



EFFECT OF CHEMICAL MODIFICATION OF A COTTON CELLULOSE BY ANTHRANILIC ACID ON THE SORPTION OF Cu(II) AND Fe(II) IONS

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Abstract. The authors modified cotton cellulose with anthranilic acid to obtain a new sorbent capable of efficient extraction of heavy metal ions from aqueous solutions. We conducted the modification in two stages: at the first stage, we obtained dialdehyde cellulose by oxidation of cellulose with sodium metaperiodate; at the second stage, we treated dialdehyde cellulose with anthranilic acid to obtain a ready-made sorbent. The authors determined the optimum conditions for modifying cotton cellulose to achieve maximum sorption of iron(II) and copper(II) ions. We studied the equilibrium-kinetic characteristics of the original and modified cotton cellulose. Also, we have processed the results of the kinetic experiment within the framework of pseudo-first- and pseudo-second-order kinetics models. We selected sorption isotherms, processed them within the framework of the Langmuir model, and determined the values of the ultimate sorption capacity (A_{∞}). The modification of cotton cellulose enables to increase its sorption capacity significantly. According to the results, the A_{∞} of the modified sorbent is about 4-5 times higher than the ultimate sorption capacity of native cotton cellulose to Cu(II) and Fe(II) ions. In contrast, we obtained and compared the IR spectra of anthranilic acid-modified cellulose and native cellulose. Additionally, we obtained SEM images of the modified sorbent and the native cotton cellulose surface structure.

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Introduction

Nowadays, there is a worldwide growth of environmental pollution by harmful substances of different nature - heavy metals, radionuclides, petroleum products, etc. Studies devoted to the environmental pollution by heavy metals note their high toxicity to living organisms even in relatively low concentrations, as well as their ability to bioaccumulation [1]. Their introduction into the environment is caused by the activity of various industries, motor transport, boiler housing, incinerators, and agriculture. Volcanic eruptions, destruction of rocks, etc. are among the natural sources of environmental pollution by heavy metals. [2]. To reduce the environmental hazard of various industries, different methods of heavy metal



removal from wastewater, such as adsorption, precipitation, ion exchange, membrane treatment, electrocoagulation, electrodeposition, etc. are developed and applied [3].

The sorption is a very effective method of purification of water contaminated with heavy metal ions. It allows one to extract contaminants in a relatively wide range of concentrations. Sorption method is a challenging approach to wastewater treatment in terms of the environment. Nowadays, activated carbon is the most used adsorbent due to its high specific surface area. However, the application of activated carbon is limited due to the high cost of its production and regeneration process. Therefore, the actual task is the search for new, cheaper, and more effective sorption materials [4].

Mesoporous silica, zeolite, magnetic adsorbents, alumina, clay are widely used among sorbents of inorganic nature. Modern methods of mineral sorbents synthesis are presented in [5-7].

Biosorbents of polysaccharide nature, especially agro-industrial wastes, generated during the processing of agricultural raw materials, attract scientist's attention recently. Researchers have widely used plant biomass based on sorbents, particularly agricultural wastes, as an alternative to conventional sorbents due to their low cost, availability, renewability, biodegradability, and sorption potential. The feasibility of industrial applications and cost-effectiveness are the key factors playing the most important role in selecting the most suitable sorbent for biosorption of heavy metals from aqueous effluents [8].

The adsorption capacity of biosorbents can be significantly improved by chemical, physical, or biochemical methods. The use of agro-industrial wastes in unmodified (rice husks, chitosan, coffee cake, wheat bran, soya flour, ground olive seeds, apple pomace, mushroom biomass, yeast, algal and bacterial biomass), and in modified form (sugar cane, modified wheat bran, modified coconut waste, modified orange peel waste, modified sawdust, modified eggshells), which are the most studied adsorbents [9-10].

The main advantages of biosorbents are their nontoxicity and safety for humans and the environment. Biosorbents are able to remove heavy metals in low concentrations effectively and are relatively widely used for this purpose [11].

Sorption materials can be both water-soluble and insoluble in water, including cross-linked. They can be used in the form of membranes, fibres, gels, or beads [12-13]. Notable, hybrid materials are also of great interest for the removal of metal cations from aqueous solutions. The incorporation of inorganic materials such as silica, for example, can improve diffusion or physical properties, increase the stability of the sorbents, and facilitate separation at the end of the sorption process [14].

The efficiency of a sorbent is known to depend both on its specific surface area and on the number and type of sorption centres [14-16]. Polymeric sorbents containing acidic groups (carboxylic, sulfogroups, etc.) are of great interest. Depending on the nature of the functional groups, the polymeric sorbent can demonstrate either chelate properties or act as a polyelectrolyte, which determines the mechanism of metal ion binding [16]. Therefore, the development and application of biopolymeric sorbents with acidic functional groups for the removal of heavy metal ions from aqueous solutions, including wastewater, is an urgent scientific task.

The purpose of this study is to develop a sorbent based on cotton cellulose with high sorption characteristics for effective purification of aqueous media from heavy metal ions.



Main body

We used cotton cellulose (GOST 595-79) as a sorbent in the experimental part of the study. For purification from impurities we boiled the cellulose for 30 minutes with 5% NaHCO₃ solution at a solution/sorbent modulus of 20, then washed with distilled water to pH = 7 and dried to constant weight. Air-dried cellulose samples had a moisture content of 8.5%.

We used sodium metaperiodate NaIO₄ and anthranilic acid C₇H₇NO₂ as modifying agents; we used iron and copper sulfates FeSO₄·7H₂O and CuSO₄·5H₂O to prepare model solutions for sorption experiments. All reagents were "chemically pure".

We performed the modification of cotton cellulose with anthranilic acid in two steps:

- oxidation of cellulose by sodium metaperiodate forming dialdehyde cellulose;
- modification of dialdehyde cellulose with anthranilic acid.

We oxidised cellulose with sodium metaperiodate and determined the content of aldehyde groups in the sorbent as described in [17]. The dialdehyde cellulose [18] obtained during periodate oxidation was subsequently treated with anthranilic acid. For this purpose, we placed oxidized cotton cellulose containing 12% aldehyde groups in an amount of 1 g in a flask containing 1% anthranilic acid solution (solution/sorbent modulus 50). We conducted the modification process for 45-60 min at a temperature of 40–45 °C and pH = 7–10 with continuous stirring. After cooling, we washed the modified sorbent with distilled water to neutral reaction, and dried.

Kinetics and equilibrium of sorption. We studied the kinetics of heavy metal ions sorption in static under stirring by the limited solution volume method [19]. The initial concentration of metal ions (C_0) was $1.5 \cdot 10^{-4}$ mol/l. We then separated the solution from the sorbent by filtration and determined its equilibrium concentration of metal ions (C_τ) by atomic absorption spectroscopy on a 210VGP instrument.

The degree of (α , %) metal ion extraction we determined as follows:

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

To obtain sorption isotherms, we placed 0.1 g sorbent suspensions into a series of test tubes and poured them into 10 ml of aqueous metal sulfate solution with metal concentrations in the range of $1.5 \cdot 10^{-4}$ - $5 \cdot 10^{-2}$ mol/l. Then we were stirring them to establish the equilibrium. We then separated the solution from the sorbent by filtration and determined its equilibrium concentration of metal ions (C) by atomic absorption spectroscopy on a 210VGP.

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, where 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

We calculated the kinetic curves of sorption of Cu(II) and Fe(II) ions to determine the time to reach sorption equilibrium in the heterophase system "cellulose sorbent - aqueous solution of metal sulphate". The experimental results are shown on Fig. 1.

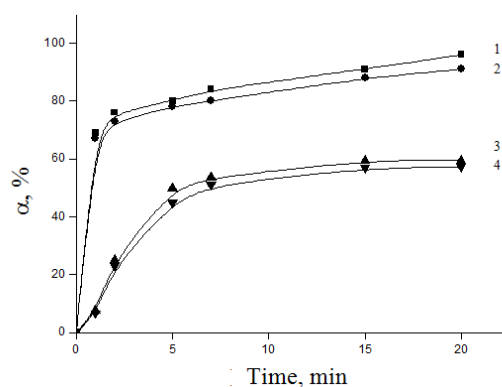


Fig. 1. Kinetic curves of sorption of Cu²⁺ (1, 3) and Fe²⁺ (2, 4) ions from aqueous solutions of native (3, 4) and modified (1, 2) cotton cellulose

Fig. 1 shows significantly increasing of heavy metal ions extraction degree in the case of using cellulose modified with anthranilic acid compared to native cellulose. According to it, the time to reach sorption equilibrium is 20 minutes.

To determine the reaction order, we processed the experimental data using pseudo-first (3) and pseudo-second (4) order kinetic models:

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

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

Table 1 shows the results of processing the kinetic curves of heavy metal ion sorption by native and modified cotton cellulose in the framework of pseudo-first-order and pseudo-second-order kinetics models using the Origin programme. However, the highest correlation coefficients (0.99) were obtained when processing the data of the kinetic experiment using the pseudo-second-order model.

Table 1. Results of the treatment of heavy metal ion sorption kinetic curves of native and modified cotton cellulose within the framework of chemical kinetics models

Ion of metal	Equilibrium sorption value	Pseudo-first-order model			Pseudo-second-order model		
		q_e , mg/g	k_1 , min ⁻¹	R^2	q_e , mg/g	k_2 , mg min/g	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
Anthranilic acid modified cellulose							
Cu(II)	0.93	0.61	0.27	0.98	0.95	1.17	0.99
Fe(II)	0.87	0.69	0.25	0.97	0.81	1.08	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 native cotton cellulose and cellulose modified with anthranilic acid. The experimental results are shown on Fig. 2.

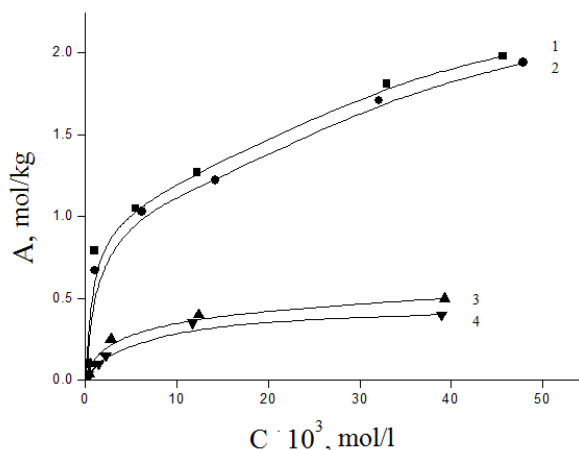


Fig. 2. Sorption isotherms of Cu²⁺ (1, 3) and Fe²⁺ (2, 4) ions from aqueous solutions of native (3, 4) and modified (1, 2) cotton cellulose

The experimental data obtained can be described by the Langmuir adsorption isotherm equation

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

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.

Linearization 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 in accordance with the experimental data on the tested sorbate distribution in the heterophase system "aqueous solution - cellulose sorbent".

Table 2 shows the results of processing of heavy metal ion sorption isotherms using Langmuir model of native cotton pulp and cotton pulp modified with anthranilic acid.

Table 2. Processing parameters of heavy metal ion sorption isotherms of original cellulose and cotton modified cellulose using the Langmuir least squares model

Metal cation	K , l/mol	$1/A_{\infty}$	Correlation coefficient	A_{∞} , mol/kg
Non-modified cellulose				
Cu(II)	909.1	$2,0 \pm 0,02$	0.99	0.50
Fe(II)	961.5	$2,5 \pm 0,02$	0.99	0.40
Anthranilic acid modified cellulose				
Cu(II)	217.4	0.50 ± 0.03	0.99	2.00
Fe(II)	325.5	0.51 ± 0.04	0.98	1.96



The experimental data on the sorption of copper and iron ions by native and modified cotton cellulose are well approximated by the Langmuir equation. As follows from the data presented on Fig. 2 and Table 2, the ultimate sorption capacity (A_{∞}) of cotton pulp modified with anthranilic acid is four times higher than A_{∞} of native pulp for Cu(II) ions and about five times higher for Fe(II) ions. The values of $A_{\infty} \approx 2$ mol/kg obtained for the sorption of Cu(II) and Fe(II) ions by modified cellulose indicate good binding capacity of the sorbent towards these metals.

We can explain the significant increase in the ultimate sorption capacity of modified cotton cellulose in comparison with native cellulose by the fact that, as a result of modification, new functional groups capable of effectively binding heavy metal ions appear in the fibre structure.

IR spectra analysis. We obtained IR spectra of the original cotton cellulose as well as cellulose oxidized with sodium metaperiodate (dialdehyde cellulose) and cellulose modified with anthranilic acid to detect new sorption centres formed on the sorbent surface during the modification process (Fig. 3, curves 1-3).

Comparison of the IR spectra obtained reveals the differences among the cellulose samples under study. In the range 1780–1600 cm^{-1} the presence of absorption bands is due to valence vibrations of the C=O bond for aldehydes, ketones, and carboxylic acids. In this range, a shift of the peak at 1729 cm^{-1} to the position 1741 cm^{-1} is observed for the cellulose sample modified with anthranilic acid compared to the original cellulose, which is due to the appearance of carboxyl groups in its structure.

We observe a band shift of the spectrum of dialdehyde cellulose from the 1640 cm^{-1} position for the original cotton cellulose to the 1632 cm^{-1} position, associated with the appearance of aldehyde groups during the oxidation of cellulose by sodium metaperiodate.

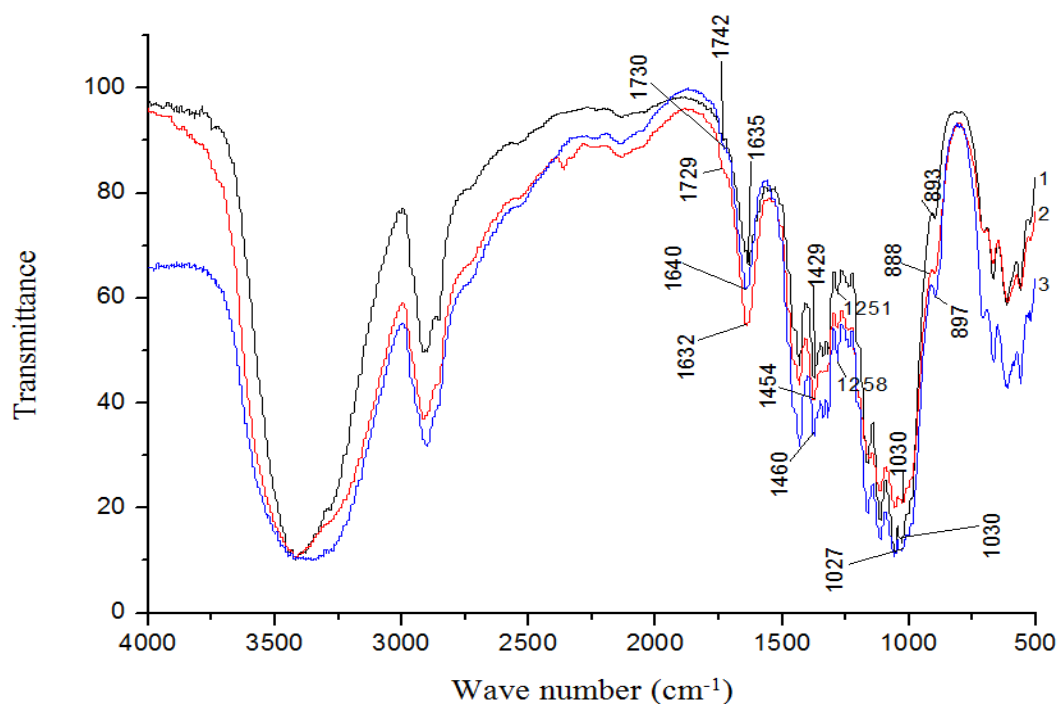


Fig. 3. IR spectra of native cotton cellulose (1), dialdehyde cellulose (2), anthranilic acid modified cellulose (3)



We also observe changes in the spectrum of cellulose modified with anthranilic acid compared to the spectrum of the original cellulose. The changes occur in the range of $1300\text{-}1250\text{ cm}^{-1}$, where the valence vibrations of the C-N bond in amides appear. Therefore, we can assert that the modification of the sorbent results in the anchoring of anthranilic acid on its surface. Thus, the results of IR spectroscopy confirm the presence of cellulose modification with anthranilic acid through the stage of dialdehyde-cellulose formation causes occurring of new sorption-active groups in the structure of sorbents.

Microscopic study of sorbents structure. The study of the surface structure of the original cotton cellulose and modified sorbent by electron microscopy showed the modification changes of the sorbent surface microrelief. Thus, the surface of the original cotton cellulose (Fig. 4, *a*) is homogeneous but has with few folds. Modification with anthranilic acid causes the surface of the sorbent to become rougher and an abundance of folds and scales is observed (Fig. 4, *b*), which indicates a change in the surface layer.

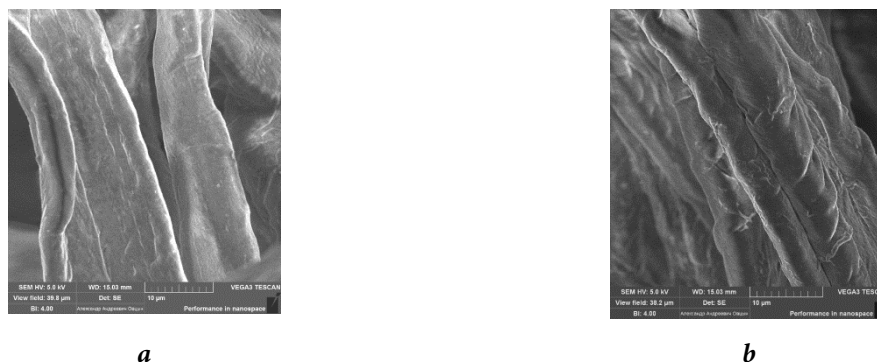


Fig. 4. SEM images of the original cotton pulp surface (*a*) and the cotton pulp surface modified with anthranilic acid (*b*)

We obtained a sorbent with a different structure from the original cotton cellulose, characterised by enhanced sorption properties towards heavy metal ions as a result of the modification.

Conclusions

We have developed a new effective sorbent for the extraction of heavy metal ions from aqueous solutions by sequential treatment of cotton cellulose with sodium metaperiodate and anthranilic acid. The authors studied the sorption process of heavy metal ions on cotton cellulose and the modified sample. We found the sorption characteristics of the modified sorbent with respect to Cu^{2+} and Fe^{2+} ions to be significantly higher than those of native cotton cellulose. The kinetics of sorption of heavy metal ions by the sorbents under study is described most adequately (with a correlation coefficient of 0.99) by the kinetic model of pseudo-second order. There is a good description of the experimental isotherms of sorption of copper and iron ions in the framework of the Langmuir model. Moreover, the maximum sorption capacity of anthranilic acid-modified cotton pulp increases compared to native cotton pulp for Cu^{2+} and Fe^{2+} ions from 0.5 and 0.4 mol/kg to 2 and 1.96 mol/kg, respectively.

IR spectra of samples of original cellulose and cellulose modified with anthranilic acid indicate occurring of new sorption-active groups in the sorbent structure.

SEM microscopic studies show the presence of changes in the surface structure of cotton cellulose based sorption material compared to the original sample.



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References

1. Humelnicu, D., Lazar, M.M., Ignat, M., Dinu, I.A., Dragan, E.S. & Dinu, M.V. (2019) 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>
2. Yadav, S., Yadav, A., Bagotia, N., Sharma, A.K. & Kumar, S. (2021) Adsorptive potential of modified plant-based adsorbents 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>
3. Agarwal, A., Upadhyay, U., Sreedhar, I., Singh, S.A. & Patel, C.M. (2020) A review on valorization of biomass in heavy metal removal from wastewater, *J. Water Proc. Eng.*, 38, 101602 [online]. Available at: <https://doi.org/10.1016/j.jwpe.2020.101602>
4. Meseldzija, S., Petrovic, J., Onjia, A., Volkov-Husovic, T., Nesic, A. & Vukelic, N. (2019) Utilization of agro-industrial waste for removal of copper ions from aqueous solutions and mining-wastewater, *Journal of Industrial and Engineering Chemistry*, 75, pp. 246–252 [online]. Available at: <https://doi.org/10.1016/j.jiec.2019.03.031>
5. Prokofev, V.Y. & Gordina, N.E. (2013) A study of thermal treatment and hydrothermal crystallization stages in production of granulated NAA zeolite from mechanically activated metakaolin, *Zhurnal prikladnoj khimii*, 86(3), pp. 332-338 (in Russian).
6. Prokofev, V.Yu., Gordina, N.E. & Zhidkova, A.B. (2011) Synthesis of granulated zeolites with NAA structure from kaolin, *Izvestija vuzov. Khimija i khimicheskaja tehnologija*, 54(12), pp. 77-80 (in Russian).
7. Gordina, N.E., Prokofev, V.Y., Hmylova, O.E. & Kul'pina, Y.N. (2017) Effect of ultrasound on the thermal behavior of the mixtures for the LTA zeolite synthesis based on metakaolin, *Journal of Thermal Analysis and Calorimetry*, 129(3), pp.1415-1427.
8. Saavedra, M.I., Miñarro, M.D., Angosto, J.M. & Fernández-López, J.A. (2019) Reuse potential of residues of artichoke (*Cynara scolymus* L.) from industrial canning processing as sorbent of heavy metals in multimetallic effluents, *Industrial Crops & Products*, 141, 111751 [online]. Available at: <https://doi.org/10.1016/j.indcrop.2019.111751>
9. Shrestha, R., Ban, S., Devkota, S., Sharma, S., Joshi, R., Tiwari, A.P., Kim, H.Y. & Joshi, M.K. (2021) Technological trends in heavy metals removal from industrial wastewater: A review, *Journal of Environmental Chemical Engineering*, 9(4), 105688 [online]. Available at: <https://doi.org/10.1016/j.jece.2021.105688>
10. Nikiforova, T.E., Kozlov, V.A., Rodionova, M.V. & Modina, E.A. (2009) Sorption of zinc ions by products containing cellulose and protein components, *Izvestija vuzov. Himija i himicheskaja tehnologija*, 52(3), pp. 27-31 (in Russian)
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. Kozlov, V.A., Nikiforova, T.E., Loginova, V.A. & Koifman, O.I. (2015) Mechanism of protodesorption – exchange of heavy metal cations for protons in a heterophase system of H₂O-H₂SO₄-MSO₄ – cellulose sorbent, *Journal of Hazardous Materials*, 299, pp. 725-732. DOI: 10.1016/j.jhazmat.2015.08.004.
13. Singha, B. & Das, S.K. (2013) Adsorptive removal of Cu(II) from aqueous solution and industrial effluent using natural/agricultural wastes, *Colloids and Surfaces B: Biointerfaces*, 107, pp. 97–106 [online]. Available at: <http://dx.doi.org/10.1016/j.colsurfb.2013.01.060>



14. **Nikiforova, T.E. & Kozlov, V.A.** (2012) Comparison of models of copper (II) and nickel (II) cations sorption from aqueous solutions by cotton cellulose, *Zhurnal fizicheskoy khimii*, 86(10), pp. 1724-1729 (in Russian).
15. **Nikiforova, T.E., Kozlov, V.A. & Islyaikin, M.K.** (2012) Acid-base interactions and complex formation while recovering copper(ii) ions from aqueous solutions using cellulose adsorbent in the presence of polyvinylpyrrolidone, *Zhurnal fizicheskoy khimii*, 86(12), pp. 1974-1984 (in Russian).
16. **Nikiforova, T.E., Kozlov, V.A. & Islyaikin, M.K.** (2012) Acid-base interactions and complex formation while recovering copper(ii) ions from aqueous solutions using cellulose adsorbent in the presence of polyvinylpyrrolidone, *Russian Journal of Physical Chemistry*, 86(12), pp. 1974-1984.
17. **Beaugeard, V., Muller, J., Graillot, A., Ding, X., Robin, J.-J. & Monge, S.** (2020) Acidic polymeric sorbents for the removal of metallic pollution in water: A review, *Reactive and Functional Polymers*, 152(3), 104599 [online]. Available at: <https://doi.org/10.1016/j.reactfunctpolym.2020.104599>
18. **Nikiforova, T.E., Kozlov, V.A. & Sofronov, A.R.** (2023) Effect of chemical modification of cotton cellulose by aminoacetic acid on the sorption of Cu(II) and Fe(II) ions, *From Chemistry Towards Technology Step-By-Step*, 4(1), pp. 32-42 [online]. Available at: <http://chemintech.ru/index.php/tor/2023-4-1> (in Russian).
19. **Klemm, D., Philipp, B., Heinze, D., Heinze, U. & Wagenknecht, W.** (1998) *Comprehensive cellulose chemistry. Vol. 1: Fundamentals and Analytical Methods*. Wiley-WCH, Weinheim, Germany.
20. **Kokotov, Yu.A. & Pasechnik, V.A.** (1970) Equilibrium and kinetics of ion exchange. L.: Khimiya (in Russian).
21. **Ahnazarova, S.L. & Kafarov, V.V.** (1985) Methods of experiment optimisation in chemical technology. Moscow: Vysshaya Shkola (in Russian).

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