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SORPTION OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS BY CELLULOSE SORBENT AGENT

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Abstract. *The paper concerns the sorption of heavy metal ions from aqueous solutions by cellulose sorbents agents. We modified the wood cellulose by polyvinylpyrrolidone and carboxylic acids. Also we studied the equilibrium and kinetics of Cu(II), Co(II) and Ni(II) ions sorption from aqueous solutions by native and modified cellulose samples. We treated the sorption isotherms under study according to Langmuir models and theory for volume filling of micropores. The Langmuir model is the most correct one for description of the process of heavy metal ions sorption by cellulose sorbents agents. According to the study, the maximum sorption capacity of the modified sorbents is 1.5-2 times higher than the maximum sorption capacity of the native cellulose. The samples obtained can be arranged in the following order of increasing ultimate sorption capacity (A_∞): native cellulose < polyvinylpyrrolidone-modified pulp < citric acid-modified pulp. In addition, we studied the influence of media acidity on the sorption of heavy metal ions in pH 1-7. We observed a significant increase in the pH of the initial solution from 1 to 6; there is a rapid increase of the degree of extraction of Cu(II), Cu(II) and Ni(II) ions. Experimentally we obtained the IR spectra of native wood cellulose and its samples modified by polyvinylpyrrolidone and citric acid. Also the authors made an elemental analysis of all types of modified sorbents.*

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Introduction

Heavy metal pollution of the biosphere as a result of anthropogenic activities is a major concern worldwide. The main cause is unlike organic pollutants metals in the natural environment do not undergo decomposition processes and can concentrate in ecosystem objects - plants, water, soil and then transfer into the human body through the natural food chain with food and drinking water. It is important to constantly monitor their content not only in the environment, but also in foodstuff. The heavy metals such as Cd, Zn, Pb, Fe, Cu, Hg, Ni, Mn, Co, etc. are usually present in trace amounts; they are the most toxic and widespread components of wastewater [1]. Heavy metals are highly susceptible to a variety of chemical, physical and biological reactions and can have adverse effects on both the environment and human health [2].

Even at low concentrations, heavy metals have harmful health effects, including carcinogenic and mutagenic effects, can cause growth retardation, organ damage, disruption of the nervous and endocrine systems, digestive organs, hematopoietic organs, etc. [3].

Pollution is steadily increasing with the development of industry. Heavy metals and wastewater from various industries such as mining, metallurgy, chemicals, electrical engineering, mechanical engineering, etc., transfer into the biosphere and accumulate in plant and animal organisms [4]. The bioaccumulation of heavy metals increases as they move along the food chains. Heavy metals are not metabolized and accumulate in the body in various organs and tissues, which is dangerous to human health [5]. Therefore, the problem of water purification from heavy metal ions is currently very acute.

Currently, various methods of purification of aqueous solutions from heavy metal ions are used. The most widespread are physical, chemical, physico-chemical and biochemical; among them are precipitation, coagulation-flocculation, electrocoagulation, ion exchange, electrodialysis, membrane and ultramembrane filtration, reverse osmosis and adsorption [6]. When choosing the method, costs, efficiency, reliability, environmental impact, practicality and operational difficulties are usually taken into account [7]. Most of these methods, except the adsorption, are expensive and insufficiently effective at low metal concentrations in solutions. The ion exchange purification using synthetic ion exchange resins (ionites) allows to achieve a high degree of water purification, however, the main disadvantages of the method are the high cost and the limited possibility of application of pollutants [8].

The adsorption method is both efficient and economical. It is also convenient to use. It includes the complex equipment and can work with a wide range of adsorbents, therefore it is most widely used for cleaning aqueous solutions with a low metal content [9].

In recent years there was a great interest in developing sorbents based on multi-tonnage co-products or waste products of the agricultural, textile and pulp and paper industries. These materials are less expensive, accessible and easy to dispose, have fairly high sorption characteristics for a wide range of pollutant metals and ecofriendly. However, such sorbents have insufficiently high sorption capacity due to the low content of active centres in their composition, which can intensify the transfer of contaminants into the material structure. The modification of sorbents based on recycled cellulose-containing raw materials is therefore a topical issue [10].

In recent years there was a great interest to developing sorbents based on multi-tonnage co-products or waste products of the agricultural, textile, pulp and paper industries. These materials are less expensive, accessible and easy to dispose, have fairly high sorption characteristics for a wide range of pollutant metals and ecofriendly. There are many publications in the literature on the use of untreated cellulose-containing raw materials as sorbents. The work shows the possibility of using sugar cane press cake to remove Pb (II) and Ni (II) from wastewater [11]. The maximum adsorption capacity of the sorbent towards Pb (II) and Ni (II) ions was 1.61 mg/g and 123.46 mg/g, respectively. Wastewater treatment for Pb(II), Cd(II), Hg(II), Cu(II), Ni(II), Cr(III) and Cr(VI) ions is based on a variety of agricultural waste materials: peanut and walnut shells, green almond husks, tea leaves, olive oil waste, jute fibre, sunflower stems, tobacco leaves, and sawdust from maple, oak and fir trees. These materials are accessible and low cost [12].

However, such sorbents have insufficiently high sorption capacity due to the low content of active centres in their composition, which can intensify the transfer of contaminants into the material structure. The modification of sorbents based on recycled cellulose-containing raw materials is therefore a topical issue. The main activation methods for cellulosic sorbents are mechanical, physical, chemical and physico-chemical ones. [13, 14]. A promising trend in sorbent processing is the use of nano- and biotechnologies.

The most common physical modification methods are high temperature (coking), superheated water vapour treatment, freezing, plasma activation and infrared exposure [15]. Different reagents are used for chemical modification of cellulose sorbents: alkaline solutions, mineral and organic acids, organic compounds, active dyes; one of the promising areas of cellulose modification is the synthesis of graft copolymers [10, 12-14].

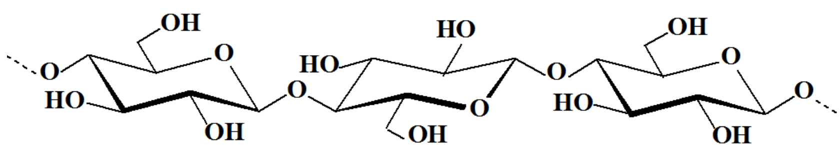
Thus, agro-industrial co-products modified in various ways are almost as good as industrial sorbents (ion exchangers, activated carbons, zeolites, etc.) in terms of their sorption capacity to metal ions. A wide range of methods for modifying plant raw materials makes it possible to obtain effective ecofriendly, biodegradable and biologically inert sorbents.

The aim of this work is to investigate the sorption of heavy metal ions from aqueous solutions by chemically modified cellulose.

Main part

The objects of study and the reagents used. In the experimental part of the work, cellulose was used as a sorbent and treated with alkali to remove impurities and increase the sorption capacity. A 0.05% NaOH solution was used for the treatment, the dwell time is 30 minutes at a solution/sorbent modulus of 20. The pulp was then washed with distilled water to neutral pH and dried to a constant weight.

Cellulose is the most abundant natural polymer, the main constituent of plant cell walls, which accounts for the mechanical strength and elasticity of plant tissue. Cellulose macromolecules are constructed of elementary D-glucose units (in pyranose form) linked by 1,4-β-glycosidic bonds to form linear, unbranched chains.



In this work we used $CuCl_2{\cdot}2H_2O$, $NiCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$ as sources of metal ions; HCl, NaOH were used to create the necessary pH level of the medium, all reagents are chemically pure. The modify cellulose we used the following reagents: succinic (ethane-1,2-dicarboxylic) - NOOS-$(CH_2)_2$-SOH, adipic (butane-1,4-dicarboxylic) - NOOS-$(CH_2)_4$-SOH and citric (2-hydroxy-1,2,3-propantricarboxylic) NOOS-CH_2-SOH-CH_2-SOH and polyvinylpyrrolidone (TU 9365-002-46270704-2001).

The elemental composition of the biopolymer sorbents under study was determined by Flash EA 1112 analyzer.

Kinetics and isotherms of sorption. We studied the kinetics of sorption by the limited solution volume method [16]. In order to obtain kinetic curves of sorption, 0.1 g sample (*m*) of sorbent was placed in a series of test tubes, filled with 10 ml (*V*) of aqueous metal chloride solution and incubated for 5 min to 24 h under stirring and temperature 293 K. The initial concentration (C_0) 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 determined in it by atomic absorption spectroscopy by apparatus "210VGP".

In order to obtain sorption isotherms, 0.1 g sample (*m*) of sorbent was placed in a series of test tubes, filled with 10 ml (*V*) of aqueous metal chloride solution with initial concentrations (C_0) of $1.5 \cdot 10^{-4}$-$5 \cdot 10^{-2}$ mol/l and incubated until equilibrium was reached at 293 K. At certain intervals the solution was separated from the sorbent by filtration and the current concentration of metal ions (*C*) was determined in it by atomic absorption spectroscopy by apparatus "210VGP".

The sorption capacity (*A*) of the sorbents was calculated according to the formula

$$A = \frac{(C_0 - C)}{m} \cdot V. \quad (1)$$

The extraction rate α (%) was determined as follows:

$$\alpha = \frac{C_0 - C}{C_0} \cdot 100. \quad (2)$$

When sorption equilibrium was reached, the solutions were filtered off and the residual concentration of metal ions in the filtrate was determined by apparatus "210VGP".

We calculated % of the indication in accordance with the data of the equilibrium and kinetic experiments; each point represents the average of two parallel experiments [17]. Experiment % of the indication

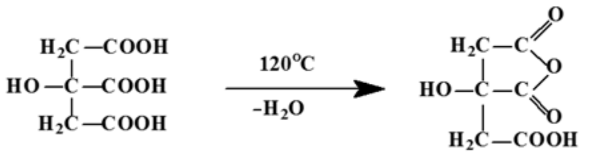
Effect of pH on the sorption of Cu(II), Co(II) and Ni(II) ions. In a study of the effect of solution pH on the sorption of heavy metal ions, a series of test tubes with the same 0.1 g sample of sorbents were filled with 10 ml of an aqueous solution with pH values of 1-7. The required acidity of the medium was achieved by using hydrochloric acid. We used the freshly prepared copper, cobalt and nickel chloride solutions for each experiment. We monitored the pH value using an IPL-311 multitest pH meter before sorption and after equilibrium was reached. When sorption equilibrium was reached, the solutions were filtered off and the residual concentration of metal ions in the filtrate was determined by apparatus "210VGP".

IR spectra of native and modified cellulose were recorded by apparatus Avatar 360 FT-IR ESP in the range 400-4000 cm^{-1}. Samples for analysis were prepared by mechanically grinding cellulose followed by thorough grinding of the sorbent in an agate mortar with spectrally pure KBr.

Results and discussion

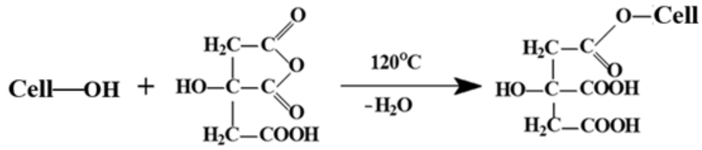
Carboxylic acids modification. In order to improve the sorption properties of the cellulose, it was modified with solutions of adipic, citric and succinic acids separately (concentration 0.5 mol/l), the solution/sorbent module being 20:1. The cellulose was kept in the acid solution for 10 min at 20 °C, then it was placed in thermostat for 60 min at 120 °C, as at higher temperature the acid decarboxylation processes are possible [18]. The pulp was then washed with distilled water to neutral pH and dried to a constant weight. The etherification reaction produces esters of cellulose and carboxylic acid esters.

According to the equation cellulose is modified with citric acid into citric acid anhydride.



Citric acid   Citric acid anhydride

The anhydride reacts with the hydroxyl groups of the cellulose to form the ester:



Cellulose   Cellulose citrate

The treatment of cellulose with citric acid increases the content of carboxylic groups in the cellulose structure, which is confirmed by equilibrium-kinetic characteristics of the sorbent (Fig. 1, 2) as well as by infrared spectra (Fig. 3, 4).

Table 1 shows the results of experiments on the sorption of Cu(II) ions from aqueous solution for polycarboxylic acid modified sorbents compared to native cellulose.

Table 1. Effect of modification by carboxylic acids on the sorption properties of cellulose to Cu(II) ions

Modifying agent	α, %
–	70
Adipic acid	91
Succinic acids	93
Citric acid	98

By data obtained, the sorbent treated with citric acid is the most effective one. In this case a higher content of sorption-active carboxylic groups in the sorbent structure is probably achieved compared to sorbents modified with adipic acid and succinic acid. Citric acid contains three carboxylic groups, whereas adipic acid and succinic acid contain only two ones. Therefore, further studies on the sorption of Cu(II), Co(II) and Ni(II) ions were carried out for citric acid modified wood cellulose.

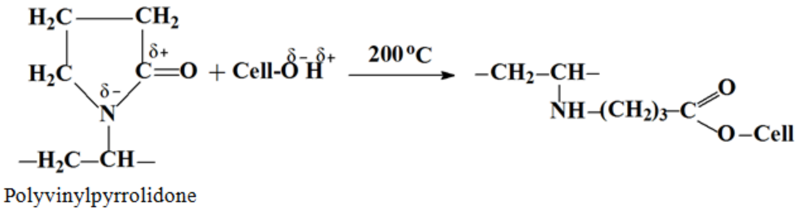
Modification by the nitrogen-containing polymer polyvinylpyrrolidone (PVP). The mechanism of these reactions is described in detail in the literature [18]. For this method the nucleophilic substitution reactions (acylation, esterification, etc.) are the most appropriate ones. Sufficiently high activation energy of this type of reactions requires high temperatures (more than 180 °C), which is confirmed by the results of elemental analysis characterizing the dependence of the nitrogen content in the sorbent after sorption on the treatment temperature (Table 2).

Table 2. The polyvinylpyrrolidone-treated wood cellulose elemental analysis

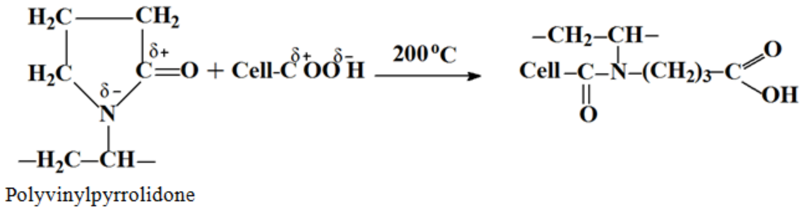
Treatment temperature, °C	Nitrogen content in sorbent, %
100	2.28
125	2.48
150	2.56
180	2.82
200	3.05

By Table 2, the nitrogen content of the sorbent increases with increasing treatment temperature. Thus, the optimum temperature for chemical modification is 200 °C.

During high-temperature fixation of a nitrogen-containing polymer on the sorbent, the amide fragment of PVP ->N - CO - CH_2 -, carboxyl and hydroxyl groups of cellulose take part in the opening of the amide cycle of PVP, which promotes its fixation (immobilisation) by covalent bonding on the cellulose sorbent when heated. The hydroxyl groups of cellulose can react with PVP as follows:



The carboxylic groups react with PVP according to the equation



Kinetics of sorption of Cu^{2+}, Ni^{2+}, Co^{2+} ions from aqueous solutions of metal chlorides.

The speed at which equilibrium is reached is an important characteristic of sorbents. We obtained the kinetic curves for the sorption of Cu(II), Co(II) and Ni(II) ions from water solutions of metal chlorides to determine the kinetic characteristics of the original sorbent and the sorbent modified with citric acid.

Kinetic studies show the time to reach sorption equilibrium in the heterophase system with the modified sorbent is markedly reduced in compare to the original sample. The extraction time for heavy metal ions was 8 min for untreated wood cellulose and 5 min for modified one (see figure 1). In compare with the original wood cellulose the recovery of metal ions increased significantly.

The extraction of heavy metal ions by citric acid-modified wood cellulose increases by an average of 30-40%. The sorption efficiency of heavy metal ions decreases for sorbents under study in the following order: Cu(II) > Co(II) > Ni(II).

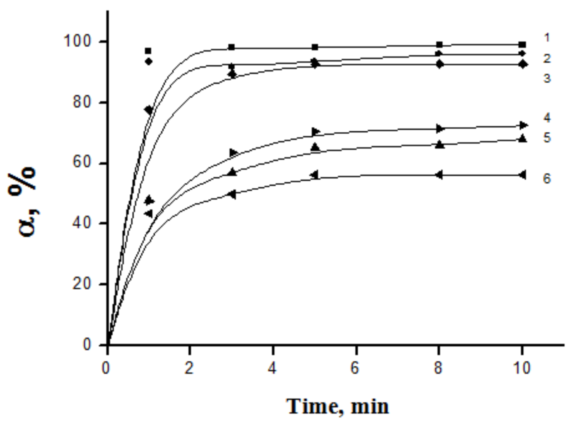


Fig. 1. Kinetics of sorption of Cu^{2+} (1, 3), Co^{2+} (2, 5) and Ni^{2+} (3, 6) ions by unmodified wood cellulose (4-6) and citric acid treated wood cellulose (1-3)

Isotherms of sorption of Co $^{2+}$, Cu^{2+}, Ni^{2+} ions by native wood cellulose. We obtained the sorption isotherms of Cu(II), Co(II) and Ni(II) ions from aqueous chloride solutions in order to determine the ultimate sorption capacity of wood cellulose at 293 K (see Figure 2).

The Langmuir sorption model is most commonly used in the literature for describing the experimental isotherms for heavy metal ions by cellulose sorbents.

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

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.

Linearisation of sorption isotherms

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

allows identify the coefficients in the Langmuir equation graphically (Table 3).

In order to describe the sorption equilibrium in heterophase system "aqueous solution of metal salt - cellulose sorbent we apply the model theory for volume filling of micropores (TVFM). By this theory, the fixation of solute occurs not only on the inner surface of pores but also in the volume of the interstitial space. TVFM establishes the relationship between the degree of filling of the adsorption space volume and the differential molar work of adsorption. The TVFM equation for adsorption from solutions in its general form is

$$\ln A = \ln A_\infty - (RT / E)^n (\ln C_S / C)^n, \quad (5)$$

in which E is the characteristic energy of adsorption, C_s is the solubility of the sorbate, C and A are the equilibrium concentrations of the distributed substance in the bulk and adsorption phases respectively, A_∞ is the limiting concentration of the sorbate in the adsorption phase, n is an integer, mostly 1, 2, 3.

The experimental isotherms were processed in two sorption models: surface (Langmuir) and volume (TVFM). Figure 2 shows the sorption isotherms of Cu^{2+}, Co^{2+} and Ni^{2+} ions by native wood cellulose from aqueous solutions of metal chlorides.

By literature review, the ultimate sorption (A_∞) on unmodified cellulose sorbents does not exceed 1 mol/kg [19]. This agrees with the data obtained from isotherms using the Langmuir adsorption model (see Table 3). Treated by these isotherms TVFM model gives overestimates of the ultimate sorption. This probably explains the predominant use of the Langmuir model to describe the sorption of heavy metal ions by swelling biosorbents from aqueous media.

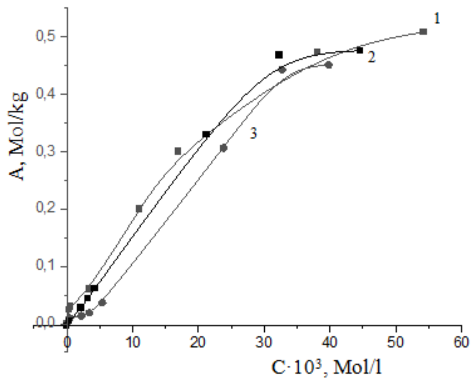


Fig. 2. Isotherms of the sorption of Cu^{2+}(1), Co^{2+}(2) and Ni^{2+}(3) ions by native wood cellulose from aqueous metal chloride solutions

Tables 3 and 4 show the results of the isotherms of heavy metal ion sorption by wood cellulose according to the Langmuir and TVFM models. The experimental data obtained are described by the Langmuir adsorption isotherm equation, the correlation coefficient is 0.98-0.99. When the TVFM model is used to treat isotherms, the A_∞ values are several times higher than the experimental A_∞ values but the correlation coefficient is lower (0.94-0.97).

Table 3. Processing parameters for heavy metal ion sorption isotherms using the Langmuir model

Metal cation	$1/A_\infty \cdot K$	$1/A_\infty$	Correlation coefficient	A_∞, mol/kg
Cu(II)	0.0010	1.42	0.99	0.70
Co(II)	0.0015	1.83	0.98	0.55
Ni(II)	0.045	1.96	0.99	0.51

Table 4. Processing parameters for heavy metal ion sorption isotherms using the TVFM model

Metal cation	$\ln A_\infty$	RT/E	Correlation coefficient	A_∞, mol/kg
Cu(II)	1,25 ± 0,27	-0,31 ± 0,04	0.94	3.49
Co(II)	1,11 ± 0,18	-0,32 ± 0,02	0.97	3.03
Ni(II)	1,30 ± 0,31	-0,33 ± 0,04	0.95	3.67

Isotherms of the sorption of Cu^{2+}, Co^{2+} and Ni^{2+} ions by citric acid-modified wood cellulose. We obtained the sorption isotherms of Cu(II), Co(II) and Ni(II) ions from aqueous chloride solutions in order to determine the ultimate sorption capacity of wood cellulose at 293 K (see Fig. 2).

According to the data obtained, the sorption properties of the modified wood cellulose increase by about one and a half times in compare with the original sample. The sorption efficiency of heavy metal ions decreases for sorbents under study in the following order: Cu(II) > Co(II) > Ni(II).

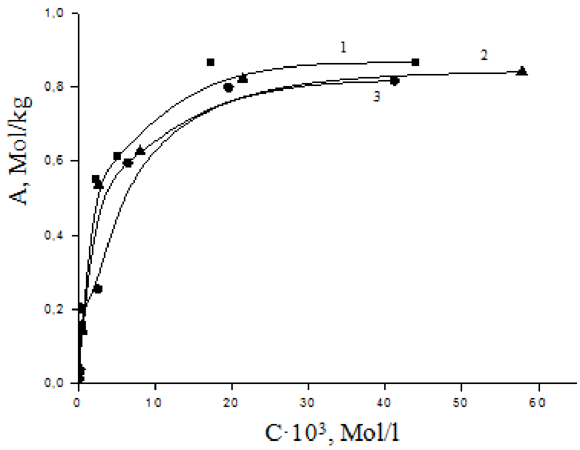


Fig. 3. Isotherms of the sorption of Cu^{2+}(1), Co^{2+}(2) and Ni^{2+}(3) ions by citric acid-treated wood cellulose

IR spectra. Fig. 4-6 show IR spectra of the original wood cellulose as well as of wood cellulose modified with citric acid and PVP.

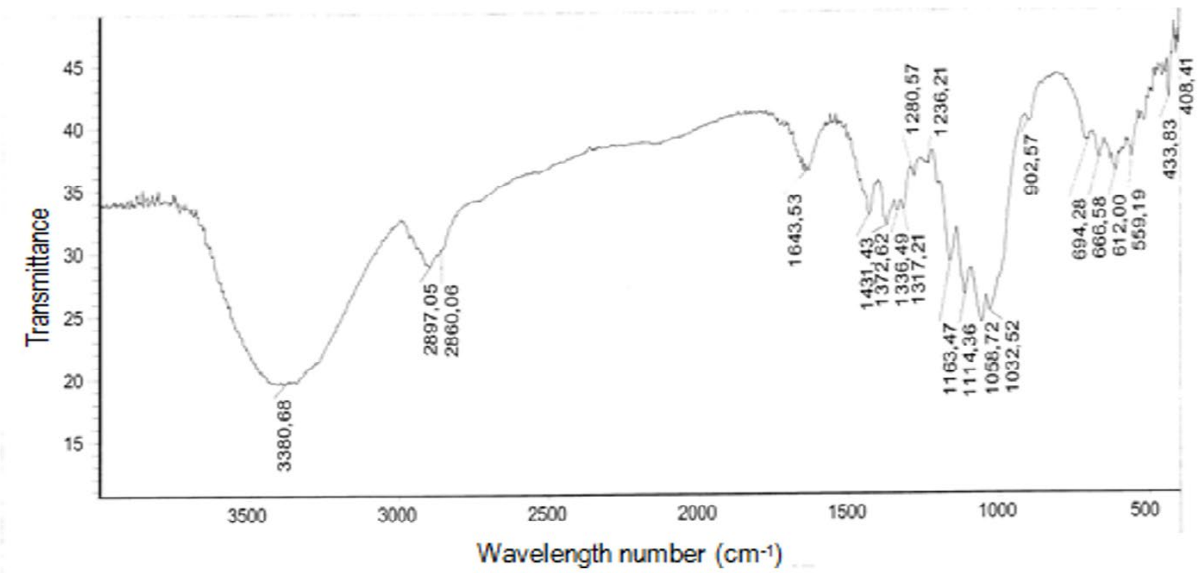


Fig. 4. IR spectrum of native wood cellulose

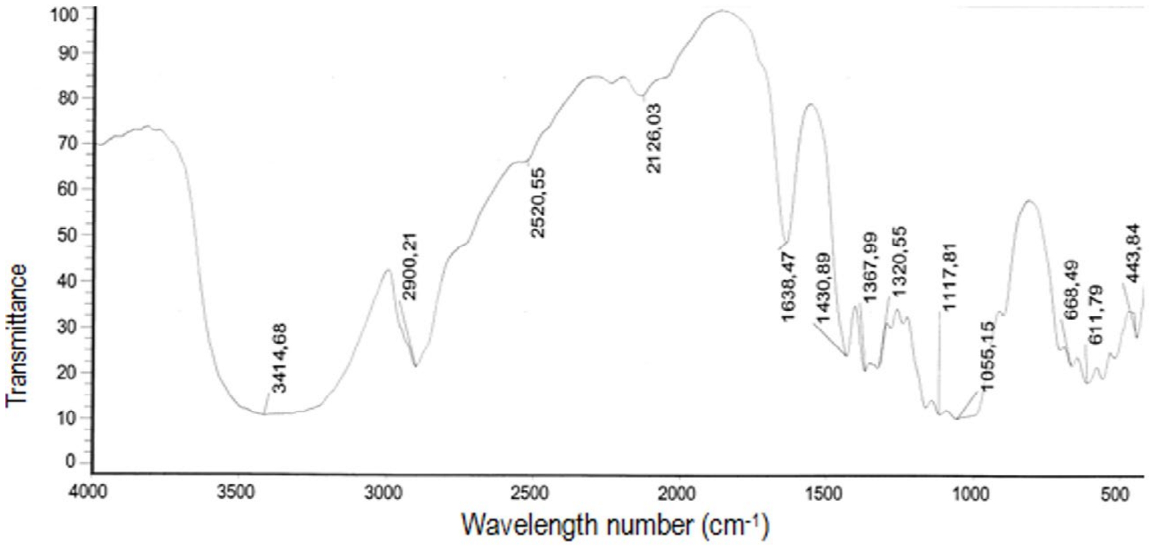


Fig. 5. IR spectrum of wood cellulose modified with citric acid

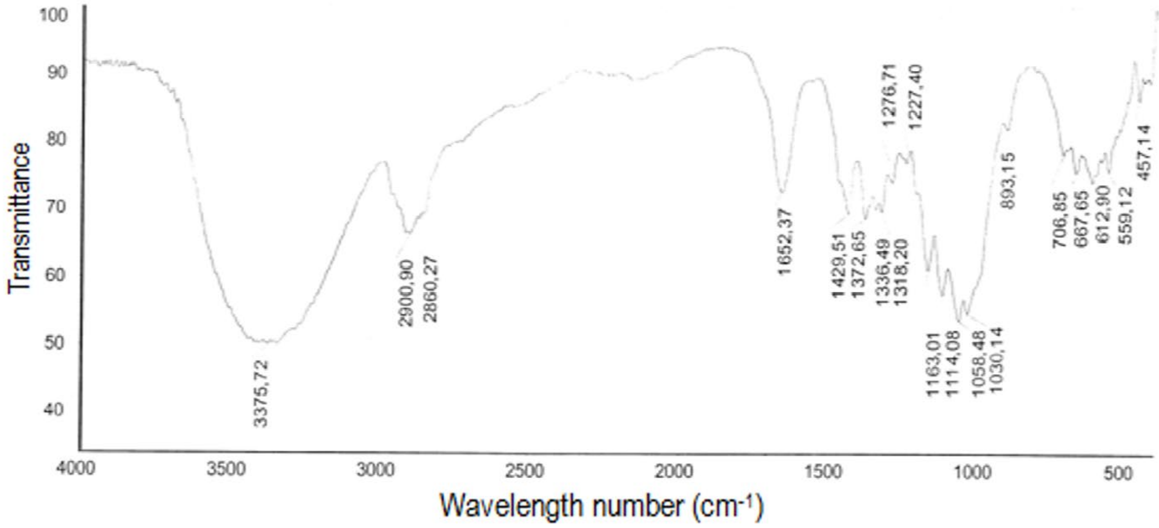


Fig. 6. IR spectrum of wood cellulose modified with PVP

The IR spectrum of the original sorbent has a characteristic set of absorption bands due to vibrations of the C=O, C-C C-O-C, C-H and O-H bonds in the cellulose structure (see Figure 4). The IR spectrum of citric acid-modified cellulose shows the significant changes in 1650-1600 cm^{-1} and 1430-1300 cm^{-1}, where valence asymmetric and symmetric vibrations of the C=O bond in the carboxylic groups appear, respectively. There is a rapid increase in the peak intensity at 1638 cm-^{1} and its shift with respect to the band in the spectrum of the original sorbent, as well as an increase in the peak intensity at 1430 cm^{-1}, indicating the appearance of additional carboxyl groups in the citric acid-modified cellulose.

Changes in the IR spectra of wood cellulose as a result of modification with polyvinylpyrrolidone are observed in 1650-1450 cm^{-1}, where deformation vibrations of N-H bond appear. In 1300-1000 cm^{-1}the valence vibrations of C-N bond appear. Therefore, the nitrogen-containing polymer becomes attached to its surface during the sorbent modifying.

Effect of pH on the sorption of Cu^{2+}, Co^{2+}, Ni^{2+} ions by wood cellulose. The acidity of the medium influenced on the value of the equilibrium exchange capacity. Therefore, we studied the effect of solution pH on the sorption of heavy metal ions from aqueous solutions of $CuCl_2$, $CoCl_2$ and $NiCl_2$ by wood cellulose.

By Fig. 7, the degree of extraction of Cu^{2+}, Co^{2+} and Ni^{2+} ions by wood cellulose increases in the pH range 1-7 of the aqueous solution and reaches a maximum at pH values of 6.0-6.5. The pH limit of 6.5 related to the precipitation of heavy metal hydroxides. The low sorption of heavy metal ions in the pH range of 1-2 is explained by the competition for the sorption centres of wood cellulose between metal ions and hydrogen H^+ ions. In the pH 2.0-5.5 the medium acidity increases the number of free sorption centres on the sorbent, which leads to a significant increase of the sorption of metal ions. At pH 5.5-6.5, the increase of extraction rate (α) slows down as the pH of the equilibrium solution increases.

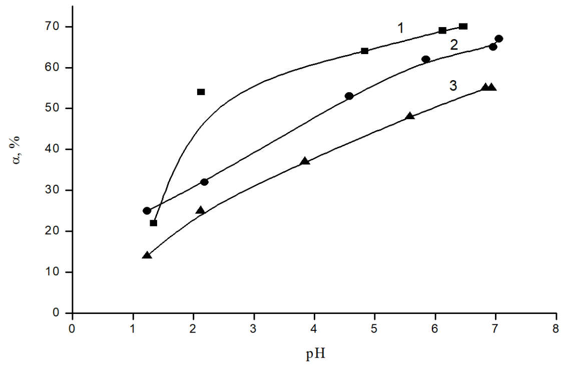


Fig. 7. Effect of aqueous solution pH on the sorption of Cu^{2+}(1), Co^{2+}(2) and Ni^{2+}(3) ions by wood cellulose

The pH of the solution increases when heavy metal ions are sorbed. The largest change are in the pH range of 3 to 5. The pH increases in the sorption process by 1-1.7 units compared to the pH of the stock solution, irrespective of the nature of the metals. Thus, the reason for the change in the acidity of the equilibrium solution in the systems under study is the competition of metal ions and hydrogen ions for the sorption centres of the sorbent and the sorption of hydrogen ions in the acidic pH. The maximum extraction of Cu(II), Co(II) and Ni(II) cations by polysaccharide sorbent is observed at pH equilibrium solutions close to neutral.

Conclusions

We carry out the modification of wood cellulose with carboxylic acids and PVP. Also we studied the sorption properties of unmodified and modified wood cellulose in compare with heavy metal ions.

Kinetic studies show the time to reach sorption equilibrium in the heterophase system "aqueous metal chloride solution - sorbent" is reduced from 8 min for native cellulose to 5 min for the sorbent modified with citric acid. The extraction rate of heavy metal ions for the sorbent under study increases by an average of 30-40% compared to native cellulose.

The experimentally obtained isotherms of heavy metal ion sorption are processed within the framework of the Langmuir and TVFM sorption models. The Langmuir model describes the sorption of heavy metal ions by wood cellulose more correctly. The ultimate sorption value of the citric acid-modified sorbent is increased by a factor of approximately 1.5 compared to the original sorbent.

We identify the effect of solution pH on the sorption of Cu^{2+}, Co^{2+}, Ni^{2+} ions from aqueous solutions of their chlorides in the pH range 1-7. The maximum extraction of Cu(II), Co(II) and Ni(II) cations by wood cellulose is observed at pH equilibrium solutions close to neutral.

Results of IR-spectroscopy confirm the different methods of modification a chemical interaction of modifying agents with wood cellulose occurs. It leads either to an increase (as in the case of citric acid modification) or to the appearance of new (in the case of PVP treatment) sorption-active groups in the structure of sorbents.

By these results, it is possible to recommend the use of modified wood cellulose for the purification of aqueous solutions from heavy metal ions.

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