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Cu(II) AND Fe(II) ION SORPTION BY COTTON CELLULOSE MODIFIED WITH DIETHYLENETRIAMINE

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Abstract. *The authors have developed new effective sorbent based on chemically modified cotton cellulose. The modification process consists of two stages, including sequential treatment of cellulose with epichlorohydrin and diethylene triamine. The authors present the optimal modification conditions for the obtained sorbent. It allows ones' to achieve the highest values of sorption capacity for the extraction of iron(II) and copper(II) ions from aqueous solutions. The authors investigated the kinetics and equilibrium of heavy metal ion sorption in the system "cellulose sorbent - aqueous solution of metal sulphate" for original and modified cotton cellulose. Processing of the kinetic experiment results indicates that the kinetics of metal ion sorption is described most correctly in the framework of the pseudo-second-order kinetics model. Isotherms of heavy metal ions sorption clearly indicate the growth of sorption capacity for the modified sorbent in comparison with the original one. Processing of experimental isotherms within the Langmuir model made it possible to determine the values of the maximum sorption capacity (A_∞) of original and modified with diethylenetriamine cotton cellulose with respect to Cu(II) and FE(II) ions. It was found that the A_∞ of the modified sorbent was about 3 times higher than the ultimate sorption capacity of original cotton cellulose towards iron(II) and Cu(II) IONS. Comparison of IR spectra of the original cellulose samples and cellulose treated with diethylenetriamine indicates the changes that occurred during chemical modification. The paper presents SEM images showing the changes in the surface structure of the modified sorbent compared to the original one.*

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Introduction

Environmental pollution by heavy metal ions has become one of the main problems worldwide in recent years [1]. Their environmental accumulation is promoted by the development of industry, transport, agriculture, and urban growth [2]. Natural sources

such as volcanic activity, weathering of rocks, etc. contribute heavy metals into the environmental pollution [3]. These types of pollutants are stable in nature, non_biodegradable and can be transported long distances with air and water flows [4].

Environmental pollution by heavy metal ions can have a negative impact on soil characteristics. They block the synthesis of enzymes by soil microorganisms, plants, animals, and disrupt the processes of nitrogen transformation and decomposition of organic matter. A number of heavy metals (chromium, copper, mercury, nickel, cadmium, lead, zinc, cobalt, etc.) are often found in water bodies, and even in trace amounts can have a harmful effect on the inhabitants of aquatic ecosystems and humans due to their bioaccumulation [5].

A lot of heavy metals, such as lead, mercury, cadmium, zinc, copper, iron, etc., have a toxic effect on the human and animal organism, affecting various organs and systems [6]. They are included in food chains. As a result, they can be transferred to the human body in high concentrations. Consequently, the protection of water and soil from heavy metal pollution is directly related to the protection of human health. Therefore, much attention is paid to the solution of the water purification problem.

Many different methods used to remove heavy metal ions from contaminated water: filtration, ion exchange, electrochemical purification, chemical precipitation, membrane filtration, reverse osmosis, and adsorption processes [7]. Most of these methods are expensive, require specialised equipment, and are not effective at low metal concentrations. This promotes the development of sorption method based on the use of clays, zeolites, ion exchange resins, activated carbon, silica gel, activated aluminium oxide, etc. as sorbents [8-10]. Furthermore, the search for cheaper, environmentally friendly and effective adsorbing materials based on wastes or by-products of the agro-industrial complex containing cellulose and protein components [11-13]. To increase their efficiency, sorbents based on cellulose [14-15], flax fibre [16], chitosan [17] wool keratin [18], etc. are modified in various ways.

The purpose of this study is to develop a sorbent based on cotton cellulose modified with diethylene triamine, which has high sorption properties towards heavy metal ions.

Main body

We used cotton cellulose (GOST 595-79) as a sorbent. It was preconditioned in NaOH solution (pH = 8-10) for 60 min and thoroughly squeezed. We modified cotton cellulose by its sequential treatment with epichlorohydrin at 50–70 °C for 0.5-1.0 h with subsequent filtration, and with diethylene triamine at 30–50 °C for 1-2 h with continuous stirring. We washed the obtained product with distilled water to neutral pH value of the wash water and dried to constant weight.

Kinetics and equilibrium of sorption. The authors studied the kinetics of Cu(II) and Fe(II) ions sorption by the method of limited volume solution at static conditions under stirring [19] with an initial concentration of metal cations (C_0) at $1.5 \cdot 10^{-4}$ mol/l. We separated the solution from the sorbent by filtration at regular intervals during the experiment and determined the current concentration of metal cations (C_τ) in it by atomic absorption spectroscopy (210 VGP unit).

The recovery rate of metal ions α (%) was calculated by the formula

$$\alpha = \frac{C_0 - C_\tau}{C_0} \cdot 100. \quad (1)$$

The authors placed 0.1 g of sorbent suspensions in a number of test tubes and poured them into 10 ml of aqueous solution of Cu(II) and Fe(II) sulfates with concentrations ranging from $1.5 \cdot 10^{-4}$ to $5 \cdot 10^{-2}$ mol/l; kept them under stirring until equilibrium was reached. We then separated the solution from the sorbent by filtration and determined its equilibrium concentration of metal cations (C_τ) by atomic absorption spectroscopy on a 210VGP unit.

We determined the equilibrium sorption capacity A (mol/kg) by the formula

$$A = \frac{(C_0 - C)}{m} \cdot V, \quad (2)$$

where C is the equilibrium concentration of metal ions, mol/l; m is the mass of the sorbent suspension, g; V is the volume of solution, litres.

We calculated the relative bias of the experiments on the basis of experimental data; each point represents the average of two parallel experiments [20]. The bias of the experiment did not exceed 10%.

Discussion of the results of the study

Figure 1 shows the scheme of cotton cellulose modification by its sequential treatment with epichlorohydrin and diethylene triamine.

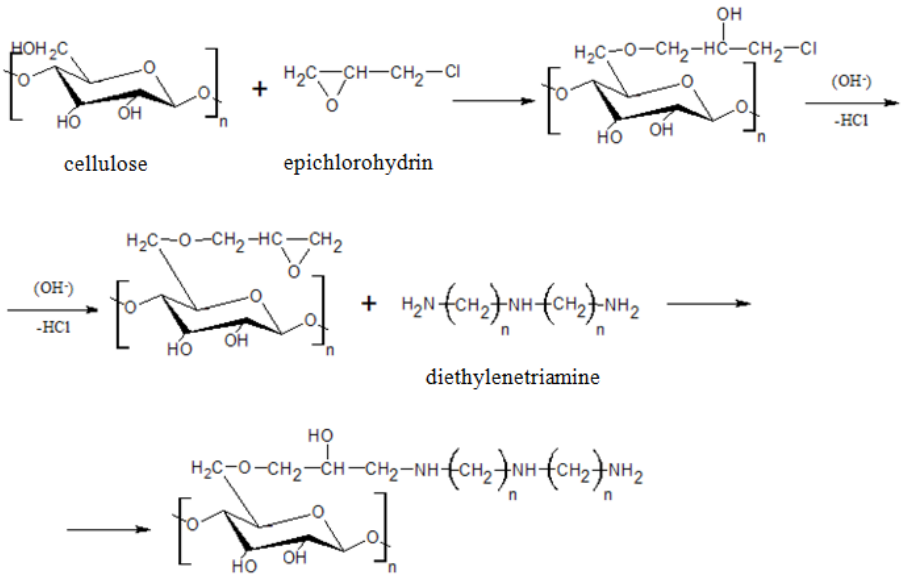


Fig. 1. Cotton cellulose modification

The time to reach sorption equilibrium in the heterophase system "cellulose sorbent - aqueous metal sulphate solution" was determined from the kinetic experiment on the extraction of Cu(II) and Fe(II) ions by the original and modified sorbent. Fig. 2 shows the experimental results.

The time to reach sorption equilibrium using original and modified cotton cellulose is 20 minutes, according to the data obtained. Indeed, the recovery rate of copper ions is slightly

higher than both sorbent samples iron ions. The recovery rate of metal cations is higher for the modified cellulose sample compared to the original one.

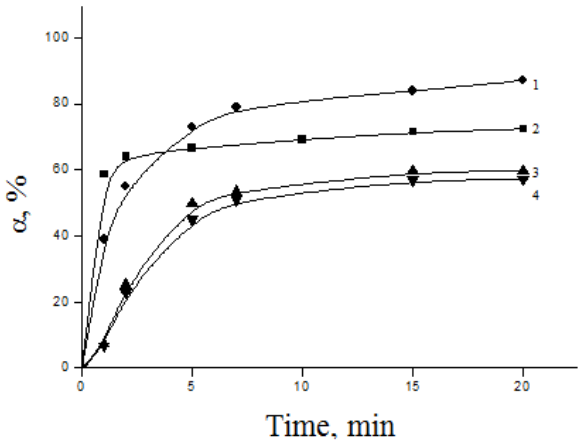


Fig. 2. Kinetic curves of sorption of Cu^{2+} (1, 3) and Fe^{2+} (2, 4) ions from aqueous solutions of original (3, 4) and modified (1, 2) cotton cellulose

The reaction order was determined using pseudo-first (3) and pseudo-second (4) order kinetic models in the processing of experimental data:

$$q_t = q_{eq}\,(1 - e^{-k_1 t}), \tag{3}$$

$$q_t = \frac{t}{\frac{1}{k_2 \cdot q_{eq}^2} + \frac{1}{q_{eq}}}. \tag{4}$$

Table 1 presents the results of processing the kinetic curves of Cu(II) and Fe(II) ion sorption by the original and modified cellulose within the framework of pseudo-first-order and pseudo-second-order kinetics models. Higher correlation coefficients (0.99) were obtained when the experimental data were processed using the pseudo-second-order kinetic model.

Table 1. Results of processing of kinetic curves of Cu(II) and Fe(II) ions sorption by original and modified cellulose within the framework of chemical kinetics models

Metal ion	Equilibrium sorption value	Pseudo-first-order model			Pseudo-second-order model		
	q_e, mg/g	q_e, mg/g	k_1, min^{-1}	R^2	q_e, mg/g	k_2, g/mg min	R^2
Non-modified cellulose							
Cu(II)	0.55	0.46	0.18	0.80	0.64	0.29	0.99
Fe(II)	0.53	0.49	0.18	0.89	0.62	0.23	0.99
Diethylene triamine modified cellulose							
Cu(II)	0.83	0.67	0.28	0.98	0.85	1.15	0.99
Fe(II)	0.74	0.62	0.24	0.97	0.78	1.10	0.99

Isotherms of sorption of Cu(II), Fe(II) ions from aqueous solutions of their sulphates were obtained to determine the ultimate sorption capacity of original cotton cellulose and cellulose modified with diethylenetriamine. Fig. 3 shows the experimental results.

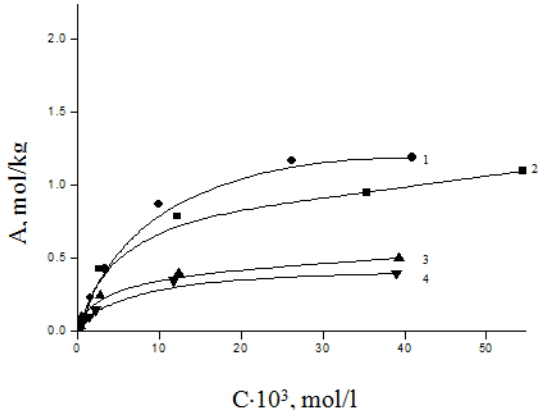


Fig. 3. Sorption isotherms of Cu^{2+} (1, 3) and Fe^{2+} (2, 4) ions from aqueous solutions of original (3, 4) and diethylenetriamine modified (1, 2) cotton cellulose

The Langmuir adsorption isotherm equation was used to process the experimental data

$$A = \frac{A_\infty \cdot K \cdot C_e}{(1 + K \cdot C_e)}, \quad (5)$$

where A_∞ is the limiting or maximum sorption capacity of the sorbent for a given metal, mol/kg; K is the concentration constant of sorption equilibrium, characterizing the intensity of the sorption process, l/mol.

Linearisation of the sorption isotherms according to the equation

$$\frac{C_e}{A} = \frac{C_e}{A_\infty} + \frac{1}{A_\infty \cdot K} \quad (6)$$

allows us to determine graphically the values of A_∞ and K in the Langmuir equation from the experimental data on the distribution of the studied sorbate in the heterophase system "aqueous solution - cellulose sorbent". The results obtained by processing the isotherms of heavy metal ions sorption by original and modified cellulose according to the Langmuir model are presented in Table 2.

Table 2. Processing parameters of sorption isotherms of Cu(II) and Fe(II) ions by original and modified cotton pulp according to the Langmuir model

Metal cation	K, l/mol	$1/A_\infty$	Correlation coefficient	A_∞, mol/kg
Non-modified cellulose				
Cu(II)	909.1	2,0±0,02	0.99	0.50
Fe(II)	961.5	2,5±0,02	0.99	0.40
Diethylene triamine modified cellulose				
Cu(II)	327.3	0,69±0,03	0.99	1.44
Fe(II)	415.1	0,77±0,05	0.98	1.29

The experimental data on the sorption of Cu(II) and Fe(II) ions by the original and modified cotton cellulose are well approximated by the Langmuir equation. The data presented in Fig. 3 and Table 2, the ultimate sorption capacity (A_∞) of cotton cellulose modified with diethylenetriamine is about three times higher than the A_∞ of the original cellulose for Cu(II) and Fe(II) ions. The obtained values of A_∞ of modified cellulose

(approximately 1.4 and 1.3 mol/kg for sorption of Cu(II) and Fe(II) ions, respectively) indicate good binding ability of the obtained sorbent towards these metals.

The sorbents were investigated by IR spectroscopy, EDS, and SEM methods. The observed increase in the ultimate sorption capacity of modified cotton cellulose compared to the A_∞ of the original cellulose is explained by the appearance of new functional groups binding ions of the studied heavy metals as a result of sorbent modification. To detect them, IR spectra of the original and modified sorbents samples were obtained (Fig. 4).

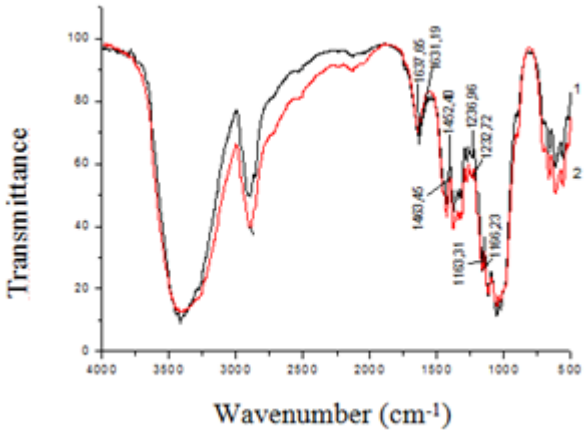


Fig. 4. IR spectra of cotton cellulose: 1 - original; 2 - cellulose treated with diethylenetriamine

By comparing the IR spectra of the original cotton cellulose and the cellulose modified with diethylenetriamine, differences were found in the region of 1650–1450 cm^{-1} and 1300-1000 cm^{-1}. There observed the deformation vibrations of the N-H bond in amines and amides and the valence vibrations of the C-N bond in amines, respectively. According to Figure 4, the most significant changes as a result of modification are related to the band shift in the spectrum of the original sorbent at 1452 cm^{-1} to the 1463 cm^{-1} position in the spectrum of cellulose modified with diethylenetriamine. Therefore, the sorbent modification results in the fixation of nitrogen-containing polymer on its surface, which is evident in the spectrum.

This is also confirmed by the results of the elemental composition analysis of the sorbent surface performed by energy dispersive X-ray spectroscopy (EDS). It indicates the appearance of nitrogen in the modified sample. Fig. 5 shows the elemental analysis of the original (***a***) and modified (***b***) sorbent samples after sorption of Fe^{2+} ions.

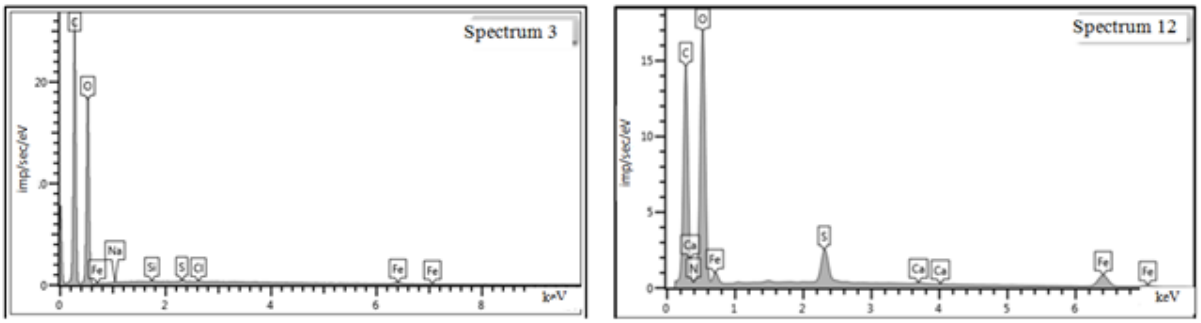
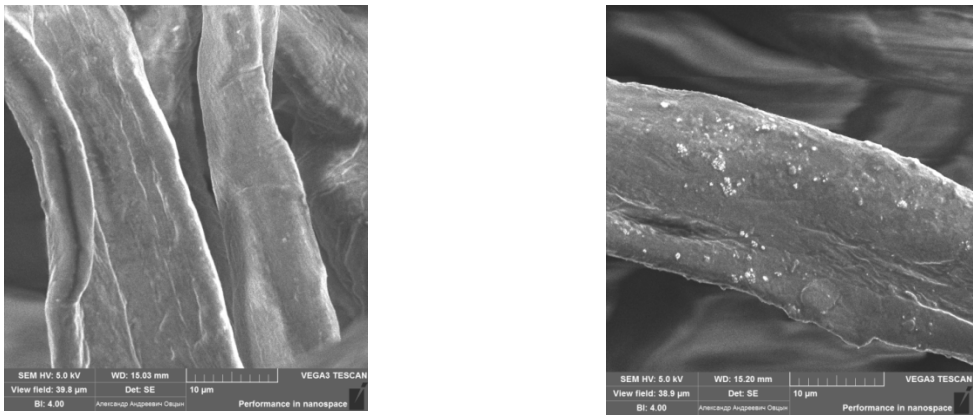


Fig. 5. The elemental analysis of cotton cellulose after Fe (II) sorption: *a* - original cellulose; *b* - cellulose modified with diethylenetriamine

Investigation of sorbents structure by SEM method. SEM-images of the original cotton cellulose and modified sorbent on its basis were made using a scanning electron microscope "VEGA3 SBH". The study of the samples surface layer structure by electron microscopy methods showed changing of the sorbent surfacemicrorelief under the modifying agent influence (Fig. 6). The surface of cellulose modified with diethylenetriamine becomes rougher (see Fig. 6, *b*) compared to the original cotton cellulose (see Fig. 6, *a*):



a ***b***

Fig. 6. SEM images of the sorbent surface layer: *a* - original cotton cellulose; *b* - cotton cellulose modified with diethylenetriamine

Thus, the SEM microscopic studies show the presence of changes in the surface structure of the modified cotton cellulose based sorption material as a result of the modification performed.

Conclusions

A novel sorbent capable of efficient extraction of Cu(II) and Fe(II) ions from aqueous solutions has been developed as a result of chemical modification of cotton cellulose with diethylene triamine. The study of heavy metal sorption indicates an increase in the efficiency of the process when using this sorbent compared to the original cellulose. The degree of metal ions extraction in the kinetic experiment increases by 15-20%. The ultimate sorption capacity of cotton cellulose modified with diethylenetriamine is 1.44 and 1.29 mol/kg for copper and iron ions, respectively.

The study of the modified sorbent by IR spectroscopy indicates that the modification of the sorbent results in the fixation of nitrogen-containing polymer on its surface. Analysis of the sorbent surface elemental composition by energy dispersive X-ray spectroscopy (EDS) indicates the presence of nitrogen in the modified sample. It was found by SEM that under the influence of the modifying agent the sorbent surface microrelief changes compared to the original cotton cellulose.

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References

1. **Syeda, H.I. & Yap, P.-S.** (2022) A review on three-dimensional cellulose-based aerogels for the removal of heavy metals from water, *Science of the Total Environment,* 807, 150606 [online]. Available at: https://doi.org/10.1016/j.scitotenv.2021.150606
2. **Aldaz, B., Figueroa, F. & Bravo, I**. (2020) Cellulose for the effective decontamination of water pollution, *Rev. Bionatura,* 5, pp. 1150–1155 [online]. Available at: https://doi.org/10.21931/RB/2020.05.02.13
3. **Yadav, S., Yadav, A., Bagotia, N. & Sharma, A.K., Kumar, S.** (2021) Adsorptive potential of modified plant-based adsor-bents for sequestration of dyes and heavy metals from wastewater, *A review Journal of Water Process Engineering,* 42, 102148 [online]. Available at: https://doi.org/10.1016/j.jwpe.2021.102148
4. **Mahurpawar, M.** (2020) Effects of heavy metals on human health, *Ann. Trop. Med. Public Heal*., 23 [online]. Available at: https://doi.org/10.36295/asro.2020.231125
5. **Humelnicu, D., Lazar, M.M., Ignat, M., Dinu, I.A., Dragan, E.S. & Dinu, M.V.** (2020) Removal of heavy metal ions from multi-component aqueous solutions by eco-friendly and low-cost composite sorbents with anisotropic pores, *J. Haz. Mat.,* 381, 120980 [online]. Available at: https://doi.org/10.1016/j.jhazmat.2019.120980
6. **Beni, A.-A. & Esmaeili, A.** (2020) Biosorption, an efficient method for removing heavy metals from industrial effluents: A Review, *Environmental Technology & Innovation,* 17, 100503 [online]. Available at: https://doi.org/10.1016/j.eti.2019.100503
7. **Aslam, A.A., Hassan, S.U., Saeed, M.H., Kokab, O., Ali, Z., Nazir, M.S., Siddiqi, W. & Aslam, A.A.** (2023) Cellulose-based adsorbent materials for water remediation: Harnessing their potential in heavy metals and dyes removal, *Journal of Cleaner Production,* 421, 138555 [online]. Available at: https://doi.org/10.1016/j.jclepro.2023.138555
8. **Prokof'ev, V.Yu. & Gordina, N.E.** (2013) A study of thermal treatment and hydrothermal crystallization stages in production of granulated zeolite from mechanically activated metakaolin, *Zhurnal Prikladnoj Khimii*, 86(3), pp. 332–338. DOI: 10.1134/S1070427213030075 (in Russian).
9. **Prokof'ev, V.Yu., Gordina, N.E. & Zhidkova, A.B.** 2011.Sintez granulirovannyh ceolitov so strukturoj NAA iz kaolina, *Izvestiya vysshih uchebnyh zavedenij. Seriya: Khimiya i khimicheskaya tekhnologiya*, 54(12), pp. 77–80 (in Russian).
10. **Burakov, A.E., Galunin, E.V., Burakova, I.V., Kucherova, A.E., Agarwal, S., Tkachev, A.G. & Gupta, V.K.** (2018) Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: a review? *Ecotoxicol. Environ. Saf.,* 148, pp. 702–712 [online]. Available at: https://doi.org/10.1016/j.ecoenv.2017.11.034
11. **Nazaripour, M., Reshadi, M.A.M., Mirbagheri, S.A., Nazaripour, M. & Bazargan, A.** (2021) Research trends of heavy metal removal from aqueous environments, *Journal of Environmental Management*, 287, 112322 [online]. Available at: https://doi.org/10.1016/j.jenvman.2021.112322
12. **Nikiforova, T.E., Kozlov, V.A., Rodionova, M.V. & Modina, Ye.A.** (2009) Sorption of zinc ions by products containing cellulose and protein components, *Izvestiya vysshih uchebnyh zavedenij. Seriya: khimiya i khimicheskaya tekhnologiya,* 52(3), pp. 27–31 (in Russian).
13. **Dey, P., Mahapatra, B.S., Juyal, V.K., Pramanick, B., Negi, M.S., Paul, J. & Singh, S.P.** (2021) Flax processing waste – A low-cost, potential biosorbent for treatment of heavy metal, dye and organic matter contaminated industrial wastewater, *Industrial Crops & Products,* 174, 114195 [online]. Available at: https://doi.org/10.1016/j.indcrop.2021.114195
14. **Nikiforova, T.E., Kozlov, V.A &, Vokurova, D.A.** (2023) Sorption of copper(II) ions in a heterophase system "aqueous solution - modified cellulose", *Izvestiya vysshih uchebnyh zavedenij. Seriya: khimiya i khimicheskaya tekhnologiya,* 66(12), pp. 91–100. DOI: 10.6060/ivkkt.20236612.6814 (in Russian).
15. **Nikiforova, T.E. Kozlov V.A. & Loginova V.A.** (2014) Peculiarities of the adsorption of heavy-metal ions from aqueous media by modified cellulose, *Adsorption Science & Technology,* 32(5), pp. 389–402**.**
16. **Nikiforova, T.E., Vokurova, D.A. & Sofronov, A.R.** (2022) Extraction of copper ions by a sorbent based on flax fiber modified with L-arginine, *From Chemistry Towards Technology Step-By-Step*, 3(3), pp. 78–86. DOI: 10.52957/27821900_2022_03_78 [online]. Available at: http://chemintech.ru/index.php/tor/2022tom3no3 (in Russian).

17. **Anantha, R.K. & Kota, S.** (2018) Bio-composites for the sorption of copper from aqueous solution: A comparative study, *Groundwater for Sustainable Development,* 7, pp. 265–276 [online]. Available at: https://doi.org/10.1016/j.gsd.2018.06.007
18. **Nikiforova, T.E., Kozlov, V.A. & Sionikhina, A.N.** (2019) Peculiarities of Sorption of Copper(II) Ions by Modified Wool Keratin, *Fizikohimiya poverhnosti i zashchity materialov*, 55(5), pp. 849–857 [online]. Available at: https://doi.org/10.1134/S2070205119050186 (in Russian).
19. **Kokotov, Yu.A.** & **Pasechnik, V.A.** (1970) *Equilibrium and kinetics of ion exchange*. L.: Khimiya (in Russian).
20. **Ahnazarova, S.L.** & **Kafarov, V.V.** (1985) *Methods of Optimizing Experiments in Chemical Technology*. Moscow: Vysshaya shkola (in Russian).

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