ARTICLE

DOI 10.36074/grail-of-science.24.09.2021.29

OUTLOOK OF USING THE ADSORPTION METHOD FOR EXTRACTION OF METALS FROM HYDROUS EFFLUENT

RESEARCH GROUP:

Ivanchenko Anna Volodymyrivna
D.Sc., professor of the Department of Chemical and Biological Technologies
Dniprovsk State Technical University, Ukraine

Yelatontsev Dmytro Oleksandrovych
Ph.D., associate professor of the Department of Chemical and Biological Technologies
Dniprovsk State Technical University, Ukraine

Soroka Olha Valeriivna
postgraduate of the Department of Chemical and Biological Technologies
Dniprovsk State Technical University, Ukraine

Tkachenko Elina Eduardivna
graduate of the Faculty of Metallurgy
Dniprovsk State Technical University, Ukraine

Summary. *Cellulose-containing waste from the agricultural industry modified by chemical methods is capable of adsorbing metal ions no worse than industrial sorbents (ion exchangers, activated carbons, zeolites, etc.). A wide range of methods for modifying plant raw materials makes it possible to obtain effective sorbents that are environmentally friendly and biologically inert. Proposed technologies of lignocellulosic sorbent manufacturing are highly economically feasible and, additionally, eco-friendly, because they ensure the proper utilization of agricultural wastes, which are very widespread in Ukraine.*
Keywords: *cellulose, chemical modification, feedstock recycling, ion exchanger, green sorbents.*

Among the substances that harm the environment and human health, the greatest prevalence and danger are heavy metals. The infiltration of these toxicants into the water comes from both man-made and various sources. Sources of man-made pollution are multifaceted, but the main ones are wastewater of man-made origin. Estimates of the number of heavy metals discharged into wastewater are contradictory, but in general, indicate not only catastrophic pollution of the environment but also a wasteful treatment of natural resources. To remove heavy metals from aqueous media, it is proposed to use the method of adsorption using cellulose-containing sorbents [1].

 Авторські права захищені | Creative Commons Attribution 4.0 International License

Despite the undeniable advantages of polymeric cellulose-containing sorbents, such as cheapness, availability, biological inertness concerning the media to be cleaned, and the ability to biodegrade in the environment, they usually have low kinetic characteristics and relatively low sorption capacity. Therefore, the task of creating new high-performance sorbents based on cellulose by various methods of modification using available inexpensive reagents and simple technological operations is urgent [2].

The main methods of activation of cellulose-containing sorbents are mechanical, physical, chemical, and physic-chemical. A promising area of sorbent processing is the use of methods of nano- and biotechnology [3].

The most common physical modification methods are exposed to high temperatures, superheated steam treatment, freezing, extrusion, plasma activation, microwave radiation, exposure to ultrasound and infrared radiation [4]. The possibility of using as sorbents heat-treated waste of different industries: wheat husk and sunflower husk, as well as wood sawdust, was investigated. The maximum effect of removal of heavy metal ions is achieved by holding the raw material at a temperature of 300 °C for 1 hour: the degree of extraction of Zn^{2+}, Cu^{2+}, and Cd^{2+} ions obtained by sorbents reaches 99.8%. Under the influence of high temperatures (300–600 ºC), rice husk was also processed to obtain a sorbent. It is shown that firing conditions significantly affect the absorption capacity of the studied samples.

Processing of crushed pine nutshell (waste of cedar oil production), pre-degreased and impregnated with water, at low temperatures (–20...–18 °C) with subsequent removal of water at a temperature of 130 °C leads to rupture of cell walls of plant tissue, increases the area of the adsorbing surface and the proportion of macro and mesopores in the material. As a result, the sorption capacity of the material increases 4 times [5].

Chemical modification of lignocellulosic plant biomaterials is most often used due to the availability, relatively low cost of chemical reagents, and selectivity of the process itself, as well as the possibility of creating sorption materials that are selective for metal ions of a certain type [6].

There are mainly two main approaches to convert cellulose into a biosorbent capable of efficiently removing heavy metal ions from aqueous solutions.

The first of these approaches is based on methods that involve a direct change in the cellulose macromolecule, which leads to the creation in its structure of functional groups capable of chelation or ion exchange with heavy metal ions from the solution. The first approach includes operations such as delignification, hydrolysis, oxidation, the addition of carboxyl, nitro, phosphate, amino groups, and using a variety of reagents: alkali solutions (sodium, potassium, or calcium hydroxides), salts, minerals, salt, salt phosphate (sulfuric) and organic acids (tartaric, citric). Polysaccharide materials of plant origin contain cellulose, hemicellulose, lignin, pectin, proteins, and others [7].

Treatment with chemical reagents allows to remove lignin, hemicellulose, reduce the crystallinity of cellulose and increase the porosity and specific surface area of such materials, increasing their sorption capacity relative to metal ions. In the process of treatment with alkaline reagents, substances that dissolve in alkalis are removed, which leads to an increase in the sorption of heavy metal ions. When using

All rights reserved | Creative Commons Attribution 4.0 International License

rice husk treated with NaOH solution, the adsorption of Cd^{2+} ions is almost doubled, from 4 to 7 mg/g [8].

In the wood process, sawdust processing was found [9] that its sorption capacity increased 2.5 times towards Cu^{2+} ions and 15 times to Zn^{2+} ions. The values of the limiting sorption capacity found by the Langmuir model were 6.92 mg/g (sawdust from poplar wood) and 12.7 mg/g (spruce sawdust) for copper and 15.83 mg/g (sawdust from poplar wood) and 13.41 mg/g (spruce sawdust) for zinc. According to the authors, this effect is achieved by increasing the availability of sorption centers on the surface of sawdust.

Treatment of wheat bran with sulfuric acid does a significant effect on the growth of the specific surface area of the material, which led to increased efficiency of sorption of ions Cu^{2+}, Pb^{2+}, and Cd^{2+}. The sorption capacity of the modified bran decreased in the range: $Cd^{2+}>Pb^{2+}>Cu^{2+}$ and amounted to 101, 55.5, and 51.5 mg/g, respectively. The authors suggest that acid treatment leads to an increase in the specific surface area due to the conversion of macropores into micropores [10].

For chemical modification of plant raw materials, orthophosphate acid can be used as a stand-alone reagent, but more often it is used in combination with other compounds [11]. When using as reagents solutions containing orthophosphate acid in a mixture with urea or dimethylformamide on the surface of cellulose-containing materials, along with residual aldehyde and carboxyl groups, phosphate and primary amino groups are formed, which causes an increase in their sorption capacity.

For chemical modification of plant raw materials, orthophosphate acid can be used as a stand-alone reagent, but more often it is used in combination with other compounds [12]. When solutions containing orthophosphate acid in a mixture with urea or dimethylformamide are used as reagents on the surface of cellulose-containing materials, along with residual aldehyde and carboxyl groups, phosphoric acid and primary amino groups are formed, which causes an increase in their sorption capacity.

Common methods of chemical modification of cellulose are shown in the table.

Table

Methods for chemical modification of cellulose

Material	Modification method (chemical reagent)	Removable ions	Sorption capacity		Reference
			mg/g	mmol/g	
Hazelnut shell	Ultrasound exposure	Cu^{2+}	239	4.5	[5]
Sugarcane millcake	Microwave radiation	Cu^{2+} Hg^{2+}	76 481	1,2 2.4	[6]
Cellulose	NaOH	Cu^{2+} Cd^{2+} Pb^{2+}	30 86 206	0.47 0.77 0.99	[7]
Cherry stones	Oxidation (O_3, H_2O_2, HNO_3)	Cu^{2+}	4–28	0.06–0.44	[8]
Date palm stones	HNO_3	Pb^{2+} Cd^{2+}	100–160 110–160	0.48–0.77 0.98–1.4	[9]
Rice husk	H_2SO_4	Zn^{2+} Hg^{2+}	11–12 100–120	0.17–0.18 0.50–0.60	[10]
Pine bumps	Fenton's reagent (H_2O_2+$FeSO_4$)	Cd^{2+} Pb^{2+}	2–11 2–10	0.02–0.10 0.01–0.05	[11]
Aspen wood	Bleaching, hydrolysis	Cu^{2+}	0.9–2.2	0.01–0.04	[12]

Авторські права захищені | Creative Commons Attribution 4.0 International License

Based on the above, scientific substantiation and development of sorption technology for purification of liquid aqueous media from heavy metal ions to the level of maximum permissible concentrations following hygienic requirements for water quality is an urgent task and requires further research to select the most effective sorbent and increase its sorption capacity.

References:

[1] Hassan S.S., Williams G.A., & Jaiswal A.K. (2018). Emerging technologies for the pretreatment of lignocellulosic biomass. *Bioresource Technology*, *262*, 310–318.

[2] Hokkanen S., Bhatnagar A., & Sillanpää M. (2016). A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. *Water research*, *91*, 156–173.

[3] Illy N., Fache M., Menard R., Negrell C., Caillol S., & David G. (2015). Phosphorylation of bio-based compounds: the state of the art. *Polymer Chemistry*, *6*(35), 6257–6291.

[4] Puzii A.M. (2011). Methods of production, structure, and physicochemical characteristics of phosphorylated carbon adsorbents. *Theoretical and Experimental Chemistry*, *47*(5), 277–291.

[5] Milenković D.D., Dašić P.V., & Veljković V.B. (2009). Ultrasound-assisted adsorption of copper (II) ions on hazelnut shell activated carbon. *Ultrasonics Sonochemistry*, *16*(4), 557–563.

[6] Orlando U.S., Baes A.U., Nishijima W., & Okada M. (2002). Preparation of chelating agents from sugarcane bagasse by microwave radiation as an alternative ecologically benign procedure. *Green Chemistry*, *4*(6), 555–557.

[7] Gurgel L.V.A., Junior O.K., de Freitas Gil R.P., & Gil L.F. (2008). Adsorption of Cu (II), Cd (II), and Pb (II) from aqueous single metal solutions by cellulose and mercerized cellulose chemically modified with succinic anhydride. *Bioresource technology*, *99*(8), 3077–3083.

[8] Jaramillo J., Gómez-Serrano V., & Alvarez P.M. (2009). Enhanced adsorption of metal ions onto functionalized granular activated carbons prepared from cherry stones. *Journal of Hazardous Materials*, *161*(2–3), 670–676.

[9] El-Hendawy A.N.A. (2009). The role of surface chemistry and solution pH on the removal of Pb2+ and Cd2+ ions via effective adsorbents from low-cost biomass. *Journal of hazardous materials*, *167*(1–3), 260–267.

[10] El-Shafey E.I. (2010). Removal of Zn (II) and Hg (II) from aqueous solution on a carbonaceous sorbent chemically prepared from rice husk. *Journal of hazardous materials*, *175*(1–3), 319–327.

[11] Argun M.E., Dursun S., Karatas M., & Gürü M. (2008). Activation of pine cone using Fenton oxidation for Cd (II) and Pb (II) removal. *Bioresource technology*, *99*(18), 8691–8698.

[12] Huang L., Ou Z., Boving T.B., Tyson J., & Xing B. (2009). Sorption of copper by chemically modified aspen wood fibers. *Chemosphere*, *76*(8), 1056–1061.

All rights reserved | Creative Commons Attribution 4.0 International License