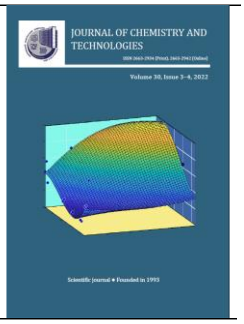
Journal of Chemistry and Technologies, 2022, *30*(4), 659-666

Journal of Chemistry and Technologies

pISSN 2663-2934 (Print), ISSN 2663-2942 (Online).

journal homepage: http://chemistry.dnu.dp.ua



UDC 63.502: 504.57

MODIFIED RICE HUSK BIOCHAR FOR BINDING Cd(II), Cu(II) IONS IN AQUEOUS SOLUTIONS

Andriy V. Khokhlov, Lyudmila I. Khokhlova*

Institute for Sorption and Problems of Endoecology of National Academy of Sciences of Ukraine, 13 General Naumov Str., Kyiv, 03164, Ukraine

Received 2 December 2022; accepted 7 January 2023; available online 26 January 2023

Abstract

The possibility of obtaining an ecosorbent based on carbon material from rice husks modified with sulfur for the removal of Cd(II), Cu(II) ions from aqueous solutions is substantiated. The features of obtaining and modifying coal material from rice husks are noted. 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 was obtained by chemical modification by one-stage co-pyrolysis of rice husks with sulfur-containing reagents at a temperature of 350–400 °C. The resulting sulfur-containing ecosorbent has thermal stability and mechanical strength. A comprehensive study of the structural-porous and sorption properties of the original and sulfur-modified biochar has been carried out. The sorption capacity of the initial biochar from rice husks and sulfur-containing biochar was estimated from the decrease in the concentration of Cd(II) and Cu(II) ions in aqueous solutions of $CuSO_4 \cdot 5H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ salts before and after treatment with ecosorbent. The initial concentrations of pollution in water and soil media were 2–6 mg/L for Cd(II) and 132–396 mg/L for Cu(II). Sulfur-containing biochar has a high absorption capacity for Cd(II) and Cu(II) ions (more than 90 %) compared to the original biochar. Its specificity is due to the formation of insoluble cadmium and copper sulfides on the surface and in the pores of the sorbent. Studies show that sulfur-modified rice husk biochar can strongly bind heavy metal ions and be used as an effective ecosorbent for the purification of aqueous solutions. The key property is the ability to form insoluble sulfide forms of metals on the surface and in the pores of the ecosorbent.

Keywords: adsorption; cadmium; copper; rice husk; pyrolysis; biochar; chemical modification; sulfides.

МОДИФІКОВАНЕ БІОВУГІЛЛЯ З РИСОВОГО ЛУШПИННЯ ДЛЯ ЗВ'ЯЗУВАННЯ ІОНІВ Cd (II), Cu (II) У ВОДНИХ РОЗЧИНАХ

Андрій В. Хохлов, Людмила Й. Хохлова

Інститут сорбції та проблем ендоекології НАН України, вул. Генерала Наумова, 13, м. Київ, 03164, Україна

Анотація

Обґрунтовано можливість отримання екосорбенту на основі вуглецевого матеріалу з рисового лушпиння, модифікованого сіркою, для видалення іонів Cd(II), Cu(II) з водних розчинів. Відзначено особливості отримання та модифікації вугільного матеріалу з рисового лушпиння. Температурні параметри та тривалість процесу піролізу визначали експериментально з умов максимального вмісту біовугілля в піролізаті. Сірковмісне біовугілля отримували шляхом хімічної модифікації одностадійним со-піролізом рисового лушпиння з сірковмісними реагентами при температурі 350–400 °С. Отриманий сірковмісний екосорбент має термічну стабільність і механічну міцність. Проведено комплексне дослідження структурно-пористих та сорбційних властивостей вихідного та модифікованого сіркою біовугілля. Сорбційну здатність вихідного біовугілля з рисового лушпиння і сірковмісного біовугілля оцінювали за зниженням концентрації іонів Cd(II) і Cu(II) у водних розчинах солей $CuSO_4 \cdot 5H_2O$ і $Cd(NO_3)_2 \cdot 4H_2O$ до та після обробки екосорбентом. Початкові концентрації забруднення водного середовища становили 2–6 мг/л для Cd(II) та 132–396 мг/л для Cu(II). Сірковмісне біовугілля має високу поглинаючу здатність відносно іонів Cd(II) і Cu(II) (більше 90 %) порівняно з вихідним біовугіллям. Його специфічність обумовлена утворенням нерозчинних сульфідів кадмію та міді на поверхні та в порах сорбенту. Дослідження показують, що біовугілля з рисового лушпиння, модифіковане сіркою, може міцно зв'язувати іони важких металів і використовуватися як ефективний екосорбент для очищення водних розчинів.

Ключові слова: адсорбція; кадмій; мідь; рисове лушпиння; піроліз; біовугілля; хімічна модифікування; сульфіди.

**Corresponding author: e-mail address: khokhlova.lyudmila@gmail.com*

doi: 10.15421/jchemtech.v30i4.268174

Journal of Chemistry and Technologies, 2022, *30*(4), 659-666

Introduction

Currently, the main and dangerous pollutants of ecosystems are heavy metals. This is due to their high toxicity to living organisms at relatively low concentrations, as well as the ability to bioaccumulate [1–3]. The source of HMs is wastewater from electroplating industries, ferrous and non-ferrous metallurgy enterprises, and machine-building plants [4–6]. The removal of heavy metals is a difficult task, since HMs often have low concentration, are capable of various chemical and physicochemical reactions, and have the ability to move, redistribute, and migrate. Heavy metals, unlike organic pollutants, are not destroyed, but only pass from one form of existence to another, are part of salts, oxides, and organometallic compounds.

To clean ecosystems from heavy metals, various methods are used, including sorption [7–8]. To this end sorbents based on activated carbons, zeolites, natural materials and minerals with a high cation exchange capacity, etc. are used. [9–10]. Reducing the toxicity of heavy metals is possible due to the binding of their mobile forms into sparingly soluble compounds (sulfides, carbonates, phosphates, hydroxides, etc.) on the surface of sorbents [11–12].

An urgent problem is the search for effective ecosorbents that can reduce environmental pollution with toxic heavy metals and meet the basic requirements – harmlessness and non-toxicity, high adsorption capacity, selective sorption of toxic compounds and the complete absence of side effects. The attraction of new types of renewable raw materials, in particular agricultural waste, in order to obtain sorbents for the detoxification of heavy metals is relevant both in scientific and practical terms [13–14]. One of the promising areas is the production of carbon sorption materials (biochar) from lignocellulosic waste [15–18]. Plant waste is a promising natural renewable material for ecosorbents. Biochar is a stable carbon-containing product that is synthesized as a result of pyrolysis (carbonization) of plant biomass [21–25].

In this study, the possibility of obtaining an ecosorbent from rice husks was studied. Rice is one of the most important food products of agriculture in the world. At the same time, large volumes (up to 20% wt.) of husks are the result of industrial processing of rice. In major rice-producing countries, rice waste amounts to millions of tons. Pyrolyzed rice husks and additionally chemically modified ones can be used in environmental technologies to reduce the toxicity of heavy metals in ecosystems.

The priority is the joint solution of two problems: environmental - the disposal of rice waste, and technological - the production of demanded solid products for solving environmental problems.

Materials and Methods

The objects of the study were: rice husks; pyrolyzed rice husk - biochar; biochar modified with sulfur. The composition of lignocellulite-containing plant waste justifies the possibility of obtaining carbon material (biochar) from them.

Rice husk is a fibrous substance that contains moisture, lignin, cellulose, pentosans, a small amount of protein and vitamins, as well as a mineral component, consisting of 92–97 % silicon dioxide. Rice husks contain about 70–85 % organic matter. When it is burned, ash is formed – about 20 %.

In the process of heat treatment of rice husks, 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. The temperature parameters and the duration of the pyrolysis process were determined experimentally from the conditions of the maximum content of biochar (Table 1) in the pyrolyzate.

Different pyrolysis conditions lead to different proportions of each final product. This means that certain pyrolysis conditions are selected depending on the need to obtain a particular product. For biochar production, slow pyrolysis produces the maximum amount of biochar. Biochar produced under different technological conditions will differ in physical and mechanical composition, namely, in porosity, bulk density, strength, hygroscopicity and moisture absorption. The porosity slightly developed in the temperature range up to 300 °C and sharply increased with an increase in temperature from 300 to 400°C. The ash content with an increase in temperature from 170 to 300 °C at the beginning decreased from 21.03 to 4.89 % wt. then increased to 8.72 % wt. at a temperature of 450 °C.

When obtaining ecosorbents, biochar modification was used to absorb complex compounds of heavy metal ions. Chemical modifiers contribute to the development of the cellular structure of biochar.

Table 1

Composition of rice husk pyrolyzate (biochar C, silica SiO_2) depending on the temperature and duration of pyrolysis.

Pyrolysis temperature, ° C	Process duration, min.	The content of pyrolysis products. %	
		C	SiO_2
250	10	20	30
	40	25	35
	60	37	27
300	10	60	40
	40	65	35
	60	72	28
400	10	78	22
	40	89	11
	60	87	13
450	10	82	18
	40	79	21
	60	77	23
500	10	60	40
	40	55	45
	60	57	43

The sulfur-containing modifier used in our case diffuses into the internal structure of the carbon matrix during pyrolysis, expanding existing pores and creating new ones. Modification of biochar with sulfur makes it possible to obtain sulfur-containing biochar. The proposed method for producing sulfur-containing biocarbon ecosorbent from rice husk is a one-stage pyrolysis of raw materials together with sulfur-containing reagents at a temperature of 350–450 °C. Sodium thiosulfate $Na_2S_2O_3$ was used as a modifier. X-ray phase analysis of the obtained samples of sulfur-containing biocoals showed the presence of up to 35 % of bound sulfur on its surface. The resulting ecosorbent has thermal stability and mechanical strength. Biochar was obtained with a specific surface area of up to 874 m^2/g and a total pore volume of up to 0.713 cm^3/g.

The properties of the surface of the carbon material were evaluated according to generally accepted methods for determining the indicators: specific surface area; the content of acid and carboxyl groups. On the basis of the results obtained, the physicochemical parameters of the raw material pyrolysis process were calculated and the optimal conditions for obtaining the carbon material were determined.

Studies of the sorption of Cd(II), Cu(II) ions were carried out under static conditions from aqueous solutions of $CuSO_4{\cdot}5H_2O$ and $Cd(NO_3)_2{\cdot}4H_2O$ salts. The sorption kinetics was studied by the limited volume method: 0.1 dm^3 of a model solution with an initial concentration of 100 mg/dm^3 was poured into a row of flasks with sorbent portions of 0.2 g and kept for 100 min at 20 °C. At certain intervals, the solutions were filtered and the equilibrium concentration of metal ions was determined by atomic absorption spectroscopy. The sorption value was estimated from the decrease in the content of the studied ion in the volume of the solution before and after sorption.

Fractographic studies were conducted to determine the number of bound Cd((II) and Cu(II) ions on the surface of the ecosorbent in the form of insoluble compounds (after intensive washing with water). The determination of the quantitative elemental composition of the ecosorbent particles was carried out by scanning electron microscopy and micro-X-ray spectral analysis, which consists of a JSM-35CF JEOL (Japan) scanning electron microscope equipped with a Link 860 X-ray energy dispersive analyzer (Oxford, Great Britain) Particle spectra of averaged powder sorbent samples indicate ion binding Cd((II) and Cu(II) on the surface of powder particles.

Results and discussion

A comprehensive study of the structural-porous and sorption properties of the original rice husk, rice husk biochar and sulfur-containing biochar was carried out. The structural-pore and ion-exchange characteristics of the feedstock, biochar, and sulfur-containing biochar were determined (Table 2). According to its structure, biochar belongs to the class of carbonized substances, due to the commonality of their characteristic structural element. The structural element of a carbonized substance is the atomic network of polymerized carbon. The constituent elements H, O, N, P, and S explain the reactivity of the resulting biochar. The presence of micro- and mesopores in biochar determines its high internal specific surface area.

Journal of Chemistry and Technologies, 2022, *30*(4), 659-666

Sulfur-containing sorption materials, like low molecular weight organic sulfur compounds, are capable of complex formation with heavy metal ions. Sulfide and hydrosulfide groups are present on the surface of the sulfur-containing carbon sorbent, and the formation of C-S-C groups on unsaturated lattice centers is also possible. The formation of sulfide, hydrosulfide and C-S-C groups in the sorption material determines its specificity with respect to a number of elements prone to the formation of poorly soluble toxic heavy metal sulfides on the surface and in the pores of the resulting sulfur-containing sorbent.

Table 2

Structural-pore and ion-exchange characteristics of the original rice husk, biochar, sulfur-containing biochar

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

The specific surface area of biochar is higher than that of sulfur-containing biochars, which is explained by the immobilization of sulfur on the biochar surface.

The obtained results show that sulfur-modified biocarbon ecosorbents from rice husks have a sufficiently high exchange capacity with respect to Cu (II) and Cd (II) ions. A comparative analysis of the adsorption capacity for Cd (II), Cu (II) cations of biochar from rice husks, biochar modified with sulfur was carried out. The sorption capacity of ecosorbents was determined under conditions of mixing for a certain time aqueous solutions of $CuSO_4 \cdot 5H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ salts and was estimated by the decrease in the concentration of Cd(II) and Cu(II) ions before and after treatment with the ecosorbent (Table 3).

It is shown that the sorption capacity of the sulfur-containing carbon sorbent obtained from rice husks ensures the extraction of cadmium ions from solutions of 70 %–90 %. The extraction of copper ions from solutions by the proposed sulfur-containing carbon sorbent is at least 60 %.

Table3

Sorption properties relative to Cd (II), Cu (II) of the initial sorbent on the biochar from rice husk and sulfur-containing biochar

Indicator	**Biochar from rice husk**		**Sulfur-containing biochar from rice husk**	
	Cd (II)	Cu (II)	Cd (II)	Cu (II)
$C_{initial.}$, mg / l.	6.01	100.00	6.00	100.00
pH	6.43	5.08	6.43	5.08
$C_{Residual}$, mg /l	0.34	7.90	2.22	42.00
pH	7.95	5.12	10.18	5.10
Sorption G, mg/g	0.28	0.65	0.19	2.55
% binding	94	13	63	51
$C_{initial.}$, mg / l.	46.00	298.00	46.00	298.00
pH	7.18	5.20	7.18	5.20
$C_{Residual}$, mg / l.	9.44	141.00	0.70	13.20
Sorption G, mg/g	1.83	7.50	2.24	14.00
% binding	79	50	97	93
$C_{initial.}$, mg / l.	151.90	550.00	151,90	550.00
pH	7.16	5.40	7.16	5.40
$C_{Residual}$, mg / l.	7.78	320.00	11.00	280.00
pH	8.33	7.00	8.20	7.30
Sorption G, mg/g	7.20	9.40	6.60	11.70
% binding	95	34	89	42

Journal of Chemistry and Technologies, 2022, *30*(4), 659-666

The efficiency of sorption depends on the pH of the solution. The acidity of the medium affects the completeness of the extraction of metal ions. Experimental data on the effect of pH solutions on the sorption efficiency of sorbents are shown in Fig. 1. It was found that Cd (II) ions are almost completely (70–90 %) extracted by sulfur-containing ecosorbent from solutions with pH 6–8, Cu (II) ions at pH 4-6 (58–65 %).

The study of the sorption kinetics of Cd (II) and Cu (II) ions by a sulfur-containing ecosorbent showed (Fig. 2) that the sorption of the studied metal ions reached its maximum value in 1–2 hours from the start of phase mixing.

The dependence of the sorption capacity of the ecosorbent with respect to Cd (II) ions and Cu (II) ions on their concentration in the medium under study was studied (Fig. 3).

The effect of the initial concentration of metal ions on the process of binding and their detoxification was studied. The initial concentration of heavy metal ions ranged from 2 to 5 MPC (maximum allowable concentration for drinking water). In the process of adsorption, the value of the sorption capacity is important - the limiting amount of the absorbed substance by the specific mass of the adsorbent (in grams). This is characteristic of the efficiency of the adsorption process, in our case, % binding (S, %). With bimetallic contamination, the % binding of Cu (II) and Cd (II) slightly decreases.

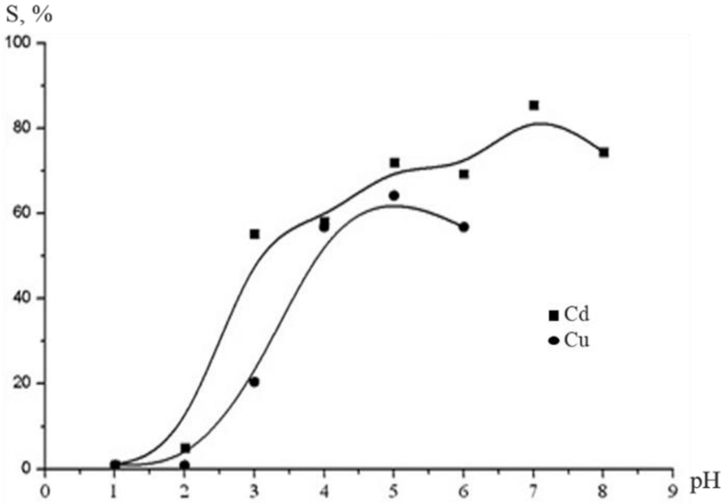


Fig. 1. Dependence of the degree of binding of Cu (II) and Cd (II) by the sulphurous rice husk biochar on the pH of the solution (C_{Cu} = 390 mg/l, C_{Cd} = 6 mg/l, V = 50 ml; ecosorbent m = 1 g, τ = 1 day, t = 20 ±2°C).

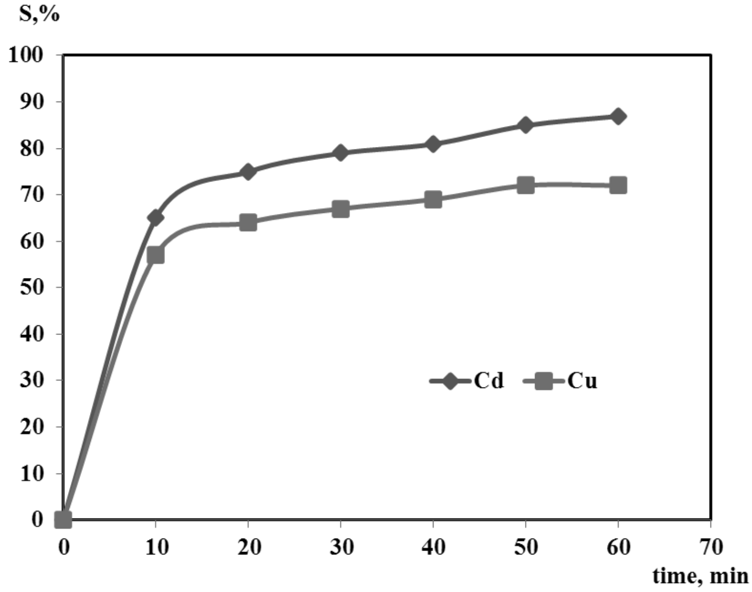


Fig. 2. Dependence of the degree of sorption of Cu(II) and Cd(II) on the sulphurous rice husk biochar on the time of contact of the solution with the sorbent (C_{Cu} = 390 mg/L; C_{Cd} = 6 mg/L; V = 50 ml; m eco sorbent = 1 g; t = 20 ± 2°C).

The study of the influence of the fractional composition of the ecosorbent on its binding capacity showed that fine fractions were more effective. The properties of ecosorbents are mainly determined by the chemical nature of the surface and, to a certain extent, depend on the features and methods of preparation.

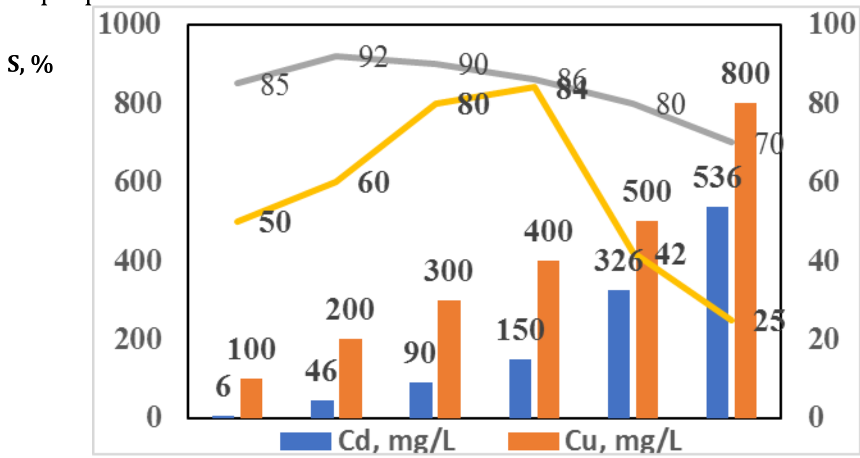


Fig. 3. Dependence of the sorption capacity of the sulphurous rice husk biochar on the concentration of Cu(II) and Cd(II) (V = 50 ml, m = 1 g, τ = 2 days, t = 20 ± 2 °C).

The studies performed have shown a correlation between a decrease in the concentration of Cd((II) and Cu(II) in a model solution and an increase in the content of metals in a bound state on the surface of sorbent particles. Figure 4 shows an electronic image of particles of sulfur-containing ecosorbent from pyrolyzed rice husk with sorbed Cd((II) and Cu(II) ions after treatment of model solutions.

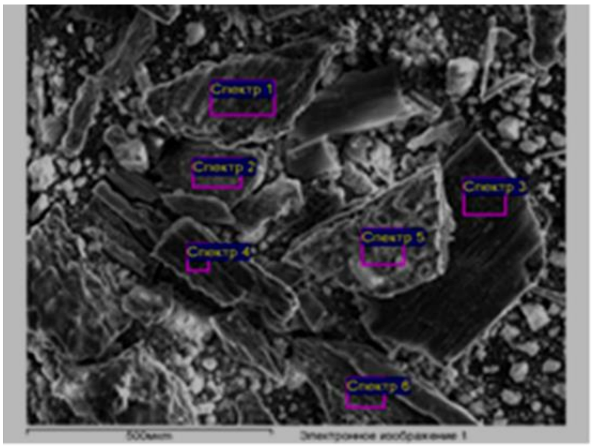


Fig. 4. Electronic image of particles of the sulphurous rice husk biochar after sorption of Cd ((II) and Cu (II) ions from aqueous solutions.

Table 4 shows the elemental composition of sorbent particles. The spectra of sorbent particles indicate the binding of Cd((II) and Cu(II) ions by the particle surface. The studies were carried out on a scanning electron microscope equipped with a Link 860 X-ray analyzer.

Table 4

Elemental composition of particles of sulfur-containing ecosorbent (%) after sorption of Cd ((II) and Cu (II) ions from aqueous solutions.

Specter	C	O	Si	S	P	Ca	Cd	Cu
Specter 1	57.15	30.16	5.53	**0.98**	0	2.32	1.99	1.87
Specter 2	66.20	24.31	2.70	**1.50**	0	1.80	2.39	1.10
Specter 3	81.58	11.94	0.96	**1.38**	0	2.15	1.30	0.71
Specter 4	70.04	21.06	2.75	**2.1**	0	0.15	2.65	1.25
Specter 5	10.22	41.94	11.32	**10.84**	0	14.62	7.66	2.90
Specter 6	32.00	39.55	21.93	**1.42**	0	1.72	2.00	1.38

Thus, the obtained results show that ecosorbents based on sulfur-modified rice husk pyrolyzate can be used as an effective, affordable and cheap sorption material for extracting copper and cadmium ions from aqueous systems.

Conclusions

Studies have been carried out on the effect of thermal treatment of rice husks and the conditions for modifying the surface of the obtained biochar on the sorption properties with respect to Cd (II) and Cu (II) ions.

The proposed method for obtaining a sulfur-containing biocarbon ecosorbent from rice husks consists of a one-stage co-pyrolysis of the feedstock with a sulfur-containing reagent $Na_2S_2O_3$ at a temperature of 350–400 °C. As a result, biochar modified with sulfur is formed. The modifier used in our case, sulfur, diffuses into the internal structure of the carbon matrix during pyrolysis, expands existing pores and creates new pores.

Sulfur-containing biochar has a high absorption capacity for Cd (II) and Cu (II) ions compared to the original biochar. Its specificity is due to the formation of insoluble heavy metal sulfides on the surface and in the pores of the sorbent. Sorption binding of ecosorbents reaches values of 70–90 %.

Referenses.

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

[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] Ahmed, M. J. K, Ahmaruzzama, M. (2016). A review on potential usage of industrial waste materials for binding Heavy metal ions from aqueous solutions, *J. Water Process. Eng.*, 10, 39–47. doi: 10.1016/j.jwpe.2016.01.014

[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] 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.

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

[7] Reddy, D. H. K., Seshaia, K., Reddy, A. V. R., Rao, M. M., Wang M. C. (2010) Biosorption of Pb2+ from Aqueous Solutions by Moringa oleifera Bark: Equilibrium and Kinetic Studies, *Journal of Hazardous Materials*, 174, 831–838. http://dx.doi.org/10.1016/j.jhazmat.2009.09.128

[8] Boonstra, J., Dijman, H., Lawrence, R. 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] 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

[10] Xu, M., Yin, P., Liu, X., Tang, Q., Qu, R., Xu Q. (2013). Utilization of Rice Husks Modified by Organomultiphosphonic 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

[11] Ibrahim M.N.M., Ngah W.S.W., Norliyana M.S., Daud W.R., Rafatullah M., Sulaiman O., et al. (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] Kwon J.S., Yun S.T., Lee J.H., Kim S.O. and 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

[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] Dahu Ding, Liang Zhou, Fuxing Kang, Shengjiong Yang, Rongzhi Chen, Tianming Cai, Xiaoguang Duan, Shaobin Wang. (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. https://doi.org/10.1021/acsami.0c15861

[15] Yunchao Li, Bo Xing, Xiaoliu Wang, Kaige Wang, Lingjun Zhu, Shurong Wang. (2019). Nitrogen-Doped Hierarchical Porous Biochar Derived from Corn Stalks for Phenol-Enhanced, *Adsorption. Energy & Fuel.*, 33, 12, 12459-12468. https://doi.org/10.1021/acs.energyfuels.9b02924

[16] Kaur R., Singh J., Khare R., Cameotra S.S. and 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. http://dx.doi.org/10.1007/s13201-012-0073-y

[17] Liang S., Guo X. and Tian Q. (2011). Adsorption of Pb2+ and Zn2+ from Aqueous Solution by Sulfured Orange Peel, *Desalination,* 275, 212-216. http://dx.doi.org/10.1016/j.desal.2011.03.001

[18] Merike Peld, Kaiato Tonsuaadu and Villem Bender. (2004). Sorption and Desorption of Cd2+ and Zn2+ Ions in Apatite-Aqueous Systems, *Environ. Sci. Technol.*, 38, 5626-5631.

Journal of Chemistry and Technologies, 2022, *30*(4), 659-666

[19] Witoon, T., Chareonpanich, M., Limtrakul, J. (2008). Synthesis of bimodal porous silica from rice husk ash via sol-gel process using chitosan as template, *Materials Letters, 62*(10-11), 1476–1479.

[20] 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.

[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.

[22] Liu, D.; Li, B.; Wu, J.; Liu, Y. (2020). Elemental mercury capture from industrial gas emissions using sulfides and selenides, *A review. Environ. Chem. Lett*, 19, 1–17.

[23] Fang, L.; Li, L.; Qu, Z.; Xu, H.; Xu, J.; Yan, N. (2018) A novel method for the sequential removal and separation of multiple heavy metals from wastewater. *J. Hazard. Mater.*, *342*, 617–624.

[24] Xia, D.; Gong, F.; Pei, X.; Wang, W.; Li, H.; Zeng, W.; Wu, M. (2018). Papavassiliou, D.V. Molybdenum and tungsten disulfides-based nanocomposite films for energy storage and conversion: A review. *Chem. Eng. J., 348*, 908–928.

[25] Annachhatre, A. P., Suktrakoolvait, S. (2001). Biological sulfate reduction using molasses as a carbon source. *Water Environment Research*, 73, 118–126.