2. Akurati, K.K., Vital, A., Hany, R., Bommer, B., Graule, T., Winterer, M. One-step flame synthesis of SnO_2/TiO_2 composite nanoparticles for photocatalytic applications // Int. J. Photoenergy, 7, 2005.

3. http://jp-minerals.org/vesta/en/

4. Kutuzova, A., Dontsova, T. Synthesis, Characterization and Properties of Titanium Dioxide Obtained by Hydrolytic Method / Proceedings of the 2017 IEEE 7 th International Conference on Nanomaterials : Applications & Properties, 2017.

5. Nagirnyak, S.V., Lutz, V.A., Dontsova, T.A., Astrelin I.M. The effect of the synthesis conditions on morphology of tin (IV) oxide obtained by vapor transport method // Nanophysics, Nanophotonics, Surface Studies, and Applications, 183, 2016.

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A.V. Khokhlov, Senior Researcher, PhD,
M.V. Titarenko, junior science,
L.I. Khokhlova, Senior Researcher, PhD
(Institute for Sorption and Problems of Endoecology
of The National Academy of Sciences of Ukraine, Kyiv)

SULFUR-CONTAINING BIOCARBON MATERIAL FOR STRONG BINDING OF HEAVY METALS

Pollution of soils with heavy metals (HM) is an important ecological problem. Removing heavy metals is a difficult task, since they often have a low concentration [1-3]. Heavy metals have the ability to various chemical and physico-chemical reactions. HM have the ability to move, to redistribute and to migrate. Various methods are used for ecosystems purification from heavy metals, including sorption. If we consider methods for cleaning contaminated soil, it is advisable to use the most ecological and safe methods for soil purification. It is possible to precipitate them in the form of sparingly soluble sediments, to wash them out of the soil profile, to extract from the soil by plants and microorganisms, to apply sorption by minerals with high cation exchange capacity and a mixture of sorbents. The disadvantages of the existing methods of cleaning soil from HM determine the need to find new methods of soil detoxification.

Elimination of the mobility of heavy metals on the site has a lot of advantages over the physical removal. One way to stabilize heavy metals is to add chemicals to the soil that cause the formation of minerals containing heavy metals in a fixed form. This method is called in situ (in place) fixation or stabilization. This process does not violate the environment and does not generate hazardous waste. Instead, the heavy metal combines with the added chemical to create a less toxic compound. Heavy metal remains in the soil, but in a form, that is much less harmful. Reduction of the toxicity of heavy metals in soils is possible due to the binding of their mobile forms to sparingly soluble compounds (sulfides, carbonates, phosphates, hydroxides, etc.) on the surface of sorbents when applied to soils.

Depending on the level of pollution and the assignment of soils, it is possible to single out various ways of implementing sorption purification. For example, in the case of insignificant contamination of agricultural soils, sorbents are introduced to the depth of the fertile layer and, as a rule, are not subject to extraction from the cleaned soil [46]. At present, numerous methods for obtaining sorbents have been developed, the use of which allows the purified soil to be returned to natural circulation and to reduce the volume of waste for disposal. The use of new types of reproducible raw materials, in particular agricultural wastes, with the goal of obtaining sorbents for detoxifying heavy metals in soils is relevant both scientifically and practically. The urgent task is to obtain ecological sorbents based on rice husk pyrolysate (biochar) for long-term binding of heavy metals in soils. Biochar is the "charred organic matter of plants". Biochar is a solid material obtained by carbonization of biomass. Different degrees of carbonation give an endless variety of biochars for use as adsorbents [4].

The rice husk is a fibrous substance containing moisture, lignin, cellulose, and pentosans, a small amount of protein and vitamins, and mineral ash consisting of 92-97% of silicon dioxide. In the rice husk, there is about 70-85% of organic substance. Its combustion produces about 20% of ash. The proposed technologies for rice husk recycling are mainly based on the processes of thermal destruction of material without air access (pyrolysis). An important role in obtaining demanded products with specified performance characteristics belongs to the sequence of stages of rice husk recycling, the regime parameters of the processes that are taking place, the composition of the semi-products used in production. 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 the production of biochar, slow pyrolysis makes it possible to obtain the maximum amount of biochar. In addition to the various pyrolysis conditions, the volumes and the composition of the pyrolyzate can vary (Table 1).

Table 1. Composition of rice husks pyrolyzate (biochar C, SiO_2 silica), depending on the temperature and duration of pyrolysis

Pyrolysis temperature, °C	Duration of the process, min	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

At average pyrolysis, temperatures in the 400-450°C range (low-temperature pyrolysis); biomass passes through exothermic processes and releases a lot of gaseous substances and the maximum amount of carbon material. In its structure, the biochar belongs to the class of carbonized substances, due to the common nature of their characteristic structural element. The structural element of the carbonized substance is the atomic grid of polymerized carbon. Atomic carbon grids in such a polymer are valently connected to each other. In the structure, H, O, N, P and S elements are included as heteroatoms, which explains the reactivity of the biochar. Bio-coal produced at different technological conditions will differ in the physical-mechanical composition, namely, in porosity, density, strength, hygroscopicity and moisture absorption.

The initial biomass influences the pore size (macro-, meso- and micropores) and their distribution in bio-carbon. The presence of micro- and meso-pores in the biochar determines its high internal specific surface, which plays an important role in chemical reactions occurring at relatively low temperatures of soils. Macro-pores have a smaller contribution to the change in the specific surface of the biochar, but contribute to access to its internal surface and to enhance interphase interactions.

Chemical modifiers help develop the porous structure of biochar. Modifiers used in our case, sulfur containing, diffuse into the internal structure of the carbon matrix during pyrolysis, expand existing pores and create new pores. A biochar 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 was obtained. Sulfur-containing sorption materials like low-molecular-weight organo-sulfur compounds are capable of complexing with ions of heavy metals, therefore such sorbents can be used for cleaning and neutralizing wastewater and soil contaminated with heavy metals. Carbon sulfur-containing materials are sorption selective with respect to several heavy metals (cadmium, copper, mercury) by the formation and strong binding of sparingly soluble metal sulfides on their surface.

Our proposed method to produce sulfur-containing bio-carbon eco sorbents from rice husk consists in a one-stage pyrolysis of the feedstock together with sulfur-containing reagents at a temperature of 350-400°C. As a result, biochar (coal from vegetable raw materials - biochar), modified by sulfur, is formed [5]. Sorption properties of the materials obtained by the proposed method are confirmed in the example of sorption of cadmium and copper ions from aqueous and ground media. It has been shown experimentally that the capacity of samples of sulfur-containing carbon sorbent, obtained from ligne-cellulose plant raw materials, provides extraction of cadmium ions from solutions on average up to 70%, for the best samples reaches 80%. The sorption capacity of the sulfur-containing carbon sorbent was determined under conditions of mixing for a certain time of aqueous solutions of $CuSO_4 \times 5H_2O$ and Cd $(NO_3)_2$ x $4H_2O$ salts to decrease the concentration of Cd(II) and Cu(II) ions before and after treatment with an eco-sorbent. Similarly, the concentrations of the ions studied in the aqueous extracts of the contaminated soil were compared. The initial concentrations of contamination in the water and ground media were Cd(II) 2-6 mg/l and Cu(II) 132-396 mg/l. Sulfide and hydrosulphide 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 on the surface and in the pores of the resulting sulfur-containing sorbent of sparingly soluble sulfides of toxic heavy metals. Sulfur-containing bio-carbon sorbent (biochar) has ability to firmly bind Cd (II) and Cu (II) ions on the surface of the sorbent in an insoluble sulfide form, which will allow removing it from soils and waters.

The advantage of the sulfur-containing bio-carbon eco sorbent is environmental friendliness due to its ligno-cellulose raw base materials (rice husk) and harmless sulfur-containing components are used in an insignificant amount. The production technology does not require complex equipment and consists of a one-stage pyrolysis of the feedstock and a sulfur-containing component together at a temperature of 350-400°C and the production of a biochar modified from sulfur by the vegetable raw material. The resulting sulfur-containing carbon materials are selective with respect to such heavy metals as cadmium and copper and can be used to extract and neutralize they toxicity in the water and on the ground environments.

REFERENCES

1. Орлов Д.С. Экология и охрана биосферы при химическом загрязнении/ Орлов Д.С., Лозановская И.Н., Садовникова Л.К. М.: Высшая школа, 2002.
334 с.
2. Алтунина Л. К. и др. Каталитические, сорбционные, микробиологические и интегрированные методы для защиты и ремедиации окружающей среды / под ред. О. П. Таран, В. Н. Пармона. Новосибирск: Изд-во Сибирского отд-я РАН, 2013. 297 с.
3. González, J. F., Román, S., Encinar, J. M., Martinéz, G., pyrolysis of various biomass residues and char utilization for the production of activated carbons. Journal of Analytical and Applied Pyrolysis. 2009. 85, P. 134-141.
4. Witoon T., Chareonpanich M., Limtrakul J. Synthesis of bimodal porous silica from rice husk ash via sol-gel process using chitosan as template // Materials Letters. 2008. V. 62. Iss. 10-11. P. 1476-1479.
5. А.В.Хохлов , Л.Й. Хохлова Патент МПК[8] CO2F3/34; C12N1/20;G21F9/28; BO9C1/08 Сірковмісний біовуглецевий матеріал для знешкодження важких металів у водних та грунтових середовищах.опубл.10.08.2018, бюл.№ 15.

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Y.K. Kosihina, L. R. Kabirova, , N.A. Nikonova, R.A.Zilberg, D.I. Dubrovsky
(BSU, Ufa)

SELECTION OF OPTIMAL CONDITIONS FOR THE VOLTAMMETRIC DETERMINATION OF ATENOLOL ON “SMART” POLYMERS

Nowadays, polymers are an indispensable component of advanced sensor devices. The polymers which reproducibly respond to changes in the