**The mechanism of d-metal ions sorption from aqueous media and chelating sites structures of modified heterocyclic biopolymers**

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The mechanism of d-metal ions sorption from aqueous media and chelating sites structures of modified heterocyclic biopolymers

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Sorption of d-metal ions (Cu$^{2+}$, Fe$^{2+}$, and Ni$^{2+}$) from aqueous media using modified heterocyclic biopolymers takes place with the participation of sorption sites – acidic groups: α-hydroxycarboxylic (monobasic, bidentate), hydroxamic (monobasic, bidentate), and aldehyde bisulphite (dibasic) in the form of chelate metal complexes, whose structures were determined through the use of computational quantum chemistry on some modeled compounds.

Ion exchange mechanism of the components of hetero-phase system in electroneutral, molecular form reflects the implementation of the general laws of thermodynamics – Gibbs' phase rule, law of mass action, law of equivalent proportions, and law of conservation of charge at electroneutrality of phases.

Sorbents functional groups act as sorption sites whose filling goes in accordance with their amount, denticity, basicity and ability of metal cations to complex formation and solvation. The amount and the nature of acid sorption sites of sorbents permits to compare their initial and maximum sorption abilities.

Keywords: d-metal, cellulose modification, sorption mechanism.
Introduction

Chelate metal complexes are very common in natural processes, they have a unique and specific features that allows them to act in the photosynthesis of carbohydrates (chlorophyll) and in animals breathing processes (heamin) whereby the pyrrollic rings act as ligands in the macrocycle. These natural polypyrrollic ligands contain four pyrrollic rings in their unit structure (porphyrins) which are embedded in the biopolymer structures. Denticity of such sorption sites in the macroheterocycles is 4. However, the study of the peculiarities and the mechanism of the chemisorptions of metal cations to form chelate metal complexes can be made easier by beginning with one of the most common polyheterocyclic sorbent – cellulose, which has a simpler functional acid groups-sorption site with denticity not exceeding 2, cellulose being the most available polyheterocyclic biopolymer and its modified forms can be used as sorbents.

The sorption of heavy metal ions by biopolymers on the basis of β-D-glucose is of great importance in various fields of science and technology. Cellulosic materials are promising sorbents for the sorption of heavy metal ions; derived from available, cheap, renewable and biodegradable natural resources.\[1-3\]

Among the requirements placed on sorbents, the most important are high sorption capacity in relation to a wide spectrum of metal ions or selectivity to ions of one metal, ability to speedily and strongly bind metal ions, possibility of regeneration (recycling), environmental friendliness, cheapness and high availability. Most authors see the low sorption capacity while using cellulosic biopolymer sorbents as the main problem. It should be noted that the most profitable use of cellulose sorbents is in the purification of very dilute solutions, which allows achieving very low concentration of metal ions.\[4\]

Presently in the literature there is a large number of experimental data on the sorption of metal ions from aqueous solutions of their salts by various cellulose-containing materials,
also in recent years there has been a rapid growth in researches touching the use of cellulosic materials in the natural state as well as in their modified forms for the sorption of heavy metal ions from aqueous media.\[5-8\]

Thus, in the removal of divalent metals of the natural form of jute fibers its sorption capacity decreases as follows: Cu (4.23 mg·g\(^{-1}\)) > Zn (3.55 mg·g\(^{-1}\)) > Ni (3.37 mg·g\(^{-1}\)). Lignin isolated from paper wastes, removes heavy metal ions from aqueous solution of their salts in the following sequence: Pb(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II).\[9\] In the study of Zn(II) and Pb(II) on the fibers of coconut palms,\[10\] it was found that the sorbent has a stronger affinity for Pb(II) ions than for Zn(II) ions. The sequence of increasing sorption effectiveness of metal ions using wastes of grapefruit follows this: Pb(II) > Cu(II) > Ni(II) > Cd(II).\[11\]

Variety of agricultural wastes are used in sewage treatment of Pb(II), Cd(II), Hg(II), Cu(II), Ni(II), Cr(III) and Cr(VI) ions: peanut shells and walnut husk, green almond, tea leaves, olive oil production wastes, jute fiber, sunflower stalks, tobacco leaves and maple peels, oak, spruce. While the sorption values can vary within a wide range depending on the raw material used: 0.3-14.3 mg·g\(^{-1}\) for Cu(II), 0.4-10.8 mg·g\(^{-1}\) for Cd(II) and 1.47-10.9 mg·g\(^{-1}\) for Cr(III) ions.\[2\]

In addition to experimental data accumulated, the theoretical understanding of the mechanism of heavy metal ion sorption processes was formed taking in account the nature of functional groups (sorption sites) of polysaccharides, their interaction with metal ions, also the influence on sorption process by various factors, like pH, solution temperature, concentration of strong electrolyte, etc.\[12\]

During the development of new sorbents it is important to find a polysaccharide material treatment method aimed at improving their sorption properties in relation to heavy metal ions.
Works\textsuperscript{[13-17]} suggest different methods used in modifying cellulose-containing polymers by using mechanical, physical, biochemical and physico-chemical types of treatment. The main goal of modification is to increase the internal adsorption surface, the availability of active groups, also creation of new sorption-active sites on the sorbent surfaces (surface functionalization). Chemical modification allows significantly increase the sorption capacity of natural sorbents by using inexpensive and readily available reagents.

Two main approaches can be used for the conversion of cellulose containing materials to biosorbents having the ability to effectively remove heavy metal ions from aqueous solutions. First of the approaches is based on the methods by which macromolecules of cellulose are directly modified leading to the creation of functional groups in its structure, having the ability to participate in chelation or ion exchange with heavy metal ions of aqueous solutions. The other approach is associated with polymer analogous transformations by grafting of certain monomers to the cellulose macromolecules, having direct sorption reactivity towards to heavy metal ions or allowing further functionalization of the grafted polymer chains to form chelating structures.

The first approach includes operations such as delignification, hydrolysis, oxidation, attachment of carboxyl, sulfo-, nitro-, phosphate-, amino-groups, etc. with the use of various reagents: alkali solutions such as sodium, potassium and calcium hydroxides,\textsuperscript{[18, 19]} mineral acids (hydrochloric, nitric, phosphoric, sulfuric),\textsuperscript{[20]} organic acids and acid anhydrides (tartaric, citric, succinic),\textsuperscript{[21, 22]} oxidizing agents (hydrogen peroxide, potassium permanganate, potassium metaperiodate),\textsuperscript{[23, 24]} and organic compounds of different classes (ethylenediamine, formaldehyde, epichlorohydrin, methanol, amino acids, acrylonitrile), reactive dyes (monochlorotriazine types), enzymes and others used in the removal of soluble organic compounds, decolouration of treated water solutions and increasing the effectiveness of metal ions sorption.\textsuperscript{[25]}
Literature review shows that in a vast majority of papers, the Langmuir's model has been used to describe the sorption equilibrium of polysaccharide-based sorbents, due to high correlation coefficient values (0.97 – 0.99), the Freundlich's model, Dubinin-Radushkevich's models and others has been used also. Thus the Langmuir model has been successfully used in processing the isotherms of Cd(II) and Pb(II) ions sorption on grape bagasse,[26] Ni(II) and Cd(II) ions on stems of water hyacinth,[27] Cu(II) и Zn(II) ions on lignocellulose substrate based on wheat bran,[28] Cd(II) ions on coconut shell fibers.[29]

For the description of the experimental isotherms of Cu(II) and Cd(II) ions sorption on rice husk, Demirbas[2] used Langmuir and Freundlich's adsorption models. Review of research on Cr(III) ions[30] also shows that the most frequently used model for processing of heavy metal ions' sorption data are the Langmuir's and Freundlich's models. Isotherms of Th\(^{4+}\) and UO\(_2^{2+}\) ions sorption on chitosan, transversely cross linked by epichlorohydrin, and chitosan/clinoptilolite composite, were processed with three models - Langmuir's, Freundlich's and Sips'.[31] It is noted that the experimental data were more accurately described by the Langmuir's model.

In review,[32] it is noted, that, despite the fact that the Langmuir model does not provide information on the sorption mechanism, it is usually correctly (with a correlation coefficient close to unity) allows to describe the experimental isotherm of heavy metal ions sorption by cellulose biosorbents and to determine the maximum sorption capacity of sorbents.

To determine the peculiarities of the mechanism of metal cations removal from aqueous media as a chemisorptions process, it is particularly important to trace the influence of the components nature of the hetero-phase system (salts, acids, the cellulose functional groups) on the thermodynamics of metal cations sorption process.

In the works[17, 33, 34] hypothetical sorption site structures were used, which now necessitates the need of representing ion exchange mechanism as a chemisorptions process on
cellulosic sorbents, that will involve the computation of the chelate structure of some modeled compounds sorption sites. In the same place of importance and urgency, stands the development of scientific foundations, focusing on the chemical modification and clarification of the specifics involved in sorption of heavy metal cations from aqueous media by natural and modified sorbents.

The aim of this work was to study the peculiarities of the mechanism of the processes of protodesorption and sorption of metal ions Cu(II), Ni(II) and Fe(II) from aqueous solutions by cotton cellulose and its chemically modified samples with acidic sorption sites of different basicity and denticity, having the ability of bonding with cations forming chelate metal complexes and the determination of their structures through the use of computational quantum chemistry on the modeled compounds.

Experimental

Sorption kinetics was investigated by a method of limited solution volume. To obtain the kinetic sorption curves, the samples of a sorbent (m; 0.1 g) were placed into several flasks filled with 10 ml (vol) of aqueous solution of metal sulphate and kept under stirring at 273 K from 5 minutes to 24 hours. The initial concentration ($C_0$) of metal ions was $1.5 \cdot 10^{-4}$ mol $\text{L}^{-1}$. The solution was separated from the sorbent by filtration at definite time intervals; the current concentration of metal ions ($C_\tau$) was determined by atomic absorption spectroscopy (Saturn-2000 apparatus).

To obtain the sorption isotherms, the samples of a 0.1 g sorbent (m) were placed into a series of flasks, and the metal sulphate aqueous solution (10 ml portions by volume) was added into these flasks with initial concentrations ($C_0$) ranging from $1.5 \cdot 10^{-4}$ to $5 \cdot 10^{-2}$ mol $\text{L}^{-1}$. The gasterphase sorbent – water solution of the metal sulphate system was used to achieve the equilibrium state at 273 K. The solution was then separated from the sorbent by filtration.
The equilibrium concentration of metal ions in solution \((C_s)\) was determined by atomic absorption spectroscopy.

The sorption capacity \((A_s)\) of sorbents at any given period was calculated according to the following formula:

\[
A_s = \frac{(C_0 - C_s)}{m} \cdot V
\]  

(1)

After establishing the equilibrium in the system, the equilibrium concentration of metal ions in the solution \((C_s)\) was measured, and equilibrium sorption capacity of sorbents \((A_s)\) was calculated as follows:

\[
A_s = \frac{(C_0 - C_s)}{m} \cdot V
\]  

(2)

Sorption degree \(\alpha\) was determined using equation (3)

\[
\alpha = \frac{C_0 - C_s}{C_0} \cdot 100 \%
\]  

(3)

The pH of solutions was calculated using a pH meter.

The number of carboxyl groups in the original cellulose molecule was determined by a classical method based on the interaction between acid groups and calcium acetate and by titrimetric determination of the acetic acid evolved. Its content per unit mass was taken equal to the value of the carboxyl group acidity [4]:

\[
[-COOH] = V_{NaOH} \cdot C_{NaOH} / g ,
\]  

(4)

where \(V_{NaOH}\) is the volume of NaOH for titration (ml); \(C_{NaOH}\) is the concentration of NaOH solution (mol \(\text{L}^{-1}\)) and \(g\) is the weight of the sorbent.

The content of aldehyde groups in native and oxidized cotton cellulose was determined by iodometric titration.

\[
[-COH] = \frac{14.51 \cdot n \cdot (a - b) \cdot 100}{1000 \cdot q} , \%
\]  

(5)
where \( a \) is the volume of hyposulphite solution for titration in a control experiment (ml); \( b \) is volume of hyposulphite solution for titration in a basic experiment (ml); \( q \) is weight of a cotton cellulose (g); \( n \) is the normality of hyposulphite solution and \( E-\text{COH} (= 14.51) \) is the gram equivalent of aldehyde groups involved in the reaction.

The relative error of the experiments was calculated based on equilibrium and kinetic experiments in which each point represents an average value taken from three parallel experiments. The error in determining the concentration of metal ions using the Saturn-2000 apparatus was 3%, and the experimental error did not exceed 10%.

**Results and discussion**

With the purpose of improving the equilibrium-kinetic characteristics of the sorbent also for the validation of the mechanism of heavy metals sorption from aqueous media, chemical modification was carried out by selectively oxidizing the cotton cellulose with sodium metaperiodate forming dialdehyde cellulose. The periodate ions interact with cellulose without destruction of fibres. The action of sodium metaperiodate on cellulose resulted in the oxidation of two neighbouring alcoholic groups in \( C_2 \) and \( C_3 \) to aldehydes with the simultaneous rupture of the carbon–carbon bond. A dialdehyde cellulose is thus formed.

In this case, however, there is no oxidation of primary alcoholic group.[35]

The condition of selective oxidation of cellulose used, was performed is such a way, that the number of aldehyde groups formed were practically equal to the number of carboxylic groups in the initial cellulose. Further modifications were carried out by the quantitative conversion of aldehyde groups to other acidic types.

1. To hydroxamic acidic groups:

\[
\text{NH}_2\text{OH-HCl} + \text{H}_2\text{O}_2 \\
\rightarrow \text{HOOC(HO)CH-Cell-CH}=\text{O} \rightarrow \text{HOOC(HO)CH-Cell-CH}=\text{NOH} \rightarrow \\
\rightarrow \text{HOOC(HO)CH-Cell-CONHOH};
\]
2. To aldehyde bisulphite acidic groups:

\[ \text{NaHSO}_3 + \{\text{HOOC(HO)CH-Cell-CH=O} \rightarrow \text{HOOC(HO)CH-Cell-HC(OH)SO}_3\text{Na}\} \]

In the aqueous phase, due to the high dielectric constant and sufficiently high donor-acceptor activity of water, surface inactive substances dissociate to ions as a result of electrolytic dissociation. It can be said that the metal cations and protons in the aqueous media exist in the state of hydrated complexes \([M\cdot(H_2O)_n]^{2+}\) and \([H\cdot(H_2O)n]^+\).

Furthermore, the state of the metal cation and proton in the phase of the cellulose sorbent needs to be ascertained from the standpoint of chemical structure theory. Cellulose in the aqueous solution swells and due to electron-donor groups can sorb protons. In such a case the sorbents sorption space in the acid pH range will be filled exponentially, starting from the more active groups -COO\(^-\) with the formation of salt groups (-COO\(_2\))\(_M\) or acidic groups in the form of –COOH, whose structures will be largely dependent on the neighbouring electron donating groups. In cellulose α-hydroxycarboxylic groups –CHOHCOOH or α-alkoxycarboxylic groups –CHORCOOH can act as dentate groups in the formation of chelate five-membered H- and metal complexes of monobasic, bidentate type \((N = 1, n = 2)\).

The conjugation effect of carbonyl (>C=O) and N-hydroxyamide (-NH–OH) groups of the hydroxamic acid group (-CONHOH) gives it an acidic property comparable to that of carboxylic acids. Supposing that the proton of hydroxyl is more acidic, and the oxygen of carbonyl takes part in the formation of dentate bonds. However it is still not clear which of the protons in N-hydroxyamide groups is more acidic and which of the oxygen in (-CONHOH) groups is more susceptible to dentate bond formation with electron accepting agents (cations \(M^{2+}\) or protons \(H^+\)). However such an acidic group as –CONHOH should have the properties of a monobasic \((N = 1)\), bidentate \((n = 2)\), with the tendency of forming a five-membered chelate of H- and metal complexes.

The resemblance of sorption sites structures of the modified cellulose, proffers a
similar character to the α-hydroxylcarboxylic (-CHOHCOOH, \(N = 1, n = 2\)) and N-hydroxycarbamide (-CONHOH, \(N = 1, n = 2\)) groups during interfacial ion exchange interactions with \(2H^+\) and \(M^{2+}\), while the characters of hydroxamic (-CONHOH, \(N = 1, n = 2\)) and hydroxymethylsulphonic (-CHOH-O_2O^-, \(N = 2, n = 2\)) would be different.

In this work cellulose samples with the following sorption sites were used:

(I) An unmodified one containing α-hydroxylcarboxylic acid groups:
\[\text{HOOC(HO)CH]}\text{-Cell;}\]

(II) A modified one containing α-hydroxylcarboxylic and hydroxamic acid groups:
\[\text{HOOC(HO)CH]}\text{-Cell-[CONHOH];}\]

(III) A modified one containing α-hydroxylcarboxylic and aldehyde bisulphite acid groups: \([\text{OOC(HO)CH]}\text{-Cell-CH(OH)SO}_3\text{Na}.\]

The above samples were used in receiving sorption isotherms of copper, iron and nickel ions from the aqueous solutions of their sulphate salts at pH 6 (Fig. 1-3).

Earlier\(^{[17]}\) it was shown experimentally, that sulphate- anions from acidic aqueous solutions are not sorbed by cellulose sorbents, which allows to view the sorbents as cation exchanging gel sorbents.

In cellulose sorbents, the anion forms of acidic carboxylic functional groups bond with cations as salts, forming carboxylates in the acidic pH region: pH = \(pK_{a-\text{cooh}} \pm 2\), this gives the ability to study \(M^{2+}/2H^+\) and \(M^{2+}/2Na^+\) ion exchange in the acidic region (pH 2-6).

The thermodynamics of interfacial metal cation exchange is usually viewed in a context of mechanism without the participation of anions in the process, with the assumption that the multiplier of the activity coefficients of cations in the phases equals to unit.

**Scheme I.** Ion exchange of metal cations \(M^{2+}/2Na^+\)

\[M^{2+} + \{\text{Cell-(CHOH-COONa)}_2 \leftrightarrow \text{Cell-(CHOH-COO)}_2M\} + 2Na^+\]

Ion exchange \(M^{2+}/2H^+\)
From the study of protodesorption mechanism\cite{33} it was shown, that cations can not pass through the interfacial border without their anionic carriers, therefore the interpretation of the mechanism of protodesorption in the form of purely ion exchange (Scheme I) can not be substantiated with experiment.

Thus it was offered mechanism of ion-molecular type, with the participation of cations and their anionic carriers as salts or acidic molecular forms of the independent components in the heterophase system (aqueous solution of salts and acids - cellulose sorbent) with electroneutrality of the phases. It can be viewed in the scheme II.\cite{33}

Scheme II. \[\text{MSO}_4 + \{\text{Cell-(CHOH-COOH)}_2 \leftrightarrow \text{Cell-(CHOH-COO)}_2 \text{M}\} + \text{H}_2\text{SO}_4\]

\[---\uparrow\downarrow\text{K=1}---\quad \text{K = K}_{\text{salt2so24}}---\uparrow\downarrow---\]

\[\text{M}^{2+} + \text{SO}_4^{2-} \quad 2\text{H}^+ + \text{SO}_4^{2-}\]

\[\text{MCl}_2 + \{\text{Cell-(CHOH-COOH)}_2 \leftrightarrow \text{Cell-(CHOH-COO)}_2 \text{M}\} + 2\text{HCl}\]

\[---\uparrow\downarrow---\text{K=1}---\quad \text{K = K}_{\text{saltel}}---\uparrow\downarrow---\]

\[\text{M}^{2+} + 2\text{Cl}^- \quad 2\text{H}^+ + 2\text{Cl}^-\]

The justification of ion-molecular mechanism has been made from the point of view of Gibbs phase rule applied to the system of DoF (Degree of Freedom) = 1: four components (water, acid, salt, cellulose), with 2 independent components (K = 2: water and acid) connected together through concentration, two phases (P = 2: aqueous solution - cellulose sorbent), and with only one variable parameter (n = 1) – acid concentration, constant parameters of the system are - temperature, pressure, salt concentration (interface indicator), module (sorbent/solution). Such a system is (F = K + P + n = 2 – 2 + 1 = 1) monovariant. The values of other parameters in the system will depend on the acid concentration.

Schemes I and II are alternatives to the sorption mechanism and they are mutually
exclusive in occurrence. To proof, which one of them is substantiated through experiment (purely ion exchange $M^{2+}/2H^+$ by scheme I or ion exchange with the participation of acidic and salt components in their molecular forms $\text{MSO}_4/H_2\text{SO}_4$ or $\text{MCl}_2/2\text{HCl}$ by scheme II), we need to determine the degree of hydrogen ion participation in the reaction of protodesorption of cations for the multicomponent, monovariant, heterophase system.

In scheme I (the ion exchange $M^{2+}/2H^+$) the indicator of the degree of proton participation is supposed to be 2. In scheme II (the ion exchange $\text{MSO}_4/H_2\text{SO}_4$) the indicator of the degree of sulphuric acid participation should be 1, and proton ½. In the ion exchange with $\text{MCl}_2/2\text{HCl}$ participation it should be 2, and proton ¼.\textsuperscript{[17, 33]}

For checking the correlation of sorption sites structure specifics with the sorption of d-metal cations from the two-phase system “aqueous solution of salts - cellulose sorbent”, the sorption isotherms received at pH 6 (Fig. 1-3) were used, where all the acidic functional groups of the cellulose sorbents taking part in the sorption at their first stage of dissociation, were in the active anion-salt state (-CHOHCOO$^-$, -CONHO$^-$, -CHOHSO$_2$O$^-$), while the metal cations in the aqueous phase were in the thermodynamically stable hydrated state of $M(H_2O)_n$$^{2+}$. This allows to write down the process of filling of the sorbents anionic sorption sites in the region of saturation:

a) For the one-staged dissociation type of the monobasic bidentate functional groups

$$\text{MSO}_4 + \{\text{Cell}[-(\text{CHOHCOONa})_2]\leftrightarrow\text{Cell}[(\text{CHOHCOO})_2\text{M}]\} + \text{Na}_2\text{SO}_4 \quad \text{(stage I)}$$

$$\text{MSO}_4^+ + \{\text{Cell}[-(\text{CONHONa})_2]\leftrightarrow\text{Cell}[-(\text{CONHO})_2\text{M}]\} + \text{Na}_2\text{SO}_4 \quad \text{(stage I)}$$

b) For the dibasic groups of a two-staged dissociation type.

$$\text{MSO}_4 + \{\text{Cell}[\text{HCOHSO}_2\text{ONa})_2\] ↔ $\text{Cell}[(\text{HCOHSO}_2\text{O})_2\text{M}]\} + \text{Na}_2\text{SO}_4 \quad \text{(stage I)}$$

$$\text{MSO}_4^+ + \{\text{Cell}[(\text{HCOHSO}_2\text{O})_2\text{M}] ↔ $\text{Cell}[(\text{HCOSO}_2\text{O})\text{M}]_2\} + \text{H}_2\text{SO}_4 \quad \text{(stage II)}.$$

The amount of the cellulose $\alpha$-hydroxylcarboxylic groups (monobasic bidentate) is practically equal for modified samples, so such characters of isotherms result solely from the
difference apparent in the sorption sites nature of the samples: hydroxamic groups (monobasic bidentate) - sample 2; aldehyde bisulphite groups (dibasic bidentate) – sample 3.

Fig. 1.

Differences in the nature of the acid groups of the sorbents have allowed to reveal the mechanism peculiarities of cations $M^{2+}$ chemisorption with their participation in the initial (Henry's region) and ending (saturation region) sections of the isotherms helping in recording the dependence of sorption on chemical structures of sorption sites.\[17\]

1) Isotherm section of the Henry's region. At the initial linear segment of the sorption isotherm heavy metal ions sorption must occur proportionally with respect to the number of sorption sites ($C_{ss}$) and the bond strength of the d-metal cations attached to it. The later will be proportional to the denticity of the ligand $n'_D$ – number of coordinate bonds of cation - sorption site. In such a case, the sorption ($A$) must be described with a relationship, in which the Henry's constant $K_H$ will be proportional to the product of the number of sorption sites and their denticity: $C_{ss} n'_D$ for all the sorbents sorption site (finite discrete integral $\sum$). Based on the sorption sites structures one can say the denticity of $\alpha$-hydroxylcarboxyl group equals two, $n'_D = 2$, (bidentate, monobasic), for hydroxamic group - $n'_D = 2$ (bidentate, monobasic), and for the aldehyde bisulphite group, for the first filling stage - $n'_D = 1$ (monodentate, monobasic).

$$A_{ini} = K_H C_s = \alpha (\sum C_{ss} n'_D) C_s = tg\alpha C_s$$
where $\alpha$ is a proportionality coefficient, $C_s$ is the concentration of metal cations in aqueous solution, $C_{ss}$ is the concentration of sorbent sorption sites, $K_H$ is the Henry's constant.

In such a case the calculated tangents of the slope angles $\alpha \cdot (\sum C_{ss} \cdot n'_1)$ for the initial linear sections of sorption isotherms characterize Henry's law constants for each of the three type of samples. These relationships are observed from experiment and computed data (Fig. 1-3), with the condition, that the number of each sample sorption sites is practically equal, but with variations in their denticities at the first sorption stage:

$$(K_{III})/(K_{III}) = (\alpha \sum C_{ss} \cdot n'_1) : (\alpha \sum C_{ss} \cdot n'_2) : (\alpha \sum C_{ss} \cdot n'_3) \approx (2+2):(2+1):(2) \approx (2):(1,5):(1).$$
In this case the tangents of the slope angles follow the sequence \( \text{tg} \alpha_I > \text{tg} \alpha_{III} > \text{tg} \alpha_I \) (Fig. 1-3) and the calculated quantities of Henry's constants follow suit as \((K_{III}) > (K_{II}) > (K_{I})\), showing that they correlate well enough.

With the stage-wise filling mechanism observed in the initial linear section (Henry's region), the sorption isotherm of sorbent (II) lies above that of sorbent (III) due to the fact that \( n'_{DII} > n'_{DIII} \) for the first stage.

2) Isotherm section of the saturation region. This is the final, almost linear isotherm section (saturation region), in which all the sorption sites almost completely filled out. In this case, the total sorption \( A_\infty \) of each sorbent sample will be determined by the maximum sorption value in all their steps of filling, so it should be proportional to number \( (C_{ss}) \) of sorption sites and their basicities \( (N_B) \) for all sites \( (\Sigma) \):

\[
A_\infty = \alpha (\Sigma C_{ss} N_B).
\]

The modified sorbents contain \( \alpha \)-hydroxylcarboxylic groups \( (C_{ss}, N_{BI} = 1, n_1 = 2, \text{Cell-CHOH-COO}^-) \) in combination with an equal amount of immobilized sites having different basicities: hydroxamic acid \( (C_{ss}, N_{BII} = 1, n_II = 2, \text{Cell-CONHO}^-) \) and aldehyde - bisulphite groups \( (C_{ss}, N_{BIII} = 2, n_{III} = 2, \text{Cell-HCOHSO}_2\text{O}^-) \). The isotherm of sorbent (III) lies higher than that of sorbent (II), \( A_\infty_{III} > A_\infty_{II} \) (Fig. 2, 3). As a result the isotherms for all the cations will intersect which matches the experimental and estimated results. The ratio of estimated maximum sorption values \( A_\infty \) for the three samples with an equal number of sorption sites but with different basicities \( (N_1 = 1, N_{II} = 1, N_{III} = 2) \) should follow this sequence:

\[
A_{\infty I}:A_{\infty II}:A_{\infty III} \approx (\alpha C_{ss} N_{B1}) : (\alpha C_{ss} N_{B1} + \alpha C_{ss} N_{B2}) : (\alpha C_{ss} N_{B1} + \alpha C_{ss} N_{B3}) \approx 1 : 2 : 3.
\]

This is in good agreement with the experimental \( A_{\infty I}:A_{\infty II}:A_{\infty III} = 0.4:0.8:1.2 \) (Fig. 1-3) and estimated values of the limiting sorption received from the Langmuir's model. \( A_{\infty I}:A_{\infty II}:A_{\infty III} = 0.53:0.92:1.52 \).
3) Sorption isotherms of the sorbents with the similar nature. Samples of sorbents I and II have the similar nature (n_{DI} = 2, N_{BI} = 1 for α-hydroxycarboxyl and n_{DII} = 2, N_{BII} = 1 for hydroxamic groups) but different in their sorption site amounts C_{ssl} \approx C_{ss} for sorbent I and C_{ssl} + C_{ssII} \approx 2C_{ss} for sorbent II. In such a case, with K_{LI} \approx K_{LII} from the Langmuir's model which is fair approximation for the same and equivalent sorption sites, we can expect them to have comparable values of tangents of the slope angles \( \tan \alpha_1 : \tan \alpha_2 \approx (K_{HI}) : (K_{HII}) \approx 1:2 \) for the initial section of their isotherms and for their limiting sorption values \( \tan \alpha_1 : \tan \alpha_2 \approx (K_{LI} \cdot A_{\infty I}) : (K_{LII} \cdot A_{\infty II}) \approx A_{\infty I} : A_{\infty II} \approx 1:2 \), which correspond to that of experiments (Fig. 1-2).

Samples I and II have the same mechanism of sorption, because they are of the same denticity and the same basicity of sorption sites, both for the initial, middle and final sections of their isotherms.

4) Sorption isotherms of the sorbents with the different nature. For samples II and III, sorption isotherms are convex, different in forms and intersecting with each other (\( A_{\infty II} < A_{\infty III} \), \( A_{\infty II} > A_{\infty III} \)), having differences in their mechanisms of filling for the initial (denticities dominate: that is the bond strength with cations), middle and final section of sorption isotherms (basicity of sorption sites is the dominating factor, that is the number of bonds to each adsorbed cation). In such a case, the ratio of denticity to basicity of the available sorption sites at the initial segment will favour the hydroxamic site (\( n/N = 2/1 \)), while the final isotherm segment will favour aldehyde bisulphite sites (\( N/n = 2/1 \)). It is evident that their isotherms will intersect, because of these differences in their sorption sites.

Despite a significant difference in basicities and denticities of the sorption sites of samples II and III, description of intersecting isotherms involving the law of mass action (Langmuir's model) gives reliable results of the maximum sorption values. They are proportional to the basicity of sorption sites (\( N_{BI} = 1, N_{BII} = 1, N_{BIII} = 2 \)) for samples with equal sorption site amounts (C_{ss}).
The estimated (calculated) data based on the number and structure (denticity and basicity) of sorption sites and experimental data obtained by processing of isotherms of metal ions (Cu^{2+}, Fe^{2+}, Ni^{2+}) sorption are in good agreement with each other: \((A_{\infty II}):(A_{\infty III}) \approx 2:3\) (estimated) \((0,92):(1,52)\) (Langmuir's model). While the values of the constants \(K_L\) obtained for samples II and III are significantly different \((K_{LII} = 279) > (K_{LIII} = 83)\). With the same amount of sorption sites and different denticity \((n''_II = 2\) and \(n''_III = 1\) for the initial section of isotherm) and basicity of sorption sites \((N_{BII} = 1\) and \(N_{BIII} = 2\)), these differences in the constants suggests great influence of the nature of functional groups on the shape of the sorption isotherms.

The shape of the initial section of the isotherm \((t g\alpha = K_H)\) is determined by the metal cation binding strength, and the more adsorption centers number and their denticity, the greater the tangent of slope angle of the initial section of the isotherm (the higher the Henry's constant \(K_H\)), the contribution of the basicity of sorption sites (the degree of sites filling) thus negligible.

Maximum sorption value is achieved at the final section of the isotherm (saturation region) and is determined by the amount and and basicities of the available sorption sites. In this region the role of their denticities (bond strength) will be negligible. In this region the role of their denticities (bond strength) will be negligible. The quantitative characteristics of initial and final sections of the sorption isotherms, reflect the specifics associated with the nature, structure and characteristics of sorption sites structures.

The values of the maximum sorption for all sorbents with different sorption sites follow this relationship \(A_{\infty II} < A_{\infty III}\) while reversed to that of Langmuir's constants \(K_{LII} > K_{LIII}\). Differences in sorption sites of a particular sorbent is highly cited as an argument against the applicability of the Langmuir's model for explaining the sorption processes.
The limitations of the Langmuir's model are valid for weak interactions at sorption like universal solvation or quasi chemisorptions of nonpolar substances. In a case of distribution of particles between phases (ion exchange) with strong (specific) interactions in the phases, the Langmuir's model will correspond to the law of mass action in this case. With the correlation coefficient close to unity, this shows the good applicability of the Langmuir's model to explaining ion exchange processes on sorbents, both for similar or different sorption sites types.

The posed interpretation for the sorption mechanism for the similar sorption site types (I, II) and the different site types (II, III) of sorbent samples is fully consistent with thermodynamics of reversible processes, whereby the sorption of ions and ion exchange can be considered as a variety of chemical processes occurring between the components of the heterophase system with the participation of the sorbent's active groups in these processes.

Such approach to elucidation of the mechanism of chemisorptions of metal cations $M^{2+}$ from aqueous media by cellulose sorbents, based on knowledge of the nature, quantity and structure of the sorption sites and the solvation of ions in the phases allows to identify the causes of noncompliance or compliance involved in the description of sorption isotherms through various theories of sorption and to determine the limits of their application, especially for the models most frequently used for explaining the sorption of metal cations from aqueous media.

Sorption equilibrium depends on the nature both of sorbate and phases. Phases and their constituent components act as reagents that quantitatively and qualitatively affect the solvated-complexes of cations in the phases of sorption sites.

The salts of Cu(II), Fe(II) and Ni(II) sulphates are strong electrolytes, in water they are in the form of hydrated ions. In the solid phase of the sorbent, they are in the coordinated – salt forms bonded to the anionic sites of the sorbent. Such solvated complexes in the phases
differ in energy and structure. That is reflected on their salts solubility in the aqueous phase
and on the distribution of cations in the hetero-phase system “aqueous solutions of salts -
cellulose sorbent”.

In aqueous solutions of metal sulfates with higher solubilities, the cations are largely
hydrated and, as a consequence, it will be more difficult to sorb them. The series of salt
solubility and sorption of the cations are inversely related.

These allows to interpret the mechanism of the processes of metal cations sorption
from aqueous media by natural and modified cellulose as a conjugated and equivalent ion
exchange process, with the acidic groups acting as sorption sites, forming coloured and
colourless chelate metal complexes with Cu\(^{2+}\), Fe\(^{2+}\), Ni\(^{2+}\):

In the α-hydroxylcarboxyl groups:

\[
\text{MSO}_4 + \{\text{Cell-(CHOH-COOH)}\}_2 \leftrightarrow \text{Cell-[(CHOH-COO)}_2\text{M}\} + \text{H}_2\text{SO}_4
\]

colourless colourless

In the hydroxamic groups:

\[
\text{MSO}_4 + \{\text{Cell-(CO-NH-OH)}\}_2 \leftrightarrow \text{Cell-[(COH=N-O)}_2\text{M}\} + \text{H}_2\text{SO}_4
\]

colourless coloured

Colours of the complexes are reddish-brown with iron(II) and green with copper(II).

In the aldehyde-bisulphite groups (substitution in I and II dissociation steps):

\[
\text{MSO}_4 + \{\text{Cell-(CHOH-SO}_3\text{Na)}\}_2 \leftrightarrow \text{Cell-[(CHOH-SO}_3\text{)}_2\text{M}\} + \text{Na}_2\text{SO}_4
\]

\[
\text{MSO}_4 + \{\text{Cell-[(CHOH-SO}_3\text{)}_2\text{M}\} \leftrightarrow \text{Cell-[(CHO-SO}_3\text{)}_2\text{M}\} + \text{H}_2\text{SO}_4
\]

colourless colourless

The sorbent with hydroxamic groups forms coloured complexes of the chelate type
with d-metal ions Cell-[(COH=N-O)}_2\text{M}. The colour appears as a result of the formation of
five-membered chelate rings, with the ring atoms forming a complex due to the charge
transfer during metal–ligand interactions with the participation of a \(\pi\)-conjugated system
between key atoms of the ligand and d-atomic orbitals of the metal ions. Sorption of metal ions by cellulose on the α-hydroxylcarboxyl and aldehyde-bisulphite groups was not accompanied by a colour change of the sorbent. Colourless chelate charge-transfering complexes are formed in the absence of conjugation in the systems between the key atoms (O) of the ligand, due to the presence of (>CH–) in the chain as in the case of α-hydroxylcarboxylic (HO-C'H-COO–) and aldehyde-bisulphite (HO-C'H-SO\textsubscript{2}O–) groups.

Since the difference in denticity, basicity and the amount of sorption sites of sorbents has a different and significant impact on the initial section (region of Henry's law) and maximum (saturation region) of the sorption isotherms (Fig. 1-3), this allows to perform targeted modifications of cellulosic materials used for various purposes and in various technologies for the removal of heavy metals from aqueous media both for the static and the dynamic conditions.

Sorbents with polydentate, monobasic sorption sites are more efficient when removing the d-metal cations from dilute aqueous solutions and sorbents with the same amount as above, but with polybasic sorption sites will be more effective for sorption of d-metals cations from concentrated aqueous solutions.

Computational quantum chemistry modeling method was performed on some modeled compounds having functional groups of the same type as that of the used sample sorbents: 2-hydroxyethanoic acid, N-hydroxylacetamide and sodium ethanalbisulphite.

The quantum chemistry computation were performed using the DFT method with the B3LYP method of Hybrid Functional Theory with the 6-31+G(d, p) basis sets with the help of the software package Firefly 8.1.0 with full optimization of the geometric parameters and the verification of the conformity of the found minima of the potential energy surface by critical conditions. Preparing of the input data, and the processing and visualization of results were performed with help of the software ChemCraft.
The fragment of the carboxylic acid with the hydroxyl group in α-position is an almost planar cyclic five-membered chelate H-complex in which the proton of the carboxyl group is linked to the oxygen of the alcohol group by an intramolecular hydrogen bond. This type of configuration is more polar than other configurations. It helps to strengthen the acidic properties of such fragments.

Following the above statement; the carboxylic group in the polysaccharides which also has electronegative groups (HO- hydroxyl and RO- alkoxy) in the α-position is supposed to support the cyclic five-membered H-chelate structure and increased acidity (pKₐ-CHOHCOOH ≈ 4). It is advisable to present such structures with reflection of the nature of the neighbouring groups participating in the formation of the dentate bonds of H- or metal complexes type in the form of a Cell-(CHOH-COOH) or as shown on the modeled compound CH₃-CHOH-COOH.

Conformational structure of propene-1-triol-1,1,2 is a tautomer of lactic acid, H- chelated form of which has two flat cycles (five-membered and four-membered).

Usually compounds with a hydroxyl group at double bond or with two hydroxyls at one carbon atom are very unstable and immediately reform to the carbonyl structures, while the hydrogen atoms in the α-position retain their predisposition to the keto-enol tautomerism.

\[
\text{Cell-[CHOH-COOH]} \leftrightarrow \text{Cell-[COH=C(OH)₂]}
\]

Mobile hydrogen atoms of cyclic chelate form 2 intramolecular bonds giving some amount of stability to the enol structure. However, judging from the total energy of the isomers such tautomeric entriol structure is less stable than the structure of the lactic acid fragment. Thus the structure of cellulose sorbents sorption sites is the chelated structure of α-hydroxycarboxylic acids fragment.
In N-hydroxyacetamide, the hydrogen at the amide nitrogen atom is mobile, which allows it to be involved in keto-enol tautomerization with the formation of the enol structure in the form of alkanoloxime.

\[ R-[\text{CO-NH-OH}] \leftrightarrow R-\text{COH=N-OH} \]

Both tautomers have the cyclic five-membered H-chelate form, which are stabilized by intermolecular hydrogen bonds. Judging from \( E_{tot} \), the structure of N-hydroxyacetamide is somewhat more stable than the acetoxime structure, the hydrogen of such stable acidic group have a more high positive charge of (0.386 and 0.359, respectively). Thus hydroxamic functional groups of the modified cellulose are in the form of five-membered chelate structure (Cell-(CO-NH-OH)).

The most stable of tautomeric and conformational structures of the anionic hydroxamic acid group, is structure (1). Relative energies, \( E_{rel} \), of tautomers 1 and 4 are very close. This allows the thermodynamics of dissociation of the most stable form of hydroxamic acid to be modeled on the modeled compound (\( R^- = \text{CH}_3^- \)) in the chelate form:

\[
\{R-(\text{CO-NH-OH})_{\text{cis}} \leftrightarrow R-(\text{COH=N-OH})_{\text{cis}}\} \leftrightarrow R-(\text{CO}^-\text{N-OH})_{\text{cis}} + \text{H}^+ 
\]

The “acid” hydrogen bonded to the nitrogen atom of the amide fragment is the one that take part in the acidic dissociation of the hydroxamic acid groups (-CO-NH-OH), whose acidic properties are strengthened by the electron accepting inductive influence from the neighbouring hydroxyl group and also the shifting of electrons of \( \sigma- \) and \( \pi- \) bonds from nitrogen to the carbonyl oxygen. This unusual type of acid dissociation through the tautomeric acid forms (1) and (4) to the anionic form (1’) is due to the fact that it preserves the heterocyclic five-membered chelate form, which is stabilized by intermolecular hydrogen bond.
The chelate metal complex on the modeled compound (Cell\(\ldots\) = CH\(_3\)).

The formation of chelate metal complexes is also accompanied by the substitution of proton of the hydroxyl of (>N-OH group) by cation of the most stable chelate H-form (1) with the simultaneous transfer of the proton from nitrogen to the carbonyl oxygen, keeping the form of the cyclic five-membered chelate structure unchanged:

\[
M^{2+} + \{\text{Cell-}(\text{CO-NH-OH})_{2}\text{cis}\} \leftrightarrow \text{Cell-}[-(\text{COH}=\text{N-O}^-)_{2}M^{2+}]_{\text{cis}} + 2\text{H}^+.
\]

The transfer of cations from one phase to another occurs together with their anions at the electroneutrality of phases, in a form of the equivalent exchange of charged particles. In this case, the acetalaldehyde bisulphite – anion can exist in the sorbent phase only with oppositely charged ions in the form of sodium acetalaldehyde bisulphite. The structure of such anionic form and the form of its sodium salt are similar.

The mechanism of thermodynamics of interfacial transfer of cations as electroneutral salt or acidic components in the heterophase system (scheme II), permits the passage of the process of ion exchange with unstable intermediates. In the first and second dissociation stages, with the participation of its dibasic sorption sites in the aldehydebisulphite group complete substitution takes place of, firstly; Na\(^+\), and later H\(^+\) and their subsequent removal in conjugation with sulphate ions to the aqueous phase. While in the organic phase the neutral chelate metal complex of copper(II) in the ratio of 1:2 (in the first stage of substitution) and 1:1 (in the second stage) is formed based on coordination bond type, whose structure in the modeled compounds are of the type:
It should be noted, that the sorption of ions on the aldehyde bisulphite sorption sites always leads to the formation of chelate metal complexes both at the first stage (initial section of isotherm) and the second stage of substitution (final section of the isotherm). During the first stage of substitution $\text{M}^{2+}$ ions form a practically planar complex with four-membered chelate cycles and a coordination number of 4, in which all the four coordinate bonds are practically equal. Since the hydroxyl group of aldehydebisulphite anion having a lower electron donating capacity relative to water, doesn't take part in the coordination bond with copper. In the second stage of sorption, copper ion forms a neutral, chelate and polar complex with coordination number of 2 of a practically planar five-membered cycle.

**CONCLUSIONS**

Sorption isotherms of d-metal cations are accurately described with active masses law. In the process of sorption, the functional groups are independent sorption sites, their filling being in accordance with their amount, basicity, dentate and the ability to dissociate. Ratios of values of maximum adsorption capacities and Henry's constants are in good agreement with the amount and basicity of the same type and different types of functional groups for the cellulose samples investigated, which allows to predict the relative shapes of the isotherms and sorption capabilities of sorbents.

The chelate structures with H- and metal complexes on acidic sorption sites were computed with the methods of quantum chemistry on modeled compounds, by adhering to chemistry's best practices.

Hydroxamic groups form coloured chelate metal complexes $\text{Cell} - [(\text{COH=N-O-M})_2]$ with $\text{Cu}^{2+}$, $\text{Fe}^{2+}$, $\text{Ni}^{2+}$ cations. The colouration results from $\pi$-conjugation between key atoms of oxygen in the four-atoms chain, during complex formation with charges transfer.

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References


URI: http://www.lib.ncsu.edu/resolver/1840.2/2621


http://dx.doi.org/10.1016/j.jhazmat.2008.01.024


http://www.academicjournals.org/article/article1380188016_Kumar.pdf


http://dx.doi.org/10.1016/j.pce.2011.03.006


http://dx.doi.org/10.1016/j.jenvman.2007.01.005


http://dx.doi.org/10.1016/j.biortech.2007.11.064


doi:10.1016/S1003-6326(14)63137-X


http://dx.doi.org/10.1016/j.jhazmat.2007.05.065


http://dx.doi.org/10.1016/j.biortech.2005.11.018


12. Nikiforova, T.E.; Kozlov, V.A. Protection of Metals and Physical Chemistry of Surfaces,


  http://dx.doi.org/10.1016/j.jhazmat.2009.11.081

  http://dx.doi.org/10.1016/j.biortech.2006.07.043

  http://dx.doi.org/10.1021/ie301156y

  http://dx.doi.org/10.1007/s10311-006-0051-4

  http://dx.doi.org/10.1016/j.biortech.2008.08.051

  http://dx.doi.org/10.1016/j.jhazmat.2010.04.060

  http://dx.doi.org/10.1016/j.jhazmat.2010.09.053

  http://dx.doi.org/10.1016/j.biortech.2010.02.030

  http://dx.doi.org/10.1134/S2070205115040206

  http://dx.doi.org/10.1134/S207020511206007X

Table 1

Parameters of the Adsorption Isotherms Calculated using the Langmuir Equation

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Cation</th>
<th>1/(A∞⋅K), 10^3</th>
<th>1/A∞</th>
<th>R</th>
<th>A∞, mol⋅kg(^{-1})</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I) Initial</td>
<td>Cu(^{2+})</td>
<td>8,59±0,74</td>
<td>1,81±0,03</td>
<td>0,99</td>
<td>0,55</td>
<td>210</td>
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<tr>
<td></td>
<td>Fe(^{2+})</td>
<td>8,98±0,66</td>
<td>1,87±0,03</td>
<td>0,99</td>
<td>0,53</td>
<td>189</td>
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<tr>
<td></td>
<td>Ni(^{2+})</td>
<td>9,89±0,95</td>
<td>1,99±0,04</td>
<td>0,99</td>
<td>0,50</td>
<td>201</td>
</tr>
<tr>
<td>(II) Modified sample</td>
<td>Cu(^{2+})</td>
<td>3,85±1,54</td>
<td>1,04±0,09</td>
<td>0,98</td>
<td>0,96</td>
<td>270</td>
</tr>
<tr>
<td>containing hydroxamic groups</td>
<td>Fe(^{2+})</td>
<td>3,91±0,83</td>
<td>1,09±0,04</td>
<td>0,99</td>
<td>0,92</td>
<td>279</td>
</tr>
<tr>
<td></td>
<td>Ni(^{2+})</td>
<td>3,98±1,22</td>
<td>1,12±0,06</td>
<td>0,99</td>
<td>0,89</td>
<td>281</td>
</tr>
<tr>
<td>(III) Modified sample</td>
<td>Cu(^{2+})</td>
<td>5,99±1,51</td>
<td>0,59±0,07</td>
<td>0,98</td>
<td>1,69</td>
<td>98</td>
</tr>
<tr>
<td>containing aldehyde-bisulphite groups</td>
<td>Fe(^{2+})</td>
<td>7,95±1,38</td>
<td>0,66±0,05</td>
<td>0,99</td>
<td>1,52</td>
<td>83</td>
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<td></td>
<td>Ni(^{2+})</td>
<td>15,86±2,50</td>
<td>0,68±0,07</td>
<td>0,97</td>
<td>1,47</td>
<td>43</td>
</tr>
</tbody>
</table>
Figure captions

Fig. 1. Sorption isotherms of Cu$^{2+}$ (1), Fe$^{2+}$ (2), Ni$^{2+}$ (3) ions by unmodified cellulose

Fig. 2. Sorption isotherms of Cu$^{2+}$ (1), Fe$^{2+}$ (2), Ni$^{2+}$ (3) ions by samples of cellulose containing hydroxamic acid groups

Fig. 3. Sorption isotherms of Cu$^{2+}$ (1), Fe$^{2+}$ (2), Ni$^{2+}$ (3) ions by samples of cellulose containing aldehyde–bisulphite groups