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

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Abstract. *The paper presents the results of the cotton cellulose modification with glycine. To form dialdehyde-cellulose and its subsequent treatment with aminoacetic acid we conducted the modification through an oxidation stage of cellulose with sodium metoperiodate. We studied the sorption properties of the original and modified cellulose samples in relation to Cu(II) and Fe(II) ions. Bykinetic experiments we found the degree of extraction of copper(II) and iron(II) ions. The modified sample was approximately 25% higher compared to the original one. We obtained the most correct results when processing the kinetic sorption curves within the framework of pseudo-second order kinetics model. We determined the optimum conditions for modifying cotton cellulose to achieve maximum sorption of copper (II) and iron (II) ions and obtained the equilibrium-kinetic characteristics of modified and unmodified cotton cellulose. When studying the sorption equilibrium in the heterophase system "cellulose sorbent - aqueous solution of metal sulfate" we took sorption isotherms, processed them in the framework of Langmuir mode, and determined the values of the ultimate sorption capacity of the native and modified cellulose. We found the ultimate sorption capacity of the modified sorbent is about 1.5-2 times higher than the ultimate sorption capacity of native cotton cellulose. We have obtained IR spectra of native andmodified cellulose samples. Also we have performed elemental analysis and obtained images of the sorption materials surface structure based on cotton cellulose using SEM.*

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Introduction

Long-lasting technogenic loads on the environment led to its significant and even critical pollution with heavy metals, radionuclides, oil products and other substances harmful to wildlife, humans, air, water, and soil [1].

A number of heavy metals are highly toxic at low concentrations. They can be accumulated in living organisms, causing a number of disorders and diseases. The presence of heavy metal ions in water bodies has increased significantly over the last fifty years due to industrialisation and urbanisation. The removal of heavy metal ions from wastewater is of particular importance because of their extreme impact on the environment, public health, and the economy [2].

Heavy metal emissions into the environment are associated with human activities. Their main sources are industry, vehicles, boilers, incinerators, and agricultural production [3].

There are also natural heavy metal pollution, for example, the volcanic eruptions. Increased concentrations of toxicant metals in surface water can occur as a result of acid rain. They also can lead to the dissolution of minerals and rocks. It increases the metals pollution level of biosphere compared to the soil [4].

The treatment of water from heavy metal ions is an important modern challenge. Methods of metal extraction from wastewater are being developed and applied to reduce the environmental hazard of various industries. Substances with a high ability to extract metal ions from water are searched for and their application would be economically feasible [5-6].

Nowadays there is an interest to use renewable raw materials in the production of materials and products designed to improve the environment and solve problems related to technogenic pollution of water environments with ions of various heavy metals [7-8].

These physical, chemical, physical-chemical, and biochemical (biological) methods of aqueous solutions purification from heavy metal ions are applied in the industry [9]. The optimal solution for deep purification of water contaminated with heavy metal ions is the sorption method, which allows the extraction of contaminants with a wide range of concentrations [10].

It is possible to make sorption methods more effective, first of all, by selecting or developing inexpensive and available sorbents. Therefore, cellulose-containing agricultural wastes can be considered as a very suitable raw material, which make it possible to produce inexpensive sorption materials with a minimal quantity of technological process stages [11].

Nowadays the study of the cellulosic materials sorption properties is of practical and scientific interest. The search for compounds with high sorption activity in relation to heavy metals and the development on their basis of natural materials possessing sorption properties is an urgent challenge.

The use of the biosorption technology makes it possible to significantly reduce the concentration of heavy metal ions by using inexpensive biosorbents.

The main biosorption advantages over traditional treatment methods are its inexpensiveness, efficiency, regeneration, and reuse of sorbents, etc. [12, 13].

The lignocellulosic materials low sorption capacity as sorbents is its disadvantage. To increase the sorption capacity, untreated biosorbents are modified by various methods, including oxidation, esterification, graft copolymerisation, etc. [14, 15].

The binding of metal ions by lignocellulosic biosorbents involves carboxyl, amino groups or phenolic hydroxyls as sorption-active functional groups. Therefore, there were attempts to develop new adsorbents and improve existing ones, including the possibility of using inexpensive agro-industrial waste [16, 17].

The purpose of this study is to obtain a new effective cellulose-based sorbent by modifying it with glycine for the extraction of iron and copper ions from aqueous solutions.

Main body

We chose cotton cellulose (GOST 595-79) as the test material, which was pre-boiled with a 5% $NaHCO_3$ solution to remove impurities. Exposure time was 30 min, with a solution/sorbent modulus of 20. Then we washed the sorbent with distilled water to a neutral pH and dried to a constant weight. The dry samples had a moisture content of 8.5%.

During the experiment we used chemically pure reagents:aminoacetic acid (glycine) NH_2-CH_2-COOH, sodium metaperiodate $NaIO_4$, copper, and iron sulphates $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$.

We studied the heavy metal ions kinetics of the sorptio under static conditions with stirring by the limited volume solution method. The initial concentration of metal ions was $1.5\text{-}10^{-4}$ mol/l. We separated the solution from the sorbent at certain intervals by filtering and determined the current concentration of metal ions ($C\tau$) in it by atomic absorption spectroscopy on a 210 VGP instrument.

Isotherms of sorption in the ion-exchange system were obtained to study the influence of the concentration of heavy metal ions in solution on the equilibrium as follows: in a series of test tubes sorbent sample weighing 0.10 g was put and filled with 10 ml of water solution of metal salt with metal concentration in the range $1.5\text{-}10^{-4}\text{-}5\text{-}10^{-2}$mol/l. It kept stirred until an equilibrium was set (time to sorption equilibrium was determined by studying the kinetics of sorption). We then separated the solution from the sorbent by filtration and determined its equilibrium concentration of metal ions (C_e) by atomic absorption spectroscopy on a 210VGP instrument.

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

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

where C_0 is the initial concentration of metal ions in solution, mol/l;

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

m is mass of the sorbent suspension, kg; V - volume of the solution, l.

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

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

where C_e is equilibrium concentration of metal ions in solution, mol/l.

The degree of α extraction we determined as follows:

$$\alpha = \frac{C_0 - C_\tau}{C_0} \cdot 100\% \cdot \tag{3}$$

We calculated the relative inaccuracy of the experiments on data from kinetic experiments, where each point represents the average of two parallel experiments. The inaccuracy of the experiment did not exceed 10%.

Results and Discussion

Cellulose-based sorbents have a relatively low sorption capacity. Therefore, in order to increase their efficiency it is necessary to modify cellulose materials using available reagents and simple technological operations.

To improve the sorption properties of cellulose-containing sorbent we conducted its chemical modification. It involved the oxidation of cellulose with sodium metaperiodate to form dialdehyde cellulose and its subsequent modification with aminoacetic acid.

We chose 0.1 normal sodium metoperiodate solution as the oxidant. We poured 250 cm^3 of $NaIO_4$ solution into the pre-purified cellulose fibre (2.5 g). We conducted the oxidation reaction (Fig. 1) at pH 3-4, because the oxidative properties of periodate appear in an acidic environment. We placed a sample of cotton cellulose in sodium metaperiodate solution in a dark place for 48 hours, shook its contents periodically, and took samples for analysis. We monitored the absorption of IO_4^- ion from the oxidant solution spectrophotometrically by determining the optical density of the solutions in the UV region of the spectrum at $\lambda = 225$ nm. We filtered the insoluble fraction of the dialdehyde cellulose from the reaction products solution and washed successively with 1 l of water with hydrochloric acid solution added to pH ~ 1, then 1 l of acetone/water mixture: 1/10 and 1 l of distilled water. Then we dried the obtained dialdehyde cellulose to a constant humidity at a temperature not exceeding 80 ^{o}C and determined the content of COO groups in it.

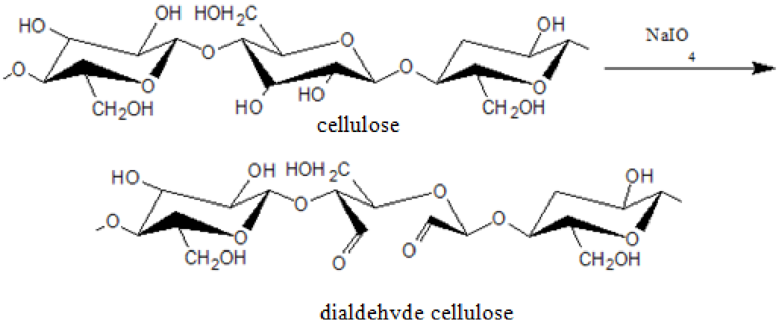


Fig. 1. Scheme for the oxidation of cellulose by sodium metoperiodate forming dialdehyde cellulose

At the next step we chose aminoacetic acid as the modifying agent. We poured pre-treated fibre with 12% aldehyde groups in a 1% aqueous glycine solution at a sorbent:solution modulus of 50. Process of modification (Fig. 2) was conducted for 1 hour at temperature 40-45 ^{o}C, pH 9-10 and constant stirring. After cooling down, we washed the reaction products with distilled water to neutral reaction.

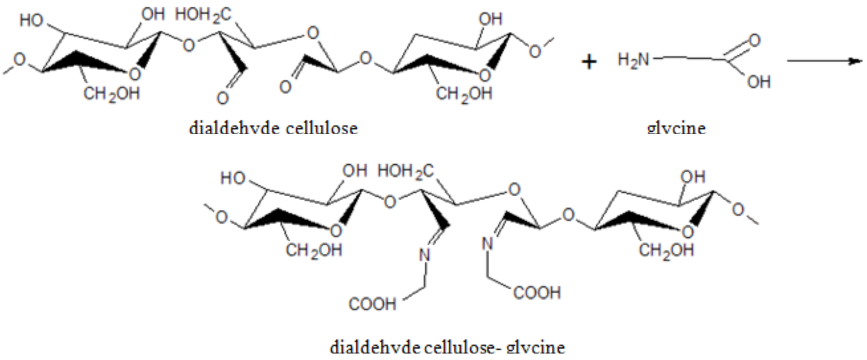


Fig. 2. Scheme for modifying cellulose with glycine

We obtained the kinetic curves of Cu(II) and Fe(II) ions sorption to determine the parameters characterizing the sorption properties of original and modified cotton cellulose. The results of the experiment are shown on Fig. 3.

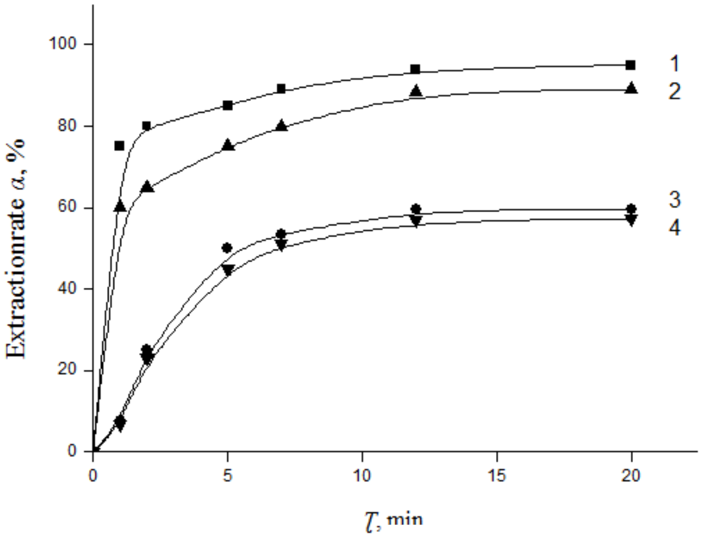


Fig. 3. Kinetic curves of sorption of heavy metal ions from aqueous solutions by modified cotton cellulose: 1 - Cu(II); 2 - Fe(II) and unmodified cellulose; 3 - Cu(II); 4 - Fe(II)

The modified cotton cellulose, in comparison with unmodified one, sorbs heavy metal ions more effectively. Indeed, the degree of extraction of Cu(II) ions is higher than that of Fe(II) ions. Time of sorption equilibrium achievement in heterophase system "water solution of metal sulphate - sorbent" is 20 min.

To determine the order of the reaction we processed the experimental data using the kinetic models most commonly applied by researchers when analyzing kinetic data - pseudo-first and pseudo-second order kinetic models (Table 1).

Table 1. Pseudo-first and pseudo-second order sorption kinetics models

Kinetic model	Integral form of the equation
Pseudo-first-order model	$q_t = q_{eq}(1 - e^{-k_1 t})$
Pseudo-second-order model	$q_t = \dfrac{t}{\dfrac{1}{k_2 \cdot q_{eq}^2} + \dfrac{1}{q_{eq}}}$

The treatment of heavy metal ion sorption kinetic curves by unmodified and modified cellulose within the framework of pseudo-first and pseudo-second order kinetics models is presented on Table 2.

As a result of treatment of kinetic sorption curves in coordinates $t/q_t - \tau$ and $\lg(q_e - q_t) - \tau$ by least-squares method using Origin program, we found the sorption of copper and iron ions from aqueous solutions is described more exactly (with correlation coefficient 0.99) using pseudo-second order kinetic model both for unmodified and for glycine-modified cellulose. The experimental equilibrium sorption values obtained from this model correlate with the experimental data well.

Table 2. Results of the treatment of heavy metal ion sorption kinetic curves of native and glycine-modified cellulose by chemical kinetics models

Ion of metal	Equilibrium sorption value	Pseudo-first-order model			Pseudo-second-order model		
	$q_{e\ experiment}$, mg/g	q_e, mg/g	k_1, min^{-1}	R^2	q_e, mg/g	k_2, mg min/g	R^2
Native cotton cellulose							
Cu(II)	0.68	0.46	0.098	0.80	0.69	0.29	0.99
Fe(II)	0.66	0.49	0.098	0.89	0.72	0.23	0.99
Aminoacetic acid modified cellulose							
Cu(II)	0.97	0.45	0.127	0.92	0.99	1.99	0.99
Fe(II)	0.87	0.27	0.086	0.93	0.86	1.34	0.99

R^2 is correlation coefficient.

We obtained the sorption isotherms of Cu(II) and Fe(II) ions to determine the maximum sorption capacity of cellulose in the heterophase system "aqueous solution of metal sulphate - sorbent" (Fig. 4).

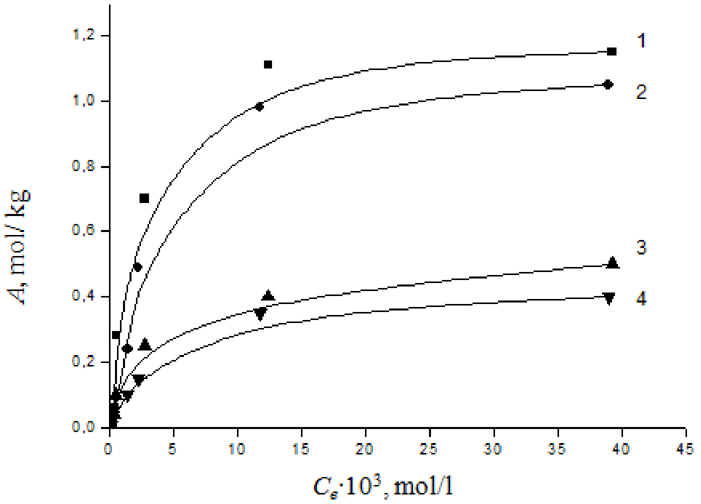


Fig. 4. Isotherms of sorption of metal ions by cellulose modified with aminoacetic acid: 1 - Cu(II); 2 - Fe(II) and unmodified cellulose; 3 - Cu(II); 4 - Fe(II)

When describing the experimental isotherms of heavy metal ion sorption by cellulose sorbents, the Langmuir sorption model is most commonly used in the literature:

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

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

$$\frac{C_e}{A} = \frac{C_e}{A_\infty} + \frac{1}{A_\infty \cdot K}$$

made it possible to determine graphically the coefficients of the Langmuir equation (Table 3).

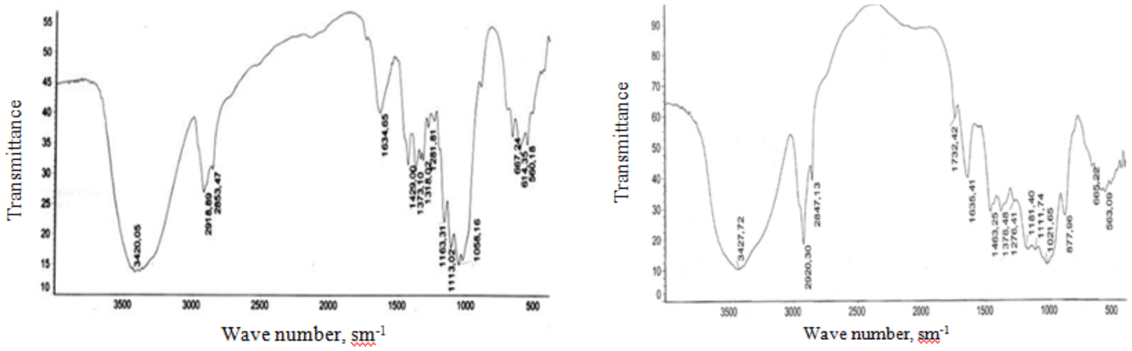
Table 3. Processing parameters of heavy metal ion sorption isotherms of original cellulose and glycine-modified cellulose using the Langmuir least squares model

Metal cation	$1/A_\infty \cdot K$	$1/A_\infty$	R^2	A_∞, mol/kg
Source cellulose				
Cu(II)	$0.0222 \pm 3 \cdot 10^{-4}$	$2{,}0 \pm 0{,}02$	0.99	0.50
Fe(II)	$0.0026 \pm 3 \cdot 10^{-4}$	$2{,}5 \pm 0{,}02$	0.99	0.40
Glycine-modified cellulose				
Cu(II)	$0.0025 \pm 3 \cdot 10^{-4}$	$0{,}78 \pm 0{,}03$	0.99	1.28
Fe(II)	$0.0027 \pm 5 \cdot 10^{-4}$	$0{,}89 \pm 0{,}02$	0.99	1.12

The experimental data on sorption of copper and iron ions by initial and modified cellulose are well approximated by the Langmuir equation (with correlation coefficient 0.99) in accordance with the Table 3. The ultimate sorption capacity (A_∞) of modified cellulose for Cu(II) and Fe(II) ions is 1.28 and 1.12 mol/kg, respectively. It is more than 2.5 times higher than A_∞ of original cellulose. The results obtained by isotherm treatment using Langmuir adsorption model (see Table 3) correlate with experimental data (see Fig. 4).

Samples under study IR spectra (Fig. 5, *a*, *b*) were obtained by using an Avatar 360 FT-IR ESP Fourier Transform Infrared Spectrometer, the range was 400-4000 cm^{-1}. Samples for the analysis were prepared by mechanical grinding of original and modified cellulose followed by thorough grinding of the sorbent in an agate mortar with spectrally pure KBr.

An analisys of the obtained IR spectra shows the changes in the structure of the cellulose during the modification process.



a *b*

Fig. 5. IR spectra of cotton cellulose: *a* - original; *b* - modified with glycine

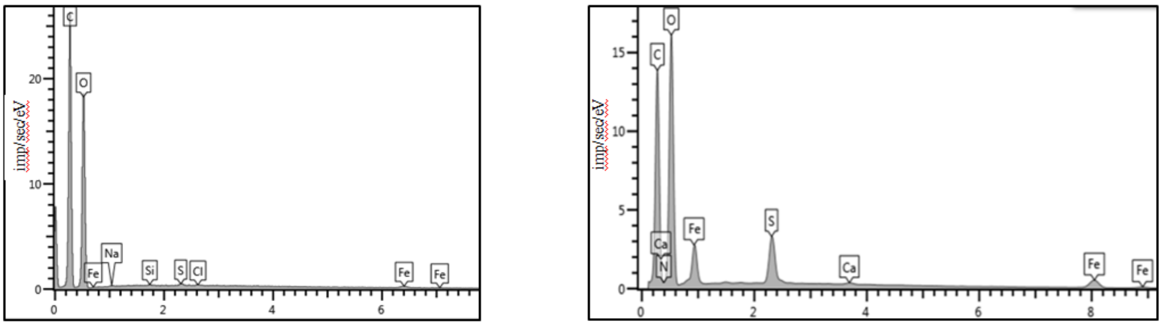
New functional groups appear in the modified sample as a result of sequential treatment with sodium metaperiodate and glycine. Therefore, we note a shift of the absorption band corresponding to the valent vibrations of the C=O bond of the carbonyl group in the modified cellulose spectrum (1732 cm^{-1}) compared to the spectrum of the original cellulose (1739 cm^{-1}). Change in the spectral pattern in the range 1650-1450 cm^{-1} for cellulose modified with aminoacetic acid as compared to the spectrum of unmodified cellulose is associated with strain vibrations of N-H bond in amides of the range. Thus, in the process of modification, aminoacetic acid becomes fixed on the surface of cellulose, which is evident on the spectrum.

Microscopic examination of the sorbents structure conducted with a scanning electron microscope "VEGA3 SB" allowed us to obtain SEM-images of the original and modified samples of cellulose and reveal the structural features of their surface (Fig. 6). Fig. 6, *a* shows the smooth surface of original cellulose fibers, while the surface of glycine-modified cellulose fibers (see Fig. 6, *b*) is rough.

a ***b***

Fig. 6. SEM images of the surface of sorbents: *a* - original cellulose; *b* - cellulose modified with glycine

Fig. 7 shows the data of elemental analysis of original and modified cotton cellulose conducted by EDS method. An increase of oxygen and nitrogen content in the modified sorbent sample (see Fig. 7, *b*) in comparison with the original cellulose (see Fig. 7, *a*) occurs during sequential modification of cellulose with sodium metaperiodate and aminoacetic acid. It indicates the addition of glycine to cellulose.



a ***b***

Fig. 7. The elemental analysis of cotton cellulose after Fe (II) sorption: *a* - original cellulose; *b* - cellulose modified with glycine

Moreover, iron content after its sorption from aqueous solutions by the sorbents under study is significantly higher on the modified sample (see Fig. 7, *b*) than on unmodified cellulose (see Fig. 7, *a*). It corresponds to the experimental data obtained in the study of sorption kinetics and equilibrium (see Fig. 3 and 4).

Conclusions and recommendations

We obtained a sorbent for the purification of aqueous solutions from iron (II) and copper (II) ions by chemical modification of cotton cellulose. We conducted it through a stage of cellulose oxidation with sodium metoperiodate to form dialdehyde cellulose and its subsequent treatment with aminoacetic acid.

The interaction of glycine amino groups with aldehyde groups of cellulose occurs with the formation of Schiff base. The observed changes in the IR spectra of the sorbentsare caused by the shift in absorption bands. It corresponds to the valence vibrations of the carbonyl group

C=O bond and strain vibrations of the amides N-H bond indicate the fixation of the aminoacetic acid modification on the surface of cellulose.

SEM/EMF examination indicates a change in the surface structure and elemental composition of the modified sample.

Cellulose modified with aminoacetic acid has good equilibrium-kinetic characteristics and can be used as a sorbent for water treatment of heavy metal ions.

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