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EXTRACTION OF COPPER IONS BY A SORBENT BASED ON FLAX FIBER MODIFIED WITH L-ARGININE

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Abstract. *This paper studies the process of Cu(II) ions extraction from aqueous solutions by cellulose-containing sorbents: native and modified by L-arginine flax fiber. We processed the experimental kinetic curves of copper ion sorption by pseudo-first and pseudo-second order models and obtain a high correlation coefficient (0.99) when used a pseudo-second order kinetics model. The results of the treatment of the sorption isotherms according to the Langmuir model indicate the model capability for the description of the process of copper ions sorption by cellulose sorbents. As a result of two-stage chemical modification through the oxidation stage of linen fibre with sodium periodate and subsequent modification with L-arginine, we obtain a new sorbent, which can be used to purify aqueous solutions from heavy metal ions. The paper also presents SEM images and elemental analysis of original and modified flax fibre samples. The infrared spectra confirms the changes occurred in the linen fibre during modification. The obtained sorbent significantly surpasses the native linen fibre in its sorption characteristics, as evidenced by the values of the ultimate sorption capacity.*

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Introduction

Nowadays, heavy metal ions contained in wastewater of various industries, including the chemical, petrochemical, mining and other industries are the main source of environmental pollution. Heavy metals are able to accumulate in the environment because, unlike organic pollutants, they are not degradable by microorganisms. High levels of heavy metals in ecosystem objects, such as plants, water bodies, soil, contribute to their accumulation in drinking water, food raw materials and food with which they get into the human body, thereby causing serious health problems.

The toxic effect of heavy metals is non-specific; they are capable of combining with proteins, nucleotides, coenzymes, phospholipids, i.e. with almost all types of substances involved in cell metabolism [1, 2].

Therefore, it is necessary to develop effective methods to purify water and aqueous solutions from heavy metal ions. Modern heavy metal removal technologies include chemical precipitation, sorption and membrane filtration. Sorption is the most common approach for removing heavy metal ions from solutions with high efficiency and ease of operation [3].

In recent years there has been great interest in developing sorbents based on multi-tonnage by-products or waste products from the agricultural, textile and pulp and paper industries. The main advantages of heavy metal ion sorption using biosorbents over traditional treatment methods are: lower cost, availability, easy disposal, treatment efficiency, possibility of sorbent regeneration and metal recovery.

The advantages of sorbents based on agricultural waste include renewability and safety. They are environmentally friendly and biologically inert towards the media to be cleaned [4]. However, sorbents in their native state generally do not have a high enough sorption capacity. The modification of sorbents based on recycled cellulose-containing raw materials is therefore a topical issue [5-7].

The cellulose-containing sorbents are modified in various ways, such as chemical, physical, physico-chemical and biochemical in order to increase their sorption capacity [8]. The authors of [9] proposed a method of removing heavy metal ions from water sources using cellulose modified with silver and zinc nanoparticles. The sorbent obtained by heat treatment of rice husk exhibits high sorption properties towards copper (II) and zinc (II) ions [10]. Wood pulp modified with multibasic carboxylic acids and polyvinylpyrrolidone is capable of efficiently extracting Cu^{2+}, Co^{2+} and Ni^{2+} ions from aqueous solutions [11]. The production of grafted copolymers of cellulose with various monomers offers great opportunities for the development of sorbents [12].

In recent years, flax fibre, produced both in our country and abroad, and its various processing products have attracted the attention of researchers. Modified waste flax meal [13] as well as short flax fibre, which is a by-product of flax processing, can be used to produce sorbents. It contains pulp, hemicellulose, lignin, pectin, etc. containing various functional groups playing an important role in the adsorption of heavy metal ions. However, electronegativity, the radius of the hydrated ion and the interaction of ions with functional groups (-COH, -ON, -$OCH_{3)}$ are the main factors affecting the biosorption process, which efficiency strongly depends on the pH of the aqueous solution, contact time, initial metal concentration and concentration of the biosorbent [14-16]. The effectiveness of untreated linen fibre as a sorbent was revealed to reach 8.32; 13.35 and 7.12 mg/g [15], and 9.9; 10.7 and 8.4 mg/g for Cu^{2+}, Pb^{2+} and Zn^{2+} ions, respectively [16]. To increase the sorption capacity of short flax fibres, they are modified in various ways [17, 18].

The aim of this study is to develop a new cellulose-containing sorbent based on short flax fibre by modifying it.

Main body

Research objects and reagents. The object of the study was flax fibre (GOST 9394-76. Flax fiber short. Technical conditions), which is a by product of flax industry processing of the following composition, %: pulp (75–78), hemicellulose (9.4–11.9), lignin (3.8), pectin substances (2.9–3.2), waxy substances (2.7), nitrogenous substances per protein (1.9–2.1), mineral substances (1.3–2.8) [19].

To remove the impurities, the flax fibre was pre-boiled in a 5% aqueous $NaHCO_3$ solution for 30 min at solution/sorbent modulus 20, washed with distilled water to pH = 7 and dried to a constant weight.

We used CP reagents: $NH\text{-}C(NH_2)NH(CH_2)_3CH(NH_2)\text{-}COOH$ (L-arginine), $NaIO_4$ (sodium iodide), $CuSO_4\text{-}5H_2O$ (copper (II) sulphate).

Kinetics and sorption isotherms. The kinetics of the sorption of heavy metal ions was studied under static conditions and periodic stirring using the limited solution volume method. The initial concentration of metal ions was $1.5 \cdot 10^{-4}$ mol/l. At certain intervals the solution was separated from the sorbent by filtration and the current concentration of metal ions (C_τ) was detected by atomic absorption spectroscopy by 210 VGP. The sorption capacity of the sorbent at particular time (q, mg/g) was calculated according to the formula

$$q = \frac{(C_0 - C_\tau)}{m} \cdot V, \quad (1)$$

where C_0 is the initial concentration of metal ions in the solution, mg/l; C_τ is the concentration of metal ions at time τ, mg/l; m is the weight of the sorbent sample, g; V is the volume of solution, l.

When sorption isotherms were taken in steady-state equilibrium conditions in the system, the equilibrium concentration of metal ions in solution was determined and the equilibrium sorption capacity (A, mol/kg) was calculated:

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

where C_0 and C are the initial and equilibrium concentration of metal ions, respectively, mol/l; m is the mass of the sorbent sample, kg; V is the volume of solution, l.

The relative error of the experiments was calculated by the data of the kinetic experiments, which point of it represents the average of two parallel experiments. The error of the experiment did not exceed 10%.

IR spectra of native and modified flax fibres were recorded by Avatar 360 FT-IR ESP in the range 400–4000 cm^{-1}. Samples for analysis were prepared by mechanically grinding and then thoroughly contusing the sorbent in an agate mortar with spectrally pure KBr.

Flax fibre modifying. In order to increase the absorption properties of the flax fibre, it was chemically modified with L-arginine. The developed method includes the oxidation of flax pulp with sodium metoperiodate to form dialdehyde cellulose and its subsequent treatment with L-arginine.

The oxidation of flax cellulose with sodium salt of iodine acid to form dialdehyde cellulose was carried out as follows. A sample of linen fibres was placed in a flask with a lapped plug and poured with 0.1 N aqueous $NaIO_4$ solution (pH ≈ 2) at a solute/sorbent modulus of 15–50. The flask was shaken thoroughly and placed in a dark place, and samples were taken periodically to detect the residual concentration of IO_4^- ions in the solution. After completing the oxidation reaction with sodium metaperiodate the insoluble fraction was separated by decantation from the solution, washed successively with 1-1.2 L water with hydrochloric acid (pH = 1), 1-1.2 L acetone/water mixture and dried. The resulting dialdehyde cellulose in flax fibre was then modified with L-arginine. For this purpose, the $NaIO_4$-oxidised flax fiber was placed in a flask with a 1% solution of L-arginine at modulo 1:50 and incubated at 40–45 °C and pH = 7-10 for 45-60 min with continuous stirring of the reaction mixture. After refrigeration, the reaction products were washed with distilled water to neutral pH and dried.

Results and Discussion

We obtained the kinetic curves of Cu (II) ions sorption in order to determine the parameters characterising the sorption properties of the modified linen fibre. Fig. 1 shows the experimental results.

According to the data obtained, the modified linen fibre is significantly more efficient at extracting copper ions than the unmodified one. The time for reaching adsorption equilibrium in the heterogeneous system "aqueous copper sulphate solution - sorbent" is 15 minutes.

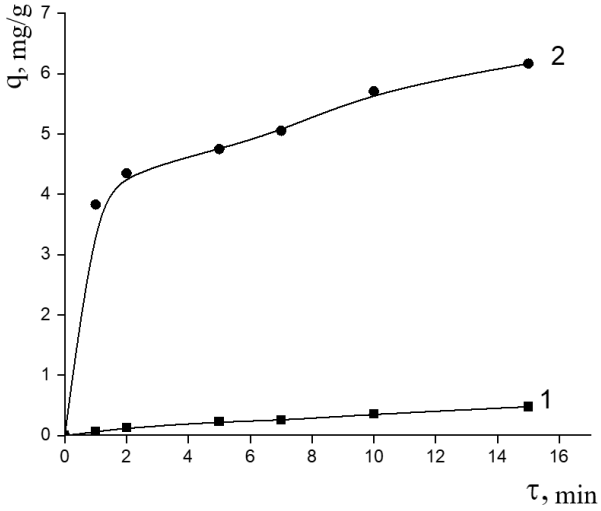


Fig. 1. Kinetics of Cu (II) ions sorption from aqueous solutions by flax fibre: 1 - unmodified; 2 - modified by L-arginine

The experimental data were processed using pseudo-first and pseudo-second kinetic models using the least squares method using OriginPro software. Kinetic parameters of copper ions sorption by native and modified by L-arginine flax fiber from aqueous solutions found as a result of processing of kinetic curves of Cu (II) ions sorption are presented in Table 1. The data obtained for native and modified flax fibres show that the treatment with a pseudo-second-order model is the most correct, with correlation coefficients of 0.99.

Table 1. Kinetic parameters of copper ions sorption by native and modified by L-arginine flax fiber from aqueous solutions

Cu (II)	Pseudo-first-order model			Pseudo-second-order model		
	q_e, mg/g	k_1, mg·min/g	R^2	q_e, mg/g	k_1, mg·min/g	R^2
Native flax fibre	0.74	0.24	0.95	0.736	1.03	0.99
Modified flax fibre	5.36	0.195	0.92	5.78	5.8	0.99

To determine and compare maximum sorption capacity (A_∞) of native and modified flax samples, isotherms of Cu(II) ions sorption from aqueous solution were obtained (Fig. 2).

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

$$A = \frac{A_\infty \cdot K \cdot C_e}{(1 + K \cdot C_e)}, \quad (3)$$

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

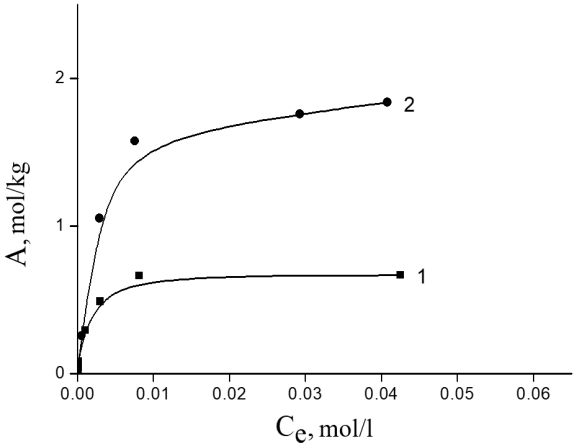


Fig. 2. Isotherms of Cu (II) ion sorption by flax fibre: 1 - native; 2 - modified by L-arginine

Linearisation of the sorption isotherm by equation (2) makes it possible to determine graphically in the Langmuir equation the values A_∞ and K from the experimental data on the distribution of the sorbate under study in the heterophase aqueous solution-sorbent system.

$$\frac{C_e}{A} = \frac{C_e}{A_\infty} + \frac{1}{A_\infty \cdot K}. \quad (4)$$

The results of the isotherm of copper ion sorption using the Langmuir least-squares model are shown in Table 2.

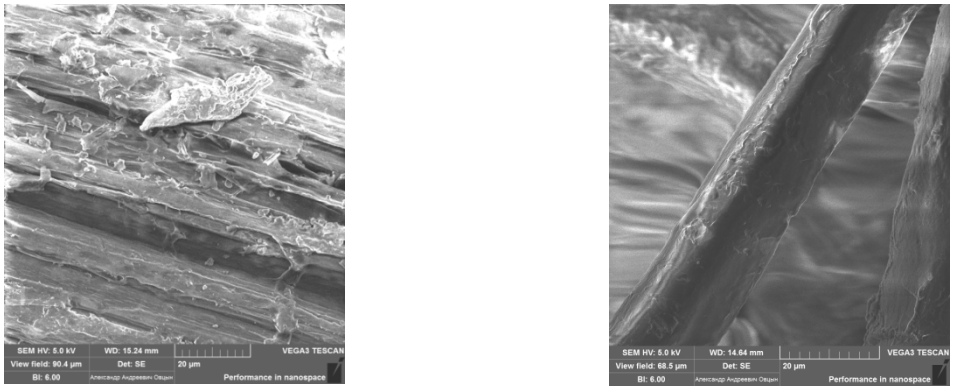
Table 2. Treatment parameters for isotherms of Cu(II) ion sorption using the Langmuir model

Sorbent	$1/A_\infty$	$1/A_\infty \cdot K$	Correlation coefficient	A_∞, mol/kg
Native flax fibre	$1{,}462 \pm 1{,}6 \cdot 10^{-2}$	$1{,}3 \cdot 10^{-3} \pm 3 \cdot 10^{-4}$	0.99	0.83
Modified flax fibre	$0{,}515 \pm 0{,}9 \cdot 10^{-2}$	$1{,}3 \cdot 10^{-3} \pm 2 \cdot 10^{-4}$	0.99	1.84

The results obtained by treating the sorption isotherm using the Langmuir adsorption model indicate that the ultimate sorption capacity of flax fibre (A_∞) increases for Cu (II) ions from 0.83 to 1.84 mol/kg when treated with L-arginine.

The examination of samples surface of raw flax fibre and flax fibre oxidised with sodium metaperiodate by scanning electron microscope (SEM) "VEGA3 SB" shows, that under the influence of modification the micro relief of surface layer of samples changes (Fig. 3, *a, b*).

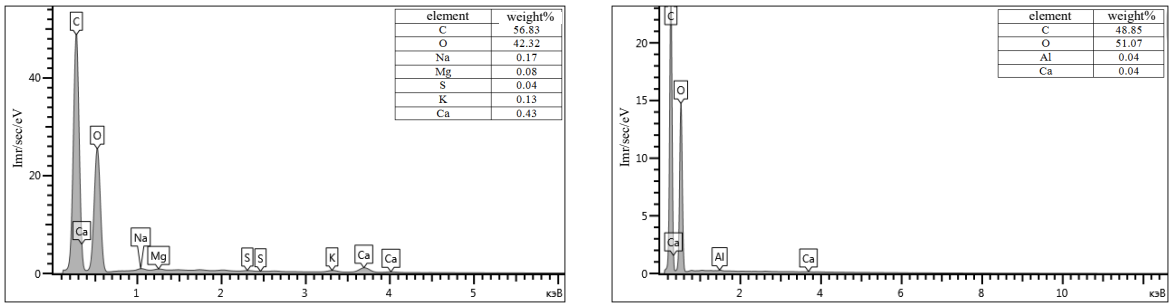
The surface of native flax fibre (see Fig. 3, *a*), is heterogeneous, with many folds and inclusions, due to the fact that flax fibres are formed from elementary fibres bonded together by lignin, pectin and amorphous polymers of the secondary cell wall When native sample is oxidised by sodium periodate (see Fig. 3, *b*), the fibre structure is smoothed and various inclusions are removed from the surface, resulting in a change in the surface layer. The surface of the sorbent becomes more homogeneous and smooth.



a *b*

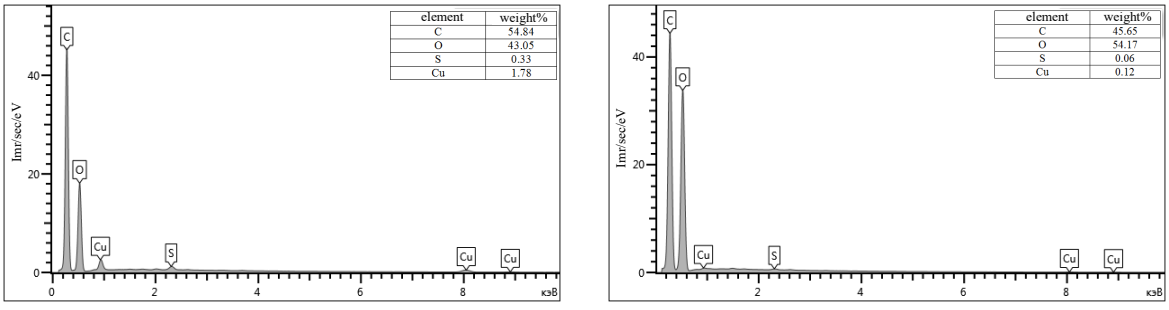
Fig. 3. SEM images of flax fibre surface: *a* - native flax fibre; *b* - flax fibre oxidised with sodium metoperiodate

The elemental composition of the flax fibre before and after oxidation with sodium metaperiodate and before and after sorption of Cu (II) ions is shown in Fig. 4 and 5, respectively. The content of oxygen in the sample of oxidized flax fibre (see Fig. 4, *b*) increases noticeably in comparison with the original sample (see Fig. 4, *a*), while the sorption of Cu ions by the oxidized sample (see Fig. 5, *b*) is almost absent, whereas 1.78 % Cu is detected on the surface of the native fibre. This indicates the presence of the meta-periodic oxidation process of dialdehyde cellulose that is not capable to sorb metal ions.



a *b*

Fig. 4. Elemental analysis of flax fibre samples: *a* - native flax fibre; *b* - flax fibre oxidised



a *b*

Fig. 5. Elemental analysis of flax fibre samples after sorption of copper (II) ions: *a* - native flax fibre; *b* - flax fibre oxidised

To confirm the formation of dialdehyde cellulose when treating flax fibre in sodium metaperiodate solution, IR spectra were taken of raw and oxidised flax fibre in $NaIO_4$ solution (Fig. 6, spectra 1-2). A comparison of the IR spectra shows the marked changes during flax fibre oxidation process. Thus, in the spectrum of flax fibre containing dialdehyde-cellulose, an increase in intensity and a slight shift of the absorption band corresponding to the valent vibrations of the C=O bond in aldehydes and acids is observed in comparison with the spectrum of

the original flax fibre from the position 1632 cm^{-1} to 1638 cm^{-1}. In the spectrum of the oxidised sample the peak at 1739 cm^{-1}, which was present in the spectrum of native flax and corresponds to the valent vibrations of the carbonyl group for carboxylic acids, has disappeared. Thus, the IR spectrum of the oxidised flax fibre indicates the appearance of aldehyde groups in the oxidized sorbent.

IR spectrum 3 in Fig. 6 is obtained for flax fibre oxidised with $NaIO_4$ and treated with L-arginine. A comparison of the IR spectrum of oxidised flax with that of oxidised and L-arginine-treated flax reveals the following differences. In the spectrum of flax fiber 3, oxidised and modified with L-arginine, a shift of absorption band as compared with the spectrum of oxidised flax fiber from position 1638 cm^{-1} to position 1648 cm^{-1} is observed, which may be due to valent vibrations of carbonyl group for aldehydes and carboxylic acids as well as strain vibrations of N-H bond in amides. In addition, a significant shift of the absorption band from the 1280 cm^{-1} position to the 1271 cm^{-1} position, where valence vibrations of the C-N bond in amides are present, is observed in the IR spectrum of flax fiber modified with L-arginine compared to the IR spectrum of oxidized flax fiber.

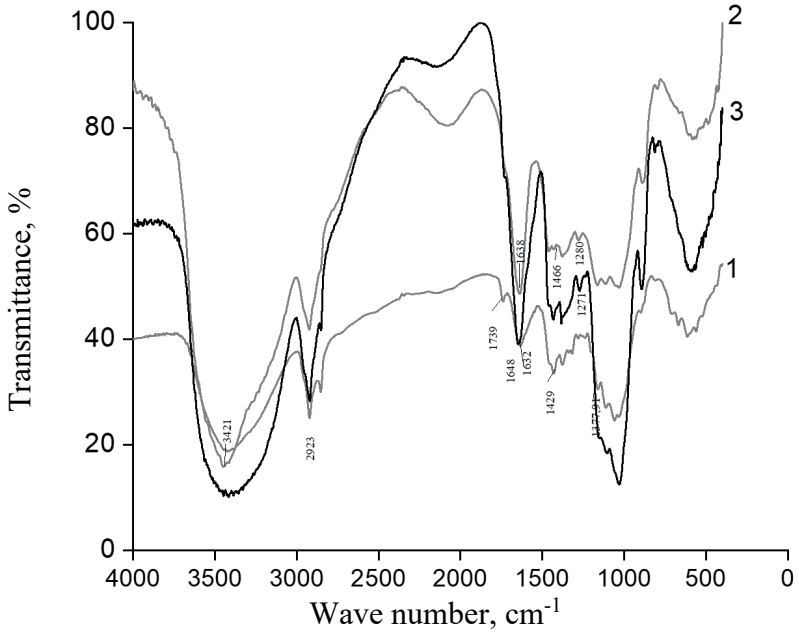


Fig. 6. IR spectra of flax fibre: 1 - native flax fibre; 2 - oxidised flax fibre; 3 - flax fibre oxidised and treated with L-arginine

Thus, when the sorbent is modified, L-arginine is fixed on its surface. The interaction of the amino acid L-arginine with aldehyde groups of flax pulp is carried out with the formation of an amide bond and an increase in the content of carboxyl groups in the fibre structure, which is confirmed by infrared spectra.

Conclusions

Thus, we obtain the sorbent for purifying aqueous solutions from heavy metal ions by chemical modification of flax fibre and study its sorption properties towards Cu(II) ions.

By the study, the modification of the natural polysaccharide material involves oxidation of flax fibre with sodium metaperiodate and subsequent treatment of the resulting dialdehyde

cellulose with L-arginine. It is providing the creation of sorption-active functional groups on the surface of the polysaccharide material during the modification process.

L-arginine-modified flax fibre has good equilibrium-kinetic characteristics and can be used as a sorbent for the purification of aqueous solutions from heavy metal ions.

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