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Study of the Effect of Oxidative-Bisulfite Modification of the Cotton Cellulose on Its Ion Exchange Properties

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Abstract—The effect of chemical modification on the sorption properties of cotton cellulose toward Cu(II) and Ni(II) ions was studied. The modification was carried out in two stages: oxidation of cellulose with the formation of dialdehydocellulose, followed by its sulfonation. The optimal conditions for modifying the cellulose to produce a sorbent capable to remove effectively the heavy metal ions from aqueous solutions of corresponding salts were elucidated. The modified sorbent exceeds the native cellulose in the sorption capacity (in terms of sorption maximum) about 3 times, therewith the time of extraction of heavy metal ions is reduced from 45 to 8 min. The high sorption properties are defined by the formation of new sorption sites –SO_3Na along with initially formed –COOH groups on the sorbent surface.

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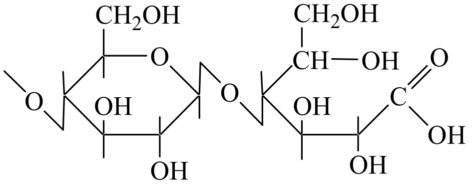
Today a very urgent task is the developing environmentally the friendly and biologically inert sorbents. This is connected with an increase in pollution of the biosphere with heavy metals, which are persistent chemical pollutants with a cumulative effect and specific toxic properties. Promising sorbents for heavy metal ions from aqueous media are different polymer cellulose-based materials produced from the accessible, cheap and renewable natural resources [1, 2]. A drawback of such materials is their relatively low equilibrium and kinetic characteristics. Therefore, at the developing new sorbents is very important to find ways of processing the polysaccharide biosorbents to improve their sorption properties toward heavy metal ions. A number of studies [3–7] offers various methods of modification of cellulose polymers, including mechanical, physical, chemical, biochemical and physicochemical treatment, such us wet grinding, freezing, plasma activation, thermoextrusion, freeze drying, processing with sodium monochloroacetate, dyeing with reactive dyes, grafting with amino acid residues, etc. The main purpose of the modification is increase of internal adsorptive surface and the accessibility of active groups, and the creation of new sorption-active sites on the sorbent surface. It seems promising to apply a chemical modification of cellulose sorbents, which allows enhance significantly the sorption capacity of natural sorbents using inexpensive and available reagents.

The aim of this work is to study the process of chemical modification of cotton cellulose for the obtaining a new sorbent containing –COOH and –SO_3H group. This process, on the one hand, is safe (ecologically friendly and biologically inert) with respect to purified medium, and, on the other hand, imparts the material with the high sorption properties in aqueous solution and capability of firmly holding the heavy metal ions.

Determination of the content of carboxyl groups is necessary for the evaluation of the limiting exchange capacity of the sorbent. Carboxyl groups may be present in cellulose predominantly as terminal groups, formed by oxidation of the carbonyl groups at the ends of macromolecules:



The potentiometric titration curves in integral and differential modes are shown in Figs. 1 and 2. The value of pK_a = 3.94 of the cellulose sorbent acidic

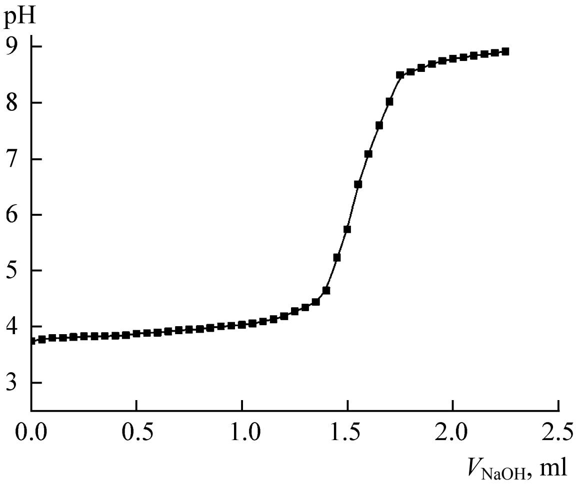


Fig. 1. Titration curve at the determining the content of carboxyl groups in the cotton cellulose.

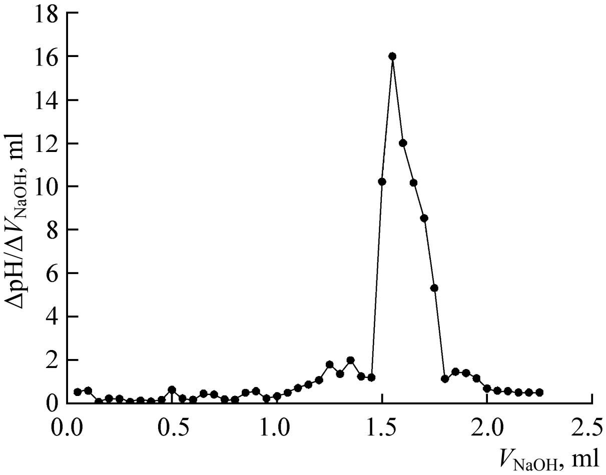


Fig. 2. Differential curve of cotton cellulose titration.

groups is fairly well consistent with the pK_a value of the carboxylic acids containing hydroxyl group in α-position (glycolic, gluconic, and lactic) [8], as well as with the data for the cellulose-containing polymer materials [pK_a(COOH) = 4.0] [9].

$$\text{RCH(OH)COOH} \leftrightarrow \text{RCH(OH)COO}^- + \text{H}^+,\ pK_a\ 3.83\text{–}3.71.$$

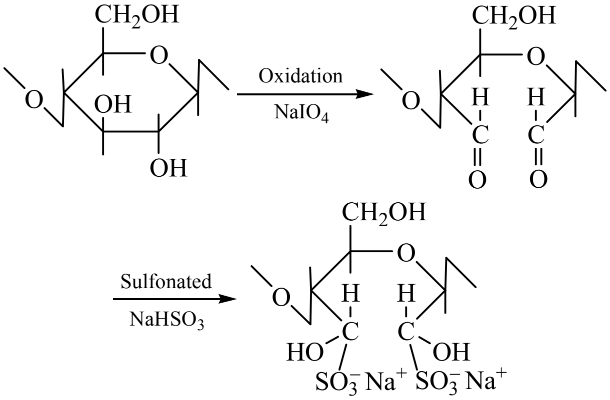
The value of carboxylic acidity of the sorbent was 0.155 mmol g^{-1}, indicating not enough high sorption capacity of the cotton cellulose as an ion exchanger.

Kinetic studies showed that equilibrium in the heterogeneous system of aqueous solution of metal sulphate–cotton cellulose reaches in 45 min. The degree of extraction of copper and nickel from solutions of the salts with a concentration of 1.5×10^{-4} M at the state of equilibrium is 59.6% and 58.0% respectively.

In order to improve the equilibrium and kinetic characteristics of the adsorbent we carried out its chemical modification in two steps: (1) oxidation of cotton cellulose with sodium metaperiodate to form dialdehydocellulose and (2) sulfonation of the dialedhydocellulose with sodium bisulfite to obtain the modified cellulose.

To achieve the greatest results were revealed the optimal conditions for modifying the cellulose in each of these stages.

Oxidation of cellulose can be carried out in various ways, for example, by using such oxidants as sodium metaperiodate, sodium paraperiodate, periodic acid, sodium hypochlorite, hydrogen peroxide, ozone, potassium dichromate, potassium permanganate and sodium chlorite [10]. However, the mode of action of the most oxidants is not specific, their use leads to the formation of carboxyl groups mainly, and may also cause rupture of the polymer chain of the cellulose macromolecule. In contrast, periodate ions interact with the cellulose without destroying the fiber. At the action of sodium metaperiodate occurs oxidation of two adjacent alcohol groups at C^2 and C^3 to aldehyde groups with the simultaneous rupture of the carbon-carbon bond between them to form dialdehydocellulose. In this case, oxidation of primary alcohol groups does not occur [11]:



To determine the optimal conditions for the oxidation of cotton cellulose we varied the concentration of oxidant and the oxidation duration. The important parameters of this process are also the solution pH, solution/adsorbent ratio and temperature.

The oxidation reaction was carried out at pH 3–4, as the oxidizing properties of periodate occur in an

Table 1. Effect of sodium metaperiodate concentration on the content of aldehyde groups in cotton cellulose (oxidation duration 1 h, pH = 3, the solution/sorbent ratio is 20, temperature 40°C)

$c(NaIO_4)$, M	Content of of aldehyde groups in cellulose, %
Untreated cotton cellulose	0.11
0.05	0.56
0.08	1.89
0.10	2.05
0.12	2.35
0.15	2.85
0.18	3.35
0.20	3.60
0.25	3.98
0.30	4.31

acidic medium [12]. At pH values above 4.6 the sodium metaperiodate is transformed to the insoluble paraperiodate.

The most preferred temperature range is 40–45°C. At a temperature below 20°C the reaction proceeds very slowly, while at a temperature above 55°C the oxidation process is too fast and causes heterogeneity of the product and decomposition of metaperiodate.

The solution/sorbent ratio 20 is selected based on the fact that in the process of modification the pulp should be completely immersed in the oxidizer solution, and the solution should be taken with a slight excess to ensure access of the oxidizer to the cellulose reaction centers and provide the process completeness.

Effect of sodium metaperiodate concentration on the content of aldehyde groups in the cotton cellulose at the oxidation duration 1 h, pH = 3, the solution/sorbent ratio 20, and the temperature 40°C is shown in Table 1.

The content of aldehyde groups in oxidized cellulose grows linearly (correlation coefficient 0.97) with increasing concentration of the sodium metaperiodate solution in the range 0–0.30 M of $NaIO_4$ (Table 1). In accordance with the oxidation potential of HIO_4 [12], we can expect the following relations between the oxidizing agent, reducing agent and the amount of aldehyde groups formed. That is, the IO_4^-/aldehyde group molar ratio is 1/2. However, from Table 1 taking into account the ratio ($NaIO_4$ solution : cellulose) ≈ 20 follows that the number of the aldehyde groups formed is much less than the expected according to the reaction equation, and the observed molar ratio IO_4^-/aldehyde groups = 1/0.3. This discrepancy can be attributed to the side reactions:

$$IO_4^- + H_2O \rightarrow H_2O_2 + IO_3^-,$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O,$$

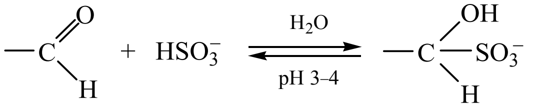
$$–COH + H_2O_2 \rightarrow –COOH + H_2O.$$

Therefore, the oxidizer must be taken in a sufficiently large excess.

The data in Table 1 show that at the increase in the sodium metaperiodate concentration from 0.05 to 0.30 M the content of aldehyde groups in cotton cellulose increases by nearly an order of magnitude. Based on these studies, for the cellulose oxidation was chosen the solution with the sodium metaperiodate concentration 0.2 M, because at the concentration of aldehyde groups in the sorbent 3.98% and higher the pulp begins to swell in aqueous solutions, which hampers its use as a sorbent.

Effect of the oxidation duration of the cotton cellulose with 0.2 M solution of $NaIO_4$ at pH = 3, the solution/sorbent ratio 20 and the temperature 40°C on the content of aldehyde groups is shown in Table 2. Obtaining the required content of aldehyde groups takes the time 20–60 min.

The next stage of modification of cotton cellulose is the treatment of aldehyde groups of oxidized cellulose with sodium bisulfite. The reaction of formation of the aldehyde bisulphite derivative is as follows:



The aldehyde bisulfite derivative

It proceeds in a weakly acidic medium defined by the values of pK_a of sulfurous acid, pH 3–4 ≈ [(pK_{a1} + pK_{a2})/2]±1:

$$H_2SO_3 \xrightleftharpoons[pK_{a1}\ 1.89]{\pm H^+} HSO_3^- \xrightleftharpoons[pK_{a2}\ 5.30]{\pm H^+} SO_3^{2-}$$

In strong acidic and alkaline media the bisulfite compound is dycomposed to form aldehyde [13]:

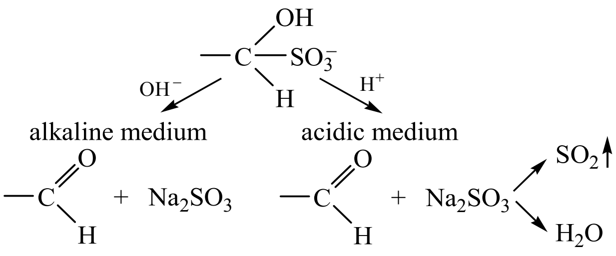


Table 2. Effect of the oxidation duration of cotton cellulose with 0.2 M solution of $NaIO_4$ on the content of aldehyde groups (pH = 3, solution/sorbent ratio 20, temperature 40°C)

Oxidation duration, min	Content of aldehyde groups, %
Untreated cotton cellulose	0.11
10	1.51
20	2.89
30	3.33
45	3.42
60	3.60
90	3.65

Table 3. Effect of $NaHSO_3$ concentration at the processing dialdehydocellulose containing 3.6% of aldehyde groups on the sorption of Cu^{2+} and Ni^{2+} ions with the sulfonated cellulose (pH = 3.5, solution/sorbent ratio 20, duration 0.5 h, room temperature)

Concentration of $NaHSO_3$ solution, %	$A\times10^3$, mol kg^{-1}		α, %	
	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}
Without treatment with sodium bisulfite	6.9	6.5	45.7	43.6
0.25	9.8	9.5	65.1	63.2
0.50	11.8	11.3	78.7	75.6
0.75	14.6	13.7	97.3	91.5
1	14.9	14.7	99.0	98.3
2	14.9	14.7	99.0	98.3
5	14.9	14.7	99.0	98.3

To determine the optimal parameters of the sulfonation of dialdehydocellulose we investigated the effect of the sodium bisulfite concentration at the processing oxidized cellulose containing 3.6% of aldehyde groups on the sorption of metal ions at pH 3.5 at the solution/sorbent ratio 20, for 0.5 h at room temperature (Table 3).

Table 3 shows that the maximum extraction of metal ions by the sulfonated cellulose is achieved when the dialdehydocellulose was treated with the sodium bisulfite solution of 1–5% concentration. Therefore, the investigation of the sulfonation of dialdehydocellulose with different content of aldehyde groups was carried out using 1% solution of $NaHSO_3$.

The effect of the content of aldehyde groups on the sorption of Cu^{2+} and Ni^{2+} by the cotton cellulose treated with 1% solution of $NaHSO_3$ at pH 3.5, solution/sorbent ratio 20, for 0.5 h at room temperature is shown in Table 4.

Table 4 shows that when the content of aldehyde groups in cellulose is 3.6% the degree of extraction of the copper and nickel cations from the aqueous solutions of the metal sulphates with concentration 1.5×10^{-4} M is 99.1% and 99.0% respectively.

By means of elemental analysis we showed that with increasing sodium bisulfite concentration the sulfur content in the modified cellulose increases, hence the content of the sorption-active $-SO_3Na$ groups also increases (Table 5).

The study of sorption kinetics of Cu^{2+} and Ni^{2+} from aqueous solutions of respective sulfates showed that the time of reaching the aqueous solution–modified sorbent equilibrium is 8 min (reduced by more than 5 times compared with unmodified pulp), the metal ions recovery is 99% (increased approximately 2-fold compared with the native cellulose).

To determine the parameters characterizing the limiting sorption capacity of native and modified cotton cellulose we obtained sorption isotherms of

Table 4. Influence the content of aldehyde groups on the sorption of Cu^{2+} and Ni^{2+} with the dialdehydecellulose treated with 1% solution of $NaHSO_3$ (pH = 3.5; solution/sorbent ratio 20, duration 0.5 h, room temperature)

Contents of aldehyde groups in cellulose, %	$A\times10^3$, mol kg^{-1}		α, %	
	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}
0.11	8.9	8.7	59.6	58
1.51	10.7	10.4	71.3	69.2
1.87	11.8	11.5	78.8	76.4
2.54	13.8	13.5	92.3	90.2
2.85	14.7	14.4	98.5	96.3
3.33	14.8	14.6	98.7	97.4
3.42	14.8	14.8	98.9	98.5
3.60	14.9	14.9	99.1	99.0
4.55	14.9	14.9	99.2	99.1

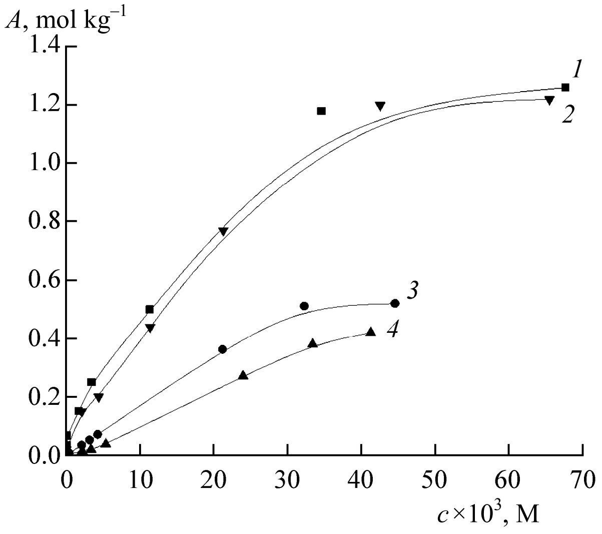


Fig. 3. Sorption isotherms of the (*1, 3*) Cu^{2+} and (*2, 4*) Ni^{2+} ions with (*3, 4*) native and (*1, 2*) modified cellulose.

copper and nickel sorption from the aqueous solutions of sulfates (Fig. 3). Experimental data can be described by the Langmuir adsorption isotherm:

$$A = \frac{A_\infty K C_{eq}}{(1 + KC_{eq})},$$

where K is the concentration constant, l mol^{-1}, of the sorption equilibrium characterizing the sorption process intensity.

Treatment of the sorption isotherms in the linear coordinates Langmuir equation performed by the method of least squares showed the applicability of this equation for the formal description of the sorption of Ni^{2+} and Cu^{2+} from aqueous solutions in the concentration range 1.5×10^{-4}–5×10^{-2} M and allowed graphical determining the value of the maximum sorption A_∞ for the original and the modified sorbent which amounted to 0.49 and 1.51 mol kg^{-1} for Cu^{2+}, and 0.45 and 1.40 mol kg^{-1} for Ni^{2+}, respectively.

$$\frac{C_{eq}}{A} = \frac{1}{A_\infty K} + \frac{1}{A_\infty} C_{eq}.$$

Table 5. Effect of the $NaHSO_3$ concentration on the content of sulfur and the sorption-active $–SO_3Na$ groups in the sorbent (aldehyde groups 3.6%)

Concentration of $NaHSO_3$ in solution, %	Sulfur content, %	Content of $–SO_3Na$ groups, mol kg^{-1}
0.25	0.02	0.006
0.5	0.06	0.019
0.75	0.12	0.038
1	1.76	0.550
2	2.56	0.800
5	3.03	0.947

The values obtained for the limiting sorption exceed the total content of carboxylic groups in the original cellulose and bisulfite groups in the modified cellulose. This can probably be explained by the formation of additional carboxyl groups in the process of oxidation–bisulfite treatment.

Thus, the chemical modification by converting alcohol groups into the aldehyde and then into the aldehyde bisulfite derivatives increases substantially (approximately 2-fold) the sorption properties of cellulose materials.

EXPERIMENTAL

As the sorbent was selected cotton cellulose (GOST 595-79), preliminary had boiled with a 5% solution of $NaHCO_3$ to remove impurities, and dried to constant weight. The air dry cellulose samples humidity was 8%.

We used: $CuSO_4·5H_2O$ and $NiSO_4·7H_2O$, $NaHSO_3$, $NaIO_4$, H_2SO_4, $Na_2B_4O_7·10H_2O$, HCl, I_2, KI, $Na_2S_2O_3·5H_2O$, NaCl, NaOH, $NaHCO_3$ of chemically pure grade.

The sorption kinetics was studied by the method of limited volume of solution [14]. To obtain the sorption kinetic curves, a series of tubes was charged with a weighted sample 0.1 g (m) of the sorbent, filled with 10 ml (V) of aqueous solution of metal sulfate and held from 5 min to 24 h while stirring at the temperature 273 K. The initial concentration (C_0) of the metal ion was 1.5×10^{-4} M. At regular intervals the solution was separated from the sorbent by filtration and determined in it the current concentration of the metal ion (C_τ) by atomic absorption spectroscopy on a Saturn instrument.

To obtain the sorption isotherms, a series of tubes was charged with weighted samples 0.1 g (m) of the sorbent, and 10 ml (V) of aqueous solution of copper sulfate with initial concentration (C_0) 1.5×10^{-4}–5×10^{-2} M and held until equilibrium at the temperature 273 K. The solution was then separated from the sorbent by filtration and equilibrium concentration of metal ions (C_{eq}) was determined in it the by atomic absorption spectroscopy on a Saturn instrument.

Sorption capacity (A_τ) of the sorbent at any given time point was calculated with the formula:

$$A_\tau = \frac{C_0 - C_\tau}{m} V. \qquad (1)$$

The equilibrium concentration of metal ions in solution (C_{eq}) after reaching equilibrium was measured and equilibrium sorption capacity of sorbents (A_{eq}) was calculated using the formula:

$$A_{eq} = \frac{C_0 - C_\tau}{m} V. \qquad (2)$$

Degree of extraction α is determined as follows:

$$\alpha = \frac{C_0 - C_{eq}}{C_0} \times 100\%. \qquad (3)$$

The solutions pH was monitored with a Multitest IPL-311 pH-meter. The number of carboxyl groups in the sorbent was determined by the classical method [15, 16] based on the reaction of acidic groups with calcium acetate and titrimetric determination of the evolved acetic acid. Its content per a weight unit is taken equal to the value of carboxylic acidity: $[\text{–COOH}] = V_{NaOH} \cdot C_{NaOH}/g$, where V_{NaOH} is the volume of NaOH solution taken at the titration, ml; C_{NaOH} is concentration of the NaOH solution, M; g is weight of the sorbent sample, g.

The content of aldehyde groups in the cotton native and oxidized cellulose was determined by iodometric titration [17, 18]. The content of aldehyde groups is given by the formula:

$$[\text{–COH}] = \frac{14.51n(a - b)\times 100}{1000q}, \qquad (4)$$

where a is the volume of the hyposulfite used at the titration in the control experiment, ml; b is the volume of the hyposulfite solution used at the titration in the basic experiment. ml; q is weigh of the cotton cellulose sample with accounting for humidity, g; n is normality of the hyposulfite solution; $E_{COH} = 14.51$ is molecular equivalent of aldehyde groups involved in the reaction.

Relative error of the experiments was calculated based on the data of equilibrium and kinetic experiments, in which each point represents the average of three parallel experiments [19]. Instrumental error of the Saturn instrument in determining the concentration of metal ions is 3%. Experimental error did not exceed 10%.

ACKNOWLEDGMENTS

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