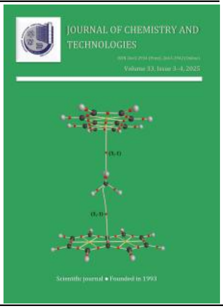
Journal of Chemistry and Technologies, 2025, *33*(3), 728-733

Journal of Chemistry and Technologies

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

journal homepage: http://chemistry.dnu.dp.ua
editorial e-mail: chem.dnu@gmail.com



UDC 63.502: 504.57

CARBON-MINERAL ECOSORBENTS BASED ON LIGNOCELLULOUS WASTE AND ZEOLITE FOR BINDING HEAVY METAL IONS

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Received 29 April 2025; accepted 10 June 2025; available online 20 October 2025

Abstract

A carbon-mineral ecosorbent was obtained by heat treatment of a mixture of rice husk and zeolite. To obtain a composite carbon-mineral ecosorbent, a mixture of rice husk and zeolite in various proportions of plant and mineral components was subjected to general pyrolysis under various temperature conditions (250–600 °C) without the use of toxic chemicals to obtain a series of biocoal-clay composites. The pyrolysis process lasted from 10 to 60 minutes. In this case, destruction of organic substances occurs, and the final decomposition product (active amorphous carbon) settles on the catalytic centers of the aluminosilicate surface of the zeolite. The carbon content in the sorbent is 8–19 %. In this case, the zeolite containing active carbon lobes on the surface is a consolidated nanostructured material. The obtained sorbent samples differed in the initial ratio of the plant and mineral components. During thermal treatment of the mixture in an oxygen-free atmosphere, activated carbon nanoparticles of 2–3 nm in size are formed on the zeolite surface. The characteristics of the composites, making them promising sorbents of pollutants, include uniform micromorphology of plate particles, improved mesoporous structure and surface area (53.0 m^2/g), as well as abundant and diverse functional groups containing oxygen / carbon. The structural-chemical and sorption properties of the obtained product in relation to Cu^{2+}, Pb^{2+}, Cd^{2+}, Sr^{2+}, Ni^{2+} ions were studied during extraction from model solutions. The composite obtained at 600 °C and 10 wt.% zeolite showed the highest removal of heavy metal ions from an aqueous solution.

Keywords: adsorption; cadmium; lead; zinc; copper; rice husk; zeolite; pyrolysis; biochar; sorption properties.

ВУГЛЕЦЬ-МІНЕРАЛЬНІ ЕКОСОРБЕНТИ НА ОСНОВІ ЛІГНОЦЕЛЮЛОЗНИХ ВІДХОДІВ І ЦЕОЛІТА ДЛЯ ЗВ'ЯЗУВАННЯ ІОНІВ ВАЖКИХ МЕТАЛІВ

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Анотація

Шляхом термообробки суміші рисового лушпиння та цеоліту отриманий вуглець-мінеральний екосорбент. Для отримання композитного вуглець-мінерального екосорбенту суміш рисового лушпиння та цеоліту в різних співвідношеннях рослинної та мінеральної складової була піддана спільному піролізу за різних температурних умов (250–600 °C) без використання токсичних хімікатів для отримання серії композитів біовугілля-глина. Процес піролізу тривав від 10 до 60 хв. У цей час відбувається деструкція органічних речовин, а кінцевий продукт розкладу (активний аморфний вуглець) осідає на каталітичних центрах алюмосилікатної поверхні цеоліту. Вміст вуглецю в сорбенті складає 8–19 %. Водночас цеоліт, що містить на поверхні часточки активного вуглецю, являє собою консолідований наноструктурований матеріал. Отримані зразки сорбентів відрізняються різним початковим співвідношенням рослинної та мінеральної складової. Після термічної обробки суміші в безкисневій атмосфері на поверхні цеоліту утворюються наночастинки активованого вугілля розміром 2–3 нм. Характеристики композитів, які роблять їх перспективними сорбентами забруднюючих речовин, включають однорідну мікроморфологію пластинчастих частинок, поліпшену мезопористу структуру й площу поверхні (53.0 м^2/г), а також рясні та різноманітні функціональні групи, що містять кисень/вуглець. Досліджено структурно-хімічні та сорбційні властивості отриманого продукту по відношенню до іонів Cu^{2+}, Pb^{2+}, Cd^{2+}, Sr^{2+}, Ni^{2+} під час вилучення з модельних розчинів. Композит, отриманий за 600 °C і 10 мас.% цеоліту, показав найвище вилучення іонів важких металів з водного розчину.

Ключові слова: адсорбція, кадмій, свинець, цинк, мідь, рисове лушпиння, цеоліт, піроліз, біовугілля, сорбційні властивості.

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doi: 10.15421/jchemtech.v33i3.328345

Journal of Chemistry and Technologies, 2025, *33*(3), 728-733

Introduction

As a result of human anthropogenic activity, excess amounts of toxic metal ions enter the environment, namely water, air and soil. Wastewater is the largest source of pollution. If not sufficiently purified, it enters water bodies in both surface and underground horizons on the soil surface [1; 2]. Heavy metals such as Cd, Cu, Hg, Ni, Pb and Zn are toxic, do not undergo biological decomposition and accumulate in the environment [3–5]. Various methods have been proposed for purifying water contaminated with metals, including chemical coagulation, oxidation, membrane filtration, extraction with various solvents, and ion exchange [6; 7]. Sorption methods of water purification using various types of adsorbents are the most accessible and cost-effective [8; 9]. Adsorption is a physicochemical process during which a pollutant (adsorbate) accumulates on the surface of a solid (adsorbent). A pressing issue is the search for effective eco-sorbents capable of reducing environmental pollution with toxic heavy metals.

Carbon materials are used as adsorbents for water purification, since they have a porous structure and a large surface area [10; 11], and meet the basic requirements – non-toxicity, high adsorption capacity. Plant waste is a priority natural renewable material for obtaining carbon materials – biochar and is relevant both in scientific and practical terms [12–14]. Large-tonnage rice production waste can also serve as a cheap raw material for obtaining carbon material. Biochar is a stable carbon-rich product synthesized as a result of pyrolysis (carbonization) of plant biomass. The main parameters controlling its properties include pyrolysis temperature, time and type of raw material. The effectiveness of biochar in neutralizing pollutants depends on the surface area, pore size distribution and ion exchange capacity [15; 16]. Pyrolysis temperature affects the properties of biochar and is a critical factor for assessing the effectiveness of removing toxicants from the environment [17–19]. In the process of formation of carbon material during pyrolysis of cellulose-containing material on the coal surface reactive groups are formed, which determine the possibility of chemical modification of the biocoal surface to improve its sorption. Modification of carbon material with mineral substances allows obtaining a composite with increased sorption capacity with respect to heavy metal ions. Therefore, such ecosorbents can be used to clean wastewater and soils contaminated with heavy metals.

Materials and methods

In this study, the possibility of obtaining a composite carbon-mineral ecosorbent from rice husk and zeolite was studied. Rice husk is a fibrous substance containing moisture, lignin, cellulose, pentosans, a small amount of protein and vitamins, and mineral ash consisting of 92–97 % silicon dioxide. Zeolite is an aluminosilicate clay (Ca^{2+}, Mg^{2+}) in the interlayer spaces and has the advantages of low cost, high ion-exchange capacity, controlled properties, and wide availability. The presented results concern the development of a technology for obtaining a carbon-mineral sorbent by thermal treatment of a mixture of rice husk and zeolite, as well as a study of the structural-chemical and sorption properties of the resulting product. During thermal treatment without oxygen access to the mixture at a temperature of 300–5000 °C, nanoparticles of activated carbon with a size of 2–3 nm are formed on the surface of the zeolite. The crushed zeolite and rice husk, selected (average particle size 2 mm, content: SiO_2 – 18.2 %, cellulose – 42.9 %, lignin – 19.0 %, nitrogenous substances –3.6 %), were mixed in various proportions and crushed in a ball 0. To obtain a composite carbon-mineral ecosorbent, a mixture of rice husk and zeolite in various ratios of plant and mineral components. A laboratory reactor was used in the heat treatment process, which provided oxygen-free conditions for the process.

The pyrolysis process lasted from 10 to 60 minutes. In this case, the destruction of organic matter occurs, and the final decomposition product (active amorphous carbon) settles on the catalytic centers of the aluminosilicate surface of the zeolite. The carbon content in the sorbent is 8–19 %. In this case, the zeolite containing active carbon lobes on the surface is a consolidated nanostructured material. The obtained sorbent samples (1–5) differed in the initial ratio of the plant and mineral components. The characteristics of the composites, producing them as promising sorbents of pollutants, include a uniform micromorphology of lamellar particles, an improved mesoporous structure and surface area (53.0 m^2/g), as well as abundant and diverse functional groups containing oxygen / carbon. The composite obtained at 600 °C and 10 wt.% zeolite showed the highest removal of heavy metal ions from an aqueous solution.

Journal of Chemistry and Technologies, 2025, *33*(3), 728-733

Nitrogen adsorption-desorption isotherms were measured using an AUTOSORB-6B gas adsorption analyzer (Quantachrome, USA). The parameters of the cellular structure were calculated using the AUTOSORB-1 program (Quantachrome, USA). The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method. The method for determining the static exchange capacity consists of determining the number of ions absorbed from a constant volume of the working solution per unit mass of the sorbent. The static exchange capacity (SEC) values indicate the ability of the material to bind ions of toxic substances. The SEC of biochar increases for both Cl- and Na+ cations, which creates the 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).

Results and discussion

The characteristics of the cellular structure (specific surface area, total pore volume, pore diameter) were determined by the low-temperature nitrogen adsorption method. The specific surface area indices of the samples of combined carbon-mineral sorbents obtained by pyrolysis are presented in Table 1. The specific surface area and pore volume are determined by the nitrogen adsorption-desorption isotherm.

Table 1

Structural and pore characteristics of combined carbon-mineral sorbents

Name of the show,size/number of the show	1	2	3	4	5
Specific surface area, m^2/g	16.1	4.6	78.7	75.9	5.4
Specific surface area of mesopores, m^2/g	16.1	4.6	47	45.1	5.4
Specific surface area of micropores, m^2/g	15.6	4.1	92.4	86.0	5.2
Total pore volume, cm3/g	0.127	0.037	0.241	0.194	0.188
Micropore volume, cm^3/g	0.005	0.001	0.033	0.031	0.002
Average (effective) pore radius, Å	158	159	61.3	51.2	691

The results of the studies of the structural and pore properties (Tables 1, 3) indicate that the carbon-mineral component of the composite ecosorbents proposed by us has fairly high indicators of the total pore volume, the volume of sorption pores, the volume of micro-macro- and especially mesopores. The development of macro- and mesoporosity can provide increased sorption activity of this sorbent both in terms of capacity indicators and the kinetics of the sorption process. These properties also play a decisive role in practical use. 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 assessing the absorption capacity of the adsorbent. The pore volume characterizes the available pore volume in the adsorbent in which adsorbates can be absorbed. The obtained sorbent samples (1–5) differed in different initial ratios of the plant and mineral components. Table 2 presents data on the ion-exchange characteristics of the obtained combined sorbents (SEC) at different ratios of the initial components (rice husk: zeolite) for obtaining combined carbon-mineral sorbents.

Table 2

Ion exchange power of combined carbon-mineral sorbents

Sample No.	Ratio of components (rice husk / zeolite), wt.%	Weight, g	Number of ml of NaOH used for titration	Equilibrium concentration of HCl, mmol/l	SEC, mmol/g
1	20:80	0.5003	4.25	0.085	0.7496
		0.5007	4.20	0.084	0.7489
2	30:70	0.5008	4.45	0.089	0.5049
		0.5009	4.50	0.090	0.4991
3	50:50	0.4999	4.00	0.080	1.0021
		0.5001	4.00	0.080	0.9998
4	70:30	0.4635	4.40	0.088	0.6473
		0.4232	4.45	0.089	0.6498
5	80:20	0.5405	4.45	0.089	0.5087
		0.5023	4.50	0.090	0.4977

Journal of Chemistry and Technologies, 2025, *33*(3), 728-733

The data obtained show that the highest efficiency of the sorbent (when purchasing standard components in total) is maximum when mixing components (wt.%): light cellulose material: zeolite 50–50. When removing from this amount of components, the efficiency of the sorbent decreases by 15–25 %.

The results of laboratory studies of the sorption capacity of composite materials evaluated by the sorption of methylene blue and vitamin B12 are given in Tables 3 and 4, respectively.

Table 3

Sorption properties of combined carbon-mineral sorbents (by methylene blue)

Sample No.	Ratio of components (rice husk: zeolite), wt.%	Optical density, od.o.h.	Dilution (times)	Concentration is equally important, mg/l	Adsorption value, mg/g
1	20:80	0.282	50	290	315
		0.360	50	385	291
2	30:70	0.272	20	117	358
		0.278	20	118	358
3	50:50	0.236	25	126	356
		0.220	25	120	358
4	70:30	0.188	5	20.5	382
		0.334	5	35.5	379
5	80:20	0.203	50	215	334
		0.207	50	218	333

The ability of the obtained material to adsorb metal ions can be quantitatively assessed by the value of the maximum adsorption capacity and the time to achieve sorption equilibrium. In this case, the value of the sorption capacity of the material is (for example, for Cu^{2+}) 10.1 mg/g, which significantly exceeds the sorption capacity of activated carbon and zeolite separately. In almost the first 5–10 minutes, significant absorption of metal ions by the sorbent occurs; the equilibrium state is achieved with a sorption duration of approximately 20–50 minutes.

Table 4

Sorption properties of combined carbon-mineral sorbents (according to B_{12})

Sample No.	Ratio of components (rice husk: zeolite), wt.%	Optical density, od.o.h.	Dilution (times)	Concentration is equally important, mg/l	Adsorption value, mg/g
1	20:80	0.172	0	35	22.5
		0.244	0	49	21.8
2	30:70	0.276	5	277.5	10.4
		0.209	5	210	14.0
3	50:50	0.144	0	28	22.8
		0.161	0	32.5	22.6
4	70:30	0.235	5	235	12.5
		0.195	5	195	15.8
5	80:20	0.232	5	232.5	13.9
		0.228	5	225	14.2

It is seen that the sorption homogeneity of the material containing Pb2+ ions is significantly higher, lower than for ions in other metals. The sorption activity series can be as follows: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+} > Sr^{2+}$. The kinetics of sorption of important metal ions from single-component solo studies in studies conducted in statistical minds is given. Kinetic studies show that when metal ions (Cu^{2+}, Pb^{2+}, Cd^{2+}, Sr^{2+} Ni^{2+}) are detected for an additional combination ecosorbent (with a 50:50 match of components) in the solid phase – liquid systems, the level persists for 30–60 minutes (Fig.).

The adsorption of heavy metal ions by carbon-mineral ecosorbent can be carried out by several sorption mechanisms, including physical interaction, cation exchange and π-π-bonding interactions, and was modulated by intrapartial diffusion. The potential of carbon-mineral composites of rice husk biochar and zeolite as a favorable adsorbent for environmental restoration and water purification is emphasized. Thus, the carbon-mineral ecosorbent obtained by the proposed technology can be successfully used for practical use for enriching soils with microelements.

Journal of Chemistry and Technologies, 2025, *33*(3), 728-733

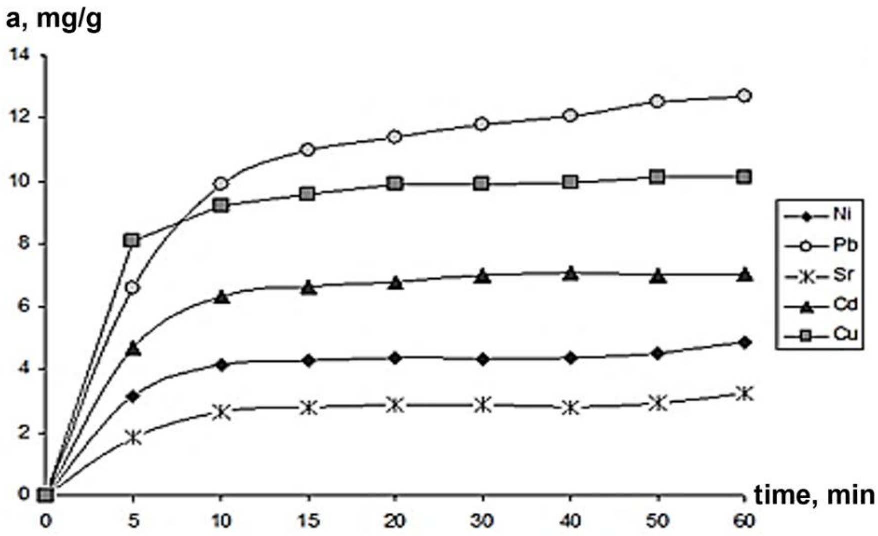

Figure. Kinetic curves for the sorption of Cu^{2+}, Pb^{2+}, Cd^{2+}, Sr^{2+}, Ni^{2+} ions by a carbon-mineral ecosorbent

Conclusions

The removal of effective carbon-mineral ecosorbent ecosorbents for the removal of Cu^{2+}, Pb^{2+}, Cd^{2+}, Sr^{2+}, Ni^{2+} ions from water sources based on biovougol from the outputs of the rural state has been demonstrated and zeolite.

To obtain a composite carbon-mineral ecosorbent, a mixture of rice husk and zeolite in various proportions of plant and mineral components was subjected to general pyrolysis under various temperature conditions (250–600 °C) without the use of toxic chemicals to obtain a series of biocoal-clay composites. The pyrolysis process lasted from 10 to 60 minutes. In this case, destruction of organic substances occurs, and the final decomposition product (active amorphous carbon) settles on the catalytic centers of the aluminosilicate surface of the zeolite. The carbon content in the sorbent is 8–19 %. In this case, the zeolite containing active carbon lobes on the surface is a consolidated nanostructured material. The obtained sorbent samples differed in the initial ratio of the plant and mineral components.

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The structural-chemical and sorption properties of the obtained product in relation to Cu^{2+}, Pb^{2+}, Cd^{2+}, Sr^{2+}, Ni^{2+} ions were studied during extraction from model solutions. The composite obtained at 600 °C and 10 wt.% zeolite showed the highest removal of heavy metal ions from an aqueous solution.

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