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SORPTION PROPERTIES OF A NEW MODIFIED FLAX FIBRE SORBENT

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Abstract. *The purpose of this study is to develop a modified sorbent of flax waste and investigate its sorption properties towards Cu (II) ions. The authors conducted the modification in two steps. The first step was oxidation of flax fibre cellulose with sodium metaperiodate to dialdehyde cellulose, the second one was the addition of taurine to increase the sorption characteristics of the modified sorbent. The paper presents the conditions for the periodate oxidation reaction of flax fibre and the treatment of the resulting dialdehyde cellulose with taurine. We determined the sorption characteristics of the modified sorbent in comparison with the original flax fibre. Kinetic studies allowed us to establish the time of reaching sorption equilibrium in the heterophase system 'aqueous solution of metal salt-sorbent' and determine the reaction order using pseudo-first and pseudo-second order kinetics models. The authors processed the sorption isotherms obtained during the experiments using the Langmuir model. The maximum sorption capacity increased by 3 times compared to the original flax fibre. IR spectroscopy confirmed the improvement of equilibrium and kinetic characteristics of flax fibre occuring as a result of the appearance of new sorption centres in its structure.*

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Introduction

Nowadays, the main pollutants of water resources include heavy metal ions contained in industrial effluents produced by chemical, petrochemical, mining and other industries. The heavy metals are accumulated in the environment. Unlike organic substances they are not decomposed by microorganisms. High concentrations of heavy metals in the wastewater of enterprises causes their accumulation in drinking water, food, etc. It provides their accumulation in the human body and causes significant harm to health.

The toxic effect of heavy metals is characterised by non-specificity. Those are able to bind to proteins, nucleotides, coenzymes, phospholipids and almost all substances involved in metabolic processes [1, 2]. This necessitates the development of new and more effective methods of purification of water and aqueous solutions against heavy metal ions. Modern heavy metal removal technologies include chemical precipitation, reduction, electrocoagulation, electrodialysis, reverse osmosis, membrane filtration, ion exchange, and adsorption. Among these methods, sorption is the most common due to its high efficiency and ease of application [3].

Particular interest has been shown in recent years for the development of sorbents based on by-products or wastes from agriculture, textile, and pulp and paper industries [4]. In addition to biosorbents based on natural components, there are a large number of synthetic sorbents based on zeolites [5]. The main advantages of using biosorbents to remove heavy metal ions compared to traditional methods include lower cost, availability, ease of disposal, cleaning efficiency, and the ability to regenerate the sorbents. The advantages of agricultural waste-based sorbents include their renewability and environmental safety as they are environmentally friendly and biologically neutral towards the media to be treated [6]. However, sorbents in the native state have, as a rule, low sorption capacity. Therefore, modification of sorbents based on secondary cellulose-containing raw materials is very relevant.

Various modification methods including chemical, physical, physicochemical, and biochemical are used to enhance the sorption capacity of cellulose-containing sorbents [4]. The paper [7] proposes a method for the removal of heavy metal ions from aqueous solutions using cellulose modified with polyethylene polyamine. The sorbent obtained by thermal treatment of rice husk shows high sorption properties towards copper (II) and zinc (II) ions [8]. The production of grafted copolymers of cellulose with different monomers is a prospective direction in the development of cellulose sorbents [9].

Flax fibre and various products of its processing are produced in large volumes both in our country and abroad. It has attracted the attention of researchers in recent years. Modified linseed flour production waste [10] and short flax fibre as waste product of flax processing, can be used to produce sorbents. The fibres include cellulose, hemicellulose, lignin, pectin substances and other components containing a variety of functional groups. They have a significant effect on the adsorption of heavy metal ions. Indeed, the radius of the hydrated ion, electronegativity, and interaction of ions with functional groups (-COOH, -OH, $-OSH_3$) are the key factors affecting the biosorption process. The efficiency of this process also depends on the pH of the aqueous solution, contact time, initial concentration of metals, and concentration of the biosorbent itself [11-12]. Flax fibre, similar to other cellulosic materials, can be modified by various methods to increase its sorption capacity [13-15].

Nowadays, in various countries there is a tendency to use annual plants as a source of cellulose (flax, jute, hemp, kenaf, etc.) [13]. Flax is the main competitor of cotton in our country. Recently, there has been an increase in the production of textile products from flax fibres. It is accompanied by an increase in the amount of wastes from these industries, such as short fibres and the woody part of flax stalks (flax refuse) as alternative sources of cellulose.

Cellulose (fibre) is one of the most abundant natural polymers and a major component of plant cell walls, providing mechanical strength and elasticity to plant tissues. Cellulose macromolecules consist of elementary links of D-glucose (in pyranose form) connected by 1,4-β-glycosidic bonds into linear unbranched chains.

The development of cellulosic sorbents and the study of their sorption properties are important practical and scientific challenges. Search for compounds with high sorption capacity towards heavy metals and creation of fillers for water treatment equipment on their basis are very actual. Cellulose is a subject of great interest due to its advantages such as affordability, renewability, and biodegradability.

The purpose of this study is to develop a new cellulose-containing sorbent based on flax fibre by modification with taurine to improve its sorption properties.

Experimental part

Short flax fibre (GOST 9394-76) – a secondary product of flax industry processing of the following composition, %, was chosen as the object of the study: (cellulose (75-78), hemicellulose (9.4-11.9), lignin (3.8), pectin substances (2.9-3.2), wax-like substances (2.7), nitrogen-containing substances per protein (1.9-2.1), mineral substances (1.3-2.8) [16].

The modifying agent was taurine (IUPAC: 2-aminoethanesulfonic acid), a sulfur-containing amino acid. The sulfogroup is a rather active sorption centre; it explains the choice of this amino acid [17].

It was pre-boiled with 10% NaOH solution to remove impurities and increase sorption capacity. The curing time was 30 minutes; a solution/sorbent modulus was 20. Then we washed the sorbent with distilled water to neutral pH 7 and dried to constant weight.

This method of modifying flax fibre with taurine consists of two main steps:

- oxidation of cellulose by sodium metoperiodate forming dialdehyde cellulose;
- modification of dialdehyde cellulose by taurine.

We used distilled water to prepare dilute solutions, mixed the pre-purified fibre (2.5 g) with 250 ml of 0.1 n $NaIO_4$ solution. The reaction proceeds for 48 hours with periodic stirring in an opaque flask, at a temperature of 23-25 °C and pH 3-4; since the oxidative properties of metaperiodate are observed in an acidic environment. Sodium metaperiodate is reduced to insoluble para-periodate at pH above 4.6.

At the end of the periodate oxidation reaction, we filtered the insoluble fraction from the reaction product solution and washed successively with 1-1.2 L of water with the addition of hydrochloric acid solution to pH ~ 1, then 1-1.2 L of acetone/water: 1/8 mixture and finally 1-1.2 L of distilled water.

The next step in the modification of flax fibre cellulose was the treatment of the aldehyde groups of oxidised flax fibre with taurine ($C_2H_7NO_3S$).

We placed 2 g weight of treated fibre containing 8.8% aldehyde groups in a flask containing 5% taurine solution (sorbent : solution modulus 1 : 50). We determined the amount of aldehyde groups by the iodometric method described in [18]. We conducted the modification for 45-60 min at a temperature of 60-70 °C and pH 7-10 under continuous stirring. After cooling, we washed the reaction products with distilled water to neutral reaction.

Equipment used: U-2001 spectrophotometer (Japan), 210 VGP atomic absorption spectrometer, IR-spectrometer Avatar 360 FT-IR E.S.P.

We studied the sorption kinetics of heavy metal ions under static conditions under stirring using the limited solution volume method [19].

We calculated the sorption capacity of the sorbent at any given time τ using formula:

$$q = \frac{(C_0 - C_\tau)}{m} \cdot V,$$

where q is sorption capacity, mg/g;

C_0 is the initial concentration of metal ions, mg/l;

C_τ is the concentration of metal ions at time τ, mol/l;

m – mass of the sorbent, kg; V – volume of the solution, l.

We determined the degree of α extraction as follows:

$$\alpha = \frac{C_0 - C\tau}{C_0} \cdot 100\%,$$

The equilibrium concentration of metal ions in solution (Ce) was determined and the equilibrium sorption capacity was calculated by removing the sorption isotherm under steady-state equilibrium conditions in the system:

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

where A is the equilibrium sorption capacity, mol/kg;

C is the equilibrium concentration of metal ions, mol/l.

We calculated the relative inaccuracy on the basis of data from experiments. Each point represents the average of two parallel experiments [20]. The inaccuracy of the experiment was lower 10%.

The research was performed using the resources of the Center for Shared Use of Scientific Equipment of the ISUCT.

Main body

We chose sodium metaperiodate as the oxidant. It is specific one and do not break the polymer chains of the cellulose molecule like other oxidants such as sodium hypochlorite, hydrogen peroxide, ozone, potassium bichromate, potassium permanganate, etc. Sodium metaperiodate acts on the two -OH groups at C_2 and C_3 forms aldehyde groups and parallel breaking of the C-C bond between them. It also forms dialdehyde cellulose. We conducted the oxidation reaction at pH 3-4; the oxidative properties of periodate occur in an acidic environment. Sodium metaperiodate is reduced to insoluble para-periodate at pH above 4.6. Fig. 1(a) shows the scheme of cellulose oxidation by sodium metaperiodate. We then treated the resulting dialdehyde cellulose with taurine in the zwitter ion state at pH ~7 (Fig. 1(b)):

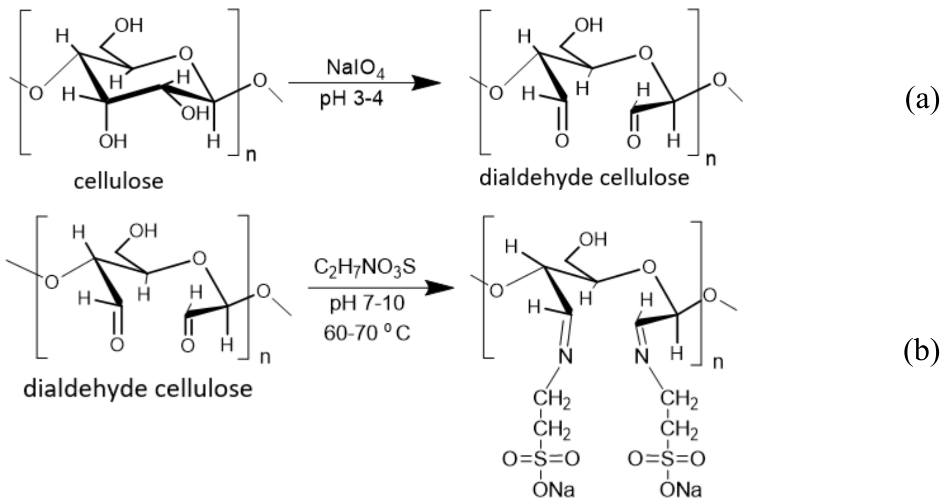

Fig. 1. Scheme of cellulose oxidation by sodium metaperiodate to form dialdehyde cellulose (a) and combining of taurine with dialdehyde cellulose (b)

To determine the kinetic characteristics of the modified sorbent, we obtained kinetic curves for the sorption of Cu(II) ions from aqueous copper sulphate solution by the original flax fibre and the taurine-modified fibre. Fig. 2 shows the experimental results.

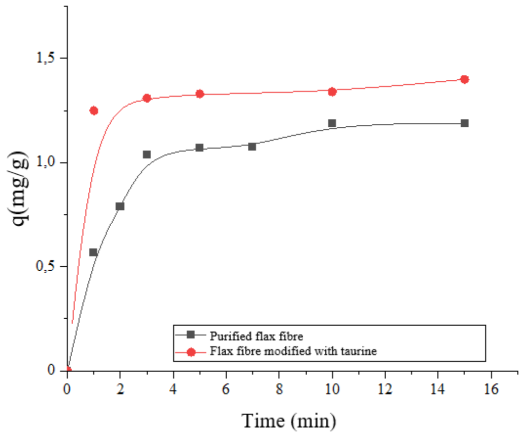

Fig. 2. Kinetic curves of copper ions sorption from aqueous solution by original and modified flax fibre

Figs. 3 and 4 and Table 1 present the kinetic curves of Cu(II) ion sorption by the original fibre and modified sorbent in terms of pseudo-first and pseudo-second order kinetics models.

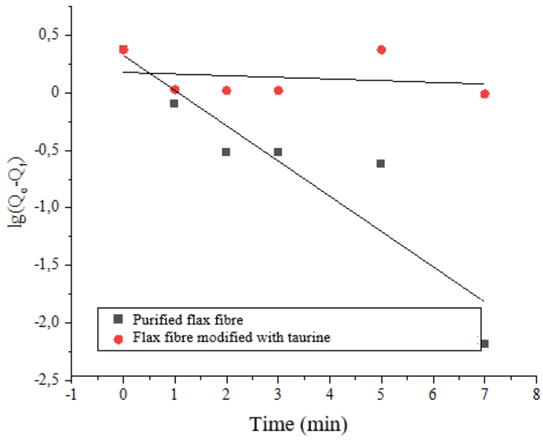

Fig. 3. Kinetics of pseudo-first order sorption of copper ions from aqueous solution by original and modified flax fibre

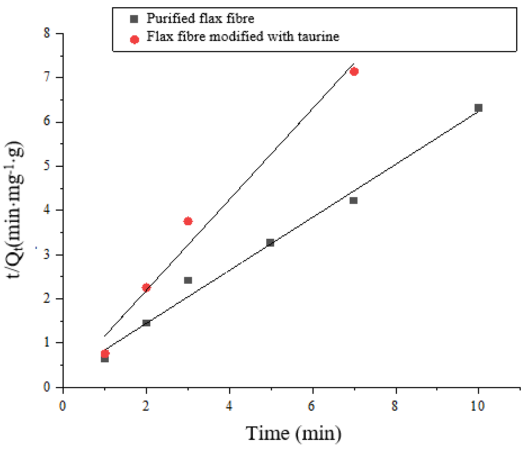

Fig. 4. Kinetics of pseudo-second order sorption of copper ions from aqueous solution by original and modified flax fibre

Table 1. Results of kinetic curves processing of copper ions sorption from aqueous solution by initial and modified flax fibre by chemical kinetics models

Kinetic model	Processing results	Native flax fibre	Modified flax fibre
pseudo-first order	q_e, mg/g	0.740±0.090	0.07±0.002
	k_1, 1/min	0.244±0.030	0.00031±0.0001
	R^2	0.95	0.82
pseudo-second order	q_e, mg/g	0.736±0.050	1.4±0.070
	k_2, g/(mg·min)	1.028±0.400	2.99±0.500
	R^2	0.99	0.99

To determine the maximum sorption capacity (A_∞) of the original and modified fibres, we obtained isotherms of Cu(II) ion sorption from aqueous solution at 293 K. Fig. 5 shows the experimental isotherms.

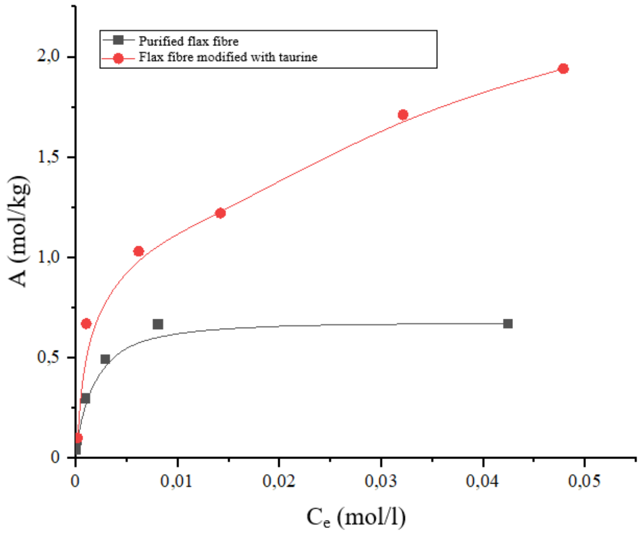

Fig. 5. Isotherms of copper ions sorption from aqueous solution by original and modified flax fibre

We present the results of copper ion sorption isotherms using the Langmuir model in Fig. 6 and Table 2.

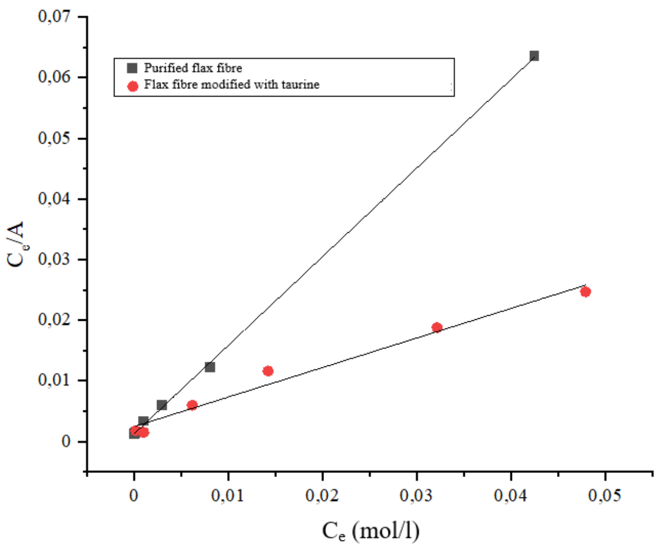

Fig. 6. Processing of isotherms of copper ions sorption from aqueous solution by modified sorbent and original fibre

Table 2. Processing parameters of copper ion sorption isotherms by initial and modified flax fibre according to Langmuir model by the least squares method

Sorbent	$1/A_\infty \cdot K$	$1/A_\infty$	Correlation coefficient	A_∞, mol/kg
Initial flax fibre	0.00129± $2.9 \cdot 10^{-4}$	1.46± 0.02	0.99	0.68
Modified fibre	0.00249 ± $8.8 \cdot 10^{-4}$	0.49 ± 0.04	0.99	2.04

The improvement of adsorption properties of flax fibre modified with taurine is explained by the occurrence of new functional groups in the fibre structure. It effectively binds heavy metal ions. To reveal such changes, we obtained IR spectra of purified flax fibre before and after modification with taurine (Figure 7).

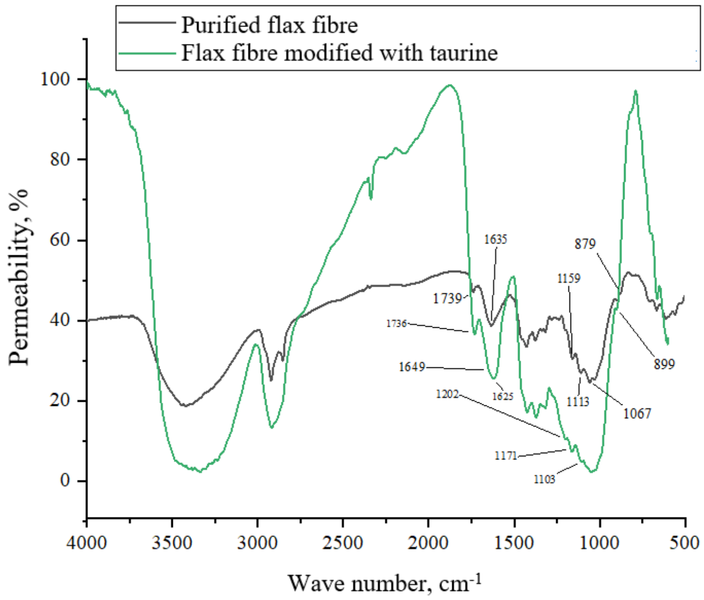

Fig. 7. IR spectra of raw and modified flax fibre

As a result of sorbent modification, Fig. 7 shows significant changes in the region 1750-1650 cm^{-1}, where the vibrations of the carbonyl group are observed. Thus, the 1739 cm^{-1} band in the spectrum of the original flax fibre shifts to the 1736 cm^{-1} position in the spectrum of the modified flax fibre. It is due to oxidation of flax cellulose with sodium metaperiodate resulting in the formation of aldehyde groups involved in the interaction with taurine (see Fig. 1 a, b). Vibrations of the C=N bond in unsaturated nitrogen-containing compounds also occur in the region 1690-1635 cm^{-1}. It is as evidenced by the appearance of a small peak at 1649 cm^{-1} in the spectrum of the modified sorbent.

The changes in the spectral region of 1650-1620 cm^{-1} and 1300-1000 cm^{-1} are due to strain and valence vibrations of the C-N bond. The band from 1635 cm^{-1} in the spectrum of the original flax fibre shifts to 1625 cm^{-1} in the spectrum of the taurine modified fibre. The band at 1159 cm^{-1} in the spectrum of unmodified flax fibre occurs at 1171 cm^{-1} in modified sample. Therefore, the modification of the sorbent results in the fixation of the nitrogen-containing compound on its surface.

The differences in the regions 1100-1000 cm^{-1} and 880-840 cm^{-1} of IR spectra of the original and modified flax fibre are due to vibrations of C-SO_3H group and S-O bond [21]. Therefore, sulfogroups are combined in the process of modification. Their occurrence is confirmed by the shift of peaks in the spectrum of the original flax fibre from 1113 cm^{-1} and 879 cm^{-1} to 1103 cm^{-1} and 899 cm^{-1} for the modified sorbent, respectively.

Therefore, the IR spectroscopy results confirm occurrence of chemical interaction of modifying agents with flax fibre cellulose through proposed processing method. It causes the presence of aldehyde groups during oxidation of flax fibre by sodium metaperiodate followed by taurine combining.

During the modification, flax fibre cellulose is sequentially reduced to dialdehyde cellulose and then to a derivative compound with taurine. It causes the occurence of new sorption-active groups in the structure of sorbents capable of effectively binding heavy metal ions. The sorption of Cu (II) ions occurs according to the mechanism shown in the scheme (Fig. 8):

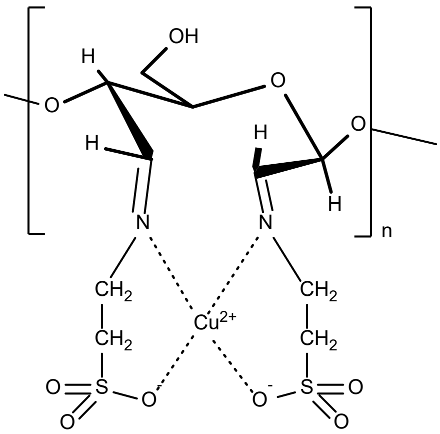

Fig. 8. Scheme of Cu (II) ions sorption by modified sorbent

Conclusions

Hence, we developed a new efficient sorbent for the extraction of heavy metal ions from aqueous solutions by modifying short flax fibre with taurine and pre-oxidising flax fibre cellulose to dialdehyde cellulose.

The authors investigated the kinetics and equilibrium of sorption of Cu(II) ions by $CuSO_4$ aqueous solutions. We processed the kinetic curves of copper ion sorption in accordance with of pseudo-first and pseudo-second-order models. The sorption is described most correctly by the pseudo-second-order model.

Indeed, the experimental sorption isotherms of copper(II) ions can be described by the Langmuir equation. Processing the isotherms in the linear form of this equation allowed us to determine the ultimate sorption capacity of taurine-modified linseed fibre as 2.04 mol/kg.

IR spectra indicate changes in the composition of flax fibre oxidised with sodium metaperiodate and modified with taurine during the modification compared to the original flax fibre.

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References

1. **Vardhan K.H., Kumar P.S., Panda R.C.** A review on heavy metal pollution, toxicity and remedial measures: current trends and future perspectives // *Journal of Molecular Liquids*. 2019. No. 290. Pp. 111-197.
2. **Lindholm-Lehto P.** Biosorption of heavy metals by lignocellulosic biomass and chemical analysis // *Bio Resources*. 2019. No. 14. Pp. 4952-4995.
3. **Yadav S., Yadav A., Bagotia N., Sharma A.K., Kumar S.** Adsorptive potential of modified plant-based adsorbents for sequestration of dyes and heavy metals from wastewater - A review // *Journal of Water Process Engineering*. 2021. No. 42. Pp. 102-148.
4. **Dawn S.S, Vishwakarma V.** Recovery and recycle of wastewater contaminated with heavy metals using adsorbents incorporated from waste resources and nanomaterials - A review // *Chemosphere*. 2021. Vol. 273. 129677. DOI: https://doi.org/10.1016/j.chemosphere. 2021.129677.
5. **Gordina N.E., Prokof'ev V.Y., Hmylova O.E., Kul'pina Y.N.** Effect of ultrasound on the thermal behavior of the mixtures for the LTA zeolite synthesis based on metakaolin // *Journal of Thermal Analysis and Calorimetry*. 2017. Vol. 129, no. 3. P. 1415-1427.
6. **Tursi A.** A review on biomass: importance, chemistry, classification and conversion // *Biofuel Research*. 2019. No. 6. Pp. 962-979.
7. **Nikiforova T.E., Kozlov V.A., Vokurova D.A., Ivanov S.N.** Vliyanie modificirovaniya l'nyanogo volokna polietilenpoliaminom na sorbciyu ionov Cu(II) i Cd(II) [Effect of modification of flax fibre polyethylene polyamine on the sorption of ions Cu(II) and Cd(II)] // *Rossijskij himicheskij zhurnal (Zhurnal Rossijskogo himicheskogo obshchestva) [Russian Chemical Journal (Journal of the Russian Chemical Society)]*. 2023. Vol. LXVII. No. 3. C. 63-72. DOI: 10.6060/RCJ.2023673.9. (In Russian).
8. **Meretin R.N., Nikiforova T.E.** Issledovanie reakcionnoj sposobnosti poverhnosti uglerodsoderzhashchego silikatnogo sorbenta rastitel'nogo proiskhozhdeniya [Investigation of the reactivity of the surface of carbon-containing silicate sorbent of plant origin] // *Izv. vuzov. Himiya i him. tekhnologiya [Proceedings of universities. Chemistry and chemical technology]*. 2021. Vol. 64. Iss. 11. Pp. 147-155. DOI: 10.6060/ivkkt.20216411.6408 (In Russian).
9. **Thakur V., Sharma E., Guleria A., Sangar S., Singh K.** Modification and management of lignocellulosic waste as an ecofriendly biosorbent for the application of heavy metal ions sorption // *Materials Today: Proceedings*. 2020. V. 32. Part 4. Pp. 608-619, DOI: 10.1016/j.matpr.2020.02.756.
10. **Nikiforova T.E., Vokurova D.A., Sofronov A.R.** Extraction of copper ions by a sorbent based on flax fiber modified with L-arginine // *From Chemistry Towards Technology Step-by-Step*. 2022. Vol. 3, Iss. 3. Pp. 17-26. URL: https://chemintech.ru/ru/nauka/issue/5031/view DOI: 10.52957/27821900_2022_03_17 (accessed 08.06.2024) (in Russian).
11. **Kajeiou M., Alem A., Mezghich S., Ahfir N.-D., Mignot M., Devouge-Boyer C., Pantet A.** Competitive and non-competitive zinc, copper and lead biosorption from aqueous solutions onto flax fibers // *Chemosphere*. 2020. No. 260. Pp. 127-505.
12. **Dey P., Mahapatra B.S., Juyal V.K., Pramanick B., Negi M.S., Paul J., Singh S.P.** Flax processing waste – A low-cost, potential bio sorbent for treatment of heavy metal, dye and organic matter contaminated industrial wastewater // *Industrial Crops & Products*. 2021. No. 174. Pp. 114-195.
13. **Razak M.R., Yusof N.A., Aris A.Z., Nasir H.M., Haron Md.J., Ibrahim N.A., Johari I.S., Kamaruzaman S.** Phosphoric acid modified kenaf fiber (K-PA) as green adsorbent for the removal of copper (II) ions towards industrial waste water effluents // *Reactive and Functional Polymers*. 2020. V. 147. DOI: 10.1016/j.reactfunctpolym.2019.104466.
14. **Liu Y., Qiao L., Wang A., Li Y., Zhao L., Du K.** Tentacle-type poly(hydroxamic acid)-modified macroporous cellulose beads: Synthesis, characterization, and application for heavy metal ions adsorption // *Journal of Chromatography A*. 2021. V. 1645. Pp. 462098. DOI: 10.1016/j.chroma.2021.462098.
15. **Hussain D., Khan S.A., Alharthi S.S., Khan T.A.** Insight into the performance of novel kaolinite-cellulose/cobalt oxide nanocomposite as green adsorbent for liquid phase abatement of heavy metal ions: Modelling and mechanism // *Arabian Journal of Chemistry*. 2022. V. 15. No. 7. P. 103925. DOI: 10.1016/j.arabjc.2022.103925.

16. **Krichevskiy G.E.** Chemical technology of textile materials: textbook for universities in 3 volumes. Vol. 1. Theoretical bases of technology. Fibres. Contaminants. Preparation of textile materials. - M. : RosZITLP, 2000. - 436 p. (In Russian).
17. **Yoshinari N., Kuwamura N., Kojima T., Konno T.** Development of coordination chemistry with thiol-containing amino acids // *Coordination Chemistry Reviews.* 2023. V. 474. P. 214857. DOI: 10.1016/j.ccr.2022.214857.
18. **Vasiliev V.P.** Analytical chemistry. In 2 volumes. Vol. 2. Physico-chemical methods of analysis: textbook for chemical-technological specialities of higher educational institutions. 6th ed. - Moscow: Higher School, 2004. - 383 p. (In Russian).
19. **Kokotov Yu.A., Pasechnik V.A.** Equilibrium and kinetics of ion exchange. L.: Khimiya, 1970. 336 p. (in Russian).
20. **Ahnazarova S.L., Kafarov V.V.** Methods of experiment optimisation in chemical technology. Moscow: Vysshaya Shkola, 1985. 327 p. (in Russian).
21. **Tarasevich B.N.** IR spectra of the main classes of organic compounds // Reference materials. Lomonosov Moscow State University. Moscow, 2012. - 55 p. (In Russian).

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