. (2013). Batch Sorption Dynamics, Kinetics and Equilibrium Studies of Cr(VI), Ni(II) and Cu(II) from Aqueous Phase Using Agricultural Residues, *Applied Water Science*, 3, 207–218

[15] dos Reis, G. S., Bergna, D., Grimm, A., Lima, E. C., Hu, T., Naushad, M., Lassi, U. (2023). Preparation of highly porous nitrogen-doped biochar derived from birch tree wastes with superior dye removal performance. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 669*, 131–493. https://doi.org/10.1016/j.colsurfa.2023.131493

[16] Liang, S., Guo, X., Tian, Q. (2011). Adsorption of Pb^{2+} and Zn^{2+} from Aqueous Solution by Sulfured Orange Peel, *Desalination, 275*, 212–216. http://dx.doi.org/10.1016/j.desal.2011.03.001

[17] Kamar, F.H., Nechifor, A.C., Mohammed, A.A., Albu, P.C., Craciun, M.E. (2015). Removal of lead and cadmium ions from aqueous solutions using walnut shells as low-cost adsorbent materials, *Revista de Chimie, 66*(5), 615–620.

[18] Ding, D., Zhou, L., Kang, F., Yang, Sh., Chen, R., Cai, T., Duan, X., Wang, Sh. (2020). Synergistic Adsorption and

Oxidation of Ciprofloxacin by Biochar Derived from Metal-Enriched Phytoremediation Plants: Experimental and Computational Insights, *ACS Applied Materials & Interfaces, 12*(48), 53788–53798.

[19] Sungsinchai, S., Niamnuy, Ch., Devahastin, S., Chen, X. D., Chareonpanich, M. (2023). Effect of the Structure of Highly Porous Silica Extracted from Sugarcane Bagasse Fly Ash on Aflatoxin B1 Adsorption. *ACS Omega, 8*(22), 19320–19328. https://doi.org/10.1021/acsomega.2c08299

[20] Hamed, R., Jodeh, S., Hanbali, G., Safi, Z., Berisha, A., Xhaxhiu, K., Dagdag, O. (2022). Eco-Friendly Synthesis and Characterizationof Double-Crossed Link 3D Graphene Oxide Functionalized with Chitosan for Adsorption of Sulfamethazine from Aqueous Solution: Experimental and DFT Calculations. *Front. Environ. Sci., 10,* 930693.

[21] El-Moselhy, K.M., Azzem, M.A., Amer, A., Al-Prol, A.E. (2017). Adsorption of Cu (II) and Cd (II) from aqueous solution by using rice husk adsorbent, *Physical Chemistry: An Indian Journal*, *12*(2), 1–13.