



REGULARITIES AND MECHANISM OF HEAVY METAL CATIONS SORPTION/PROTON-DESORPTION BY CHITOSAN FROM WATER SOLUTIONS

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**REGULARITIES AND MECHANISM OF HEAVY METAL CATIONS
SORPTION/PROTON-DESORPTION BY CHITOSAN FROM WATER SOLUTIONS**

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HIGHLIGHTS

1. Protons deactivate amino groups of chitosan by transferring to inactive H-salt form.
2. M^{2+} and $2H^+$ cations with their anions form metal- and H- complexes on amino groups.
3. pH effect on distribution of M^{2+} ions in heterophase system was studied.
4. The composition of metal complexes with amino groups of chitosan was established.
5. The structure of the complexes was confirmed by quantum chemistry methods.

Abstract

The sorption process of heavy metal ions from aqueous solutions using chitosan flakes and chitosan beads was studied. Chitosan gel beads were prepared using covalent cross-linking of chitosan chains by epichlorohydrin with the following ionic gelation by sodium tripolyphosphate. The capability of chitosan beads to absorb the heavy metal ions from aqueous solutions was studied and physicochemical characteristics of the sorbent were evaluated using SEM and FT-IR methods on model solutions treatment. It was found that competitive proton sorption takes place in acid media what has as consequence a transformation of amino groups into inactive ammonium-salt form and decreases in heavy metals sorption onto chitosan from aqueous-acid media. Batch adsorption experiments were performed to examine influence of various factors like the effects of metal salts initial concentration, pH, and agitation duration on the process. It was established that metal ion sorption is pH dependent and has an optimum effect at pH 6.0. Following Langmuir equation, maximum sorption of Cu^{2+} ions is estimated to be 1,6 mole/kg of modified chitosan. The kinetic study revealed that the adsorption kinetics is well-fitted to the kinetic equation of pseudo-second-order. Thereby a sorption of heavy metal ions by chitosan is considered to be a competitive process which occurs on amino groups of the sorbent with equivalent coordinated participation of metal cations, protons and anions.

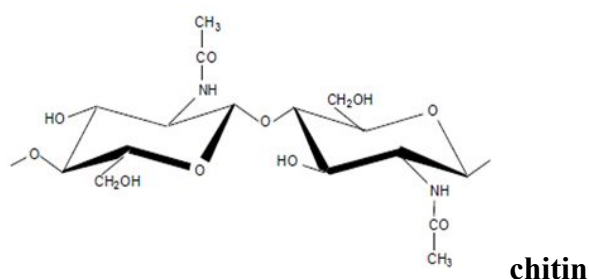
Key words: chitosan, sorption, proton-desorption, copper ions.

1. Introduction

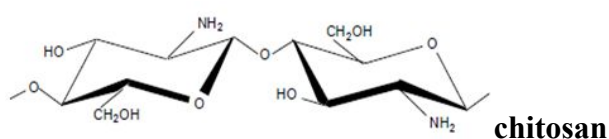
Intensive industrial exposure on the environment led to its significant pollution by heavy metals,¹ which don't decompose and tend to accumulate. They are involved in the biological cycle of substances for long time and can be transported by water currents over long distances.²

The development of inexpensive and accessible sorbents of polysaccharide or protein nature based on multi-tonnage by-products or agricultural waste of textile, pulp and paper and food industries is an important task now.³⁻⁵ These materials are available, environmentally friendly, convenient to use, inexpensive, possess a high sorption characteristics for a wide range of metal pollutants.⁶⁻⁷ To increase the sorption capacity, they are modified by various methods.⁸⁻¹⁰

Particular attention should be paid to the waste generated in huge amounts during the processing of oceanic crustaceans (crabs, shrimp, Antarctic krill), one of the important components of which is chitin, the second (after cellulose) widespread polysaccharide in nature:



Chitin has a relatively low capacity towards to heavy metals,¹¹ but its structure creates prerequisites for the successful application of its derivatives in a wide variety of fields, including medicine, pharmaceuticals, food and innovative technologies.¹² One of such derivatives is chitosan, a linear amino polysaccharide, which is formed during the deacetylation of chitin. The physical and chemical properties of chitosan are described in sufficient details.^{13, 14}



Chitosan (CS) is low cost renewable natural polymer and has perfect hydrophilicity, biocompatibility, biodegradability, non-toxicity and active for adsorb toxic metals and organic compounds.¹⁵ The presence of amino and hydroxyl groups in chitosan structure give it ability for adsorb metal ions which work as many active sites. Recently, hybrid materials based on chitosan have been developed for heavy metals removal, including polymers, metal and metal oxide nanoparticles, which give excellent synergistic effects together.¹⁶⁻¹⁸

Chitosan is quite affordable, biosafety and promising polymer for the development of new types of sorbents.¹⁹⁻²⁰ The main advantages of chitosan sorbents are: nontoxicity, biodegradability, availability, high capacitive and kinetic characteristics.^{21, 22} Chitosan is one of the most effective natural polymer ligands binding a wide range of metal ions, with the exception of alkali and

alkaline earth metals, which don't have free d- and f-orbitals. Analysis of literature data shows that the sorption capacity of chitosan varies greatly depending on the source of production, physico-chemical characteristics, the degree of chitosan deacetylation, the sorption conditions, and the nature of the sorbed metal.

Chitosan was often used to adsorb various metal ions in the form of powder or flake. But low mechanical strength, difficult separation and poor acid resistance restrict development of chitosan adsorbent. Even at $\text{pH} < 5.5$, chitosan begins to dissolve in aqueous solutions. Therefore, the search for suitable forms of chitosan application as a sorbent, which lacks the listed disadvantages, is being done.

Much of the research is aimed at creating new chitosan sorbents with increased resistance to acidic media and higher sorption characteristics, which is achieved through crosslinking processes. The insolubility of chitosan in acidic media can be achieved by using crosslinking agents such as glutaraldehyde, formaldehyde as well as epichlorohydrin²³ and ethylene glycol diglycidyl ether.²⁴ The two last cross-linkers having epoxy groups have poor solubility in water, which is an obstacle to their use.²⁵ The most commonly sorbent is used in the form of beads, in which chitosan is previously converted into a gel by dissolving in acetic or hydrochloric acids and then crosslinked with glutaraldehyde or epichlorohydrin.

High complexing properties of chitosan promote steady growth of interest in experimental and theoretical studies of the interaction of the polymer and its derivatives with various metals.^{26, 27} Different aspects of the such interaction are discussed in a number of literature reviews.^{28, 29} Despite the fact that a variety of functional groups of chitosan is able to participate in the sorption of heavy metals: $\text{CS}[-(\text{O}^-)-\text{NH}_2]$, $\text{CS}[-(\text{OH})-\text{NH}_2]$, $\text{CS}[-\text{NH}_2 \cdot \text{H}_2\text{O}]$, $\text{CS}[-\text{NH}_2]$, the problem of substantiating mechanism of sorption/desorption of M^{2+} by chitosan from/in aqueous solutions of acids remains to be unresolved.

Understanding of complex formation mechanisms and evaluation of stability of complexes are required for the prediction of the effectiveness of the developed sorbents including entherosorbents, antibacterial, anti-fouling and anti-tumor activity of metal-chitosan complex, simulation of its behavior in biological samples and food systems in the presence of other metal ions, anions, and polymeric and low-molecular ligands.³⁰

The aim of this work is to study the sorption process of heavy metal ions from aqueous solutions using chitosan gel beads prepared by cross-linking with epichlorohydrin and ionic gelation with sodium tripolyphosphate, by isotherms absorption and kinetics methods and reveal the main regularities and a probable mechanism of the sorption.

2. Materials and methods

2.1. Materials

Used salts (i.e. cadmium(II) chlorid hydrate (2.5), cobalt(II) chloride hexahydrate, copper(II) chloride dihydrate, nickel(II) chloride hexahydrate and zinc(II)chloride (anhydrous). The salts were used as received. Metal chlorides were used as sources of metal ions; sodium tripolyphosphate $\text{Na}_5\text{P}_3\text{O}_{10}$, acetic acid CH_3COOH and epichlorohydrin ($\text{C}_3\text{H}_5\text{ClO}$) were used as modifying agents. All chemicals were of analytical grade and were purchased from CJSC "Himreaktiv" Nizhny Novgorod, Russia. The chitosan (CS) was 75–85% deacetylated and had a molecular weight of 190,000–250,000. It was purchased from the Bioprogress, Schelkovo, Russia.

2.2. Preparation of chitosan beads

The chitosan gel was obtained by dissolving of 0.6 g of CS-flakes in 14 g of 1 vol. % acetic acid solution, intensive stirring for 1 h and staying at least 48 h. After that 0.7 g of epichlorohydrin (ECH) as cross-linker was added step-by-step to CS gel. The mixing went on until homogeneous mixture was received. The mixture was added by a syringe into 200 mL of aqueous solution of sodium tripolyphosphate (TPP) with a concentration of 0.05 M, under mild magnetic stirring. During this procedure chitosan beads were formed. The beads were kept for 5 h at room temperature and then were separated from the aqueous solution of TPP, intensively washed with distilled water to a neutral pH to remove the excess of TPP.

2.3. Experimental procedure

Sorption process was investigated under static conditions by a method of limited solution volume. The samples of a sorbent (m ; 0.1 g) were placed into several flasks filled with 10 ml (vol) of aqueous solution of metal chloride and kept under stirring at 273 K.

The initial concentration (C_0) of metal ions was $1.5 \cdot 10^{-4}$ mol/L in kinetic experiments; in the pH studies C_0 of each solution was the same but with a certain pH in the range of 1–6.5. Freshly prepared solutions were used for each experiment. The pH was adjusted with hydrochloric acid and controlled with Multitest PL-311 pH-meter before and after metal sorption.

To obtain the sorption isotherms initial concentrations ranging from $1.5 \cdot 10^{-4}$ to $5 \cdot 10^{-2}$ mol/L.

The sorption time was varied from 5 minutes to 24 hours in kinetic experiments. In the equilibrium and the pH studies the equilibrium time was used.

The solution was separated from the sorbent by filtration at regular time intervals (kinetic experiments) or at the equilibrium time (equilibrium and the pH studies); the initial (C_0), current (C_t)

and the equilibrium (C) concentration of metal ions were determined by atomic absorption spectroscopy (apparatus «210VGP»).

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 VGP apparatus was 3 %, and the experimental error did not exceed 10%.

The current (A_t) and equilibrium sorption capacities of sorbents (A) were calculated as follows:

$$A_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (1)$$

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

Sorption degree α was determined using equation (3):

$$\alpha = \frac{C_0 - C}{C_0} \cdot 100\% \quad (3)$$

Distribution coefficient of heavy metal ions K_D was determined as a ratio of concentrations of metal ions in the sorbent phase (C_{sorb}) and in solution (C_{sol}) at equilibrium:

$$K_D = \frac{C_{\text{sorb}}}{C_{\text{sol}}} \quad (4)$$

Sample surface and composition characterization was done using FTIR and SEM methods. The FTIR spectra were collected in a wavenumber range of 4000-400 cm^{-1} on the FT-IR Fourier Spectrometer Avatar 360 ESP. Surface morphology of the chitosan flakes and beads was characterized by SEM imaging on a TESCAN VEGA 3.

3. Results and discussion

3.1. Kinetic studies

To determine the kinetic characteristics of cross-linked chitosan and chitosan flakes, kinetic curves of copper ions sorption from water solution of copper chloride were obtained (Fig. 1). As one can see from Fig. 2, the kinetics of Cu(II) sorption is well described by the pseudo-second-order kinetics equation.

3.2. Equilibrium adsorption studies

To determine the parameters characterizing the maximum sorption capacity (A_{∞}) of chitosan, the sorption isotherm for copper ions from aqueous solution of copper chloride by cross-linked chitosan and chitosan in the form of flakes were obtained (Fig. 3). The experimental isotherms were examined within the framework of Langmuir model of sorption (Eq. (5)) which is frequently used for description of heavy metal adsorption by polysaccharide materials:

$$A = \frac{A_{\infty} \cdot K \cdot C}{(1 + K \cdot C)}, \quad (5)$$

where K - is the concentration constant of sorption equilibrium characterizing the intensity of sorption process, L/mol.

Linearization of experimental isotherm (Eq. (6)) carried out by the least squares method indicates that there is an adequate description of the process with Langmuir model:

$$\frac{C}{A} = \frac{C}{A_{\infty}} + \frac{1}{A_{\infty} \cdot K} \quad (6)$$

As can be seen from Table 1, the sorption of Cu^{2+} from aqueous solutions by chitosan is properly described by a linear function in coordinates $C_e/A - C_e$ with a high correlation coefficient, which enable to evaluate the values of A_{∞} and K .

3.3. Effect of pH on the sorption of Cu(II) ions

Sorption of heavy metals is strongly dependent on the acidity of the aqueous phase. For the given heterophase system "metal salt aqueous solution \rightarrow sorbent", there is an optimal pH when its sorption capacity reaches a maximum.

To determine the optimum pH interval, the influence of pH of aqueous solution on the sorption of Cu^{2+} by chitosan was studied. As demonstrated by the Fig. 4, the degree of copper ions sorption is sharply increased within the pH range 1-7, reaching a maximum at pH 6-6.5.

In the region with low acidity (pH > 6.5) the decrease in the copper ions content in the aqueous phase can be due to the transition of Cu^{2+} to the phase of the sorbent and to the precipitation. Many researchers combine these processes, believing that in this case copper hydroxide can also be on the surface of the sorbent in a linked form: $\text{CS}[(\text{O}^-)_2(\text{NH}_2)_2\text{Cu}^{2+}]$.

The beginning of the joint running of these processes can be determined from a blank experiment or can be calculated from the reference data of the solubility product constants of metal hydroxides. These processes proceed only at pH > 7.

One can assume that in the aqueous phase of higher acidity (pH \leq 2), the lowering in sorption of heavy metal ions is due to the strong competition between metal ions and protons for electron-donating amino groups.

Proton deactivates the sorption sites, transferring amino groups from the basic, active form ($\text{CS}[-\text{NH}_2]$) to the H-acid-salt inactive form - ($\text{CS}[\text{NH}_3^+\text{X}^-]$) for the sorption of d-metals cations. The decreasing of acidity of the medium in the interval of pH 2-6 leads to the increasing of a number of free sorption sites in the basic form and to a significant increasing in the sorption degree of chitosan.

In aqueous solutions with a lower acidity, at $\text{pH} \geq 6$ the sorption degree tends to a constant value. At $\text{pH} 6-6,5$ the sorbent shows its maximum sorption capacity. This is due to the fact that the sorption sites of the sorbent are in the basic, active form, capable to sorb metal cations (M^{2+}) in an equivalent ratio with the anions - their carriers (Cl^-). Ligands, being strong Lewis bases which can form chelate cycles, give the most stable complexes.³¹

As it can be seen from the Table 2, the pH of the solution with the sorption of Cu^{2+} increases. This indicates that there is a joint, competitive sorption of metal cations and protons on the base sorption sites of sorbent. The greatest change is observed at the $\text{pH} 3-5$ of the initial solution, in which the pH of the equilibrium solution increases during the sorption process by 1-1.7 units. Such a change in pH may occur due to the influence of the metal, or to the nature of the sorbent.

The metal ions are introduced into the heterophase system in the constant amount and the acidity of the aqueous solutions increases in a logarithmic scale. Thus the concentration of protons in the acidic region of equilibrium solutions exceeds greatly the concentration of metal cations. As a consequence, protons superior in competition with metal cations for the basic sites of the sorbent in such heterophasic system until substantially complete displacement of M^{2+} from amino groups of chitosan in acid aqueous solutions at $\text{pH} \leq 2$.

At $[-\text{NH}_2] = \text{const}$, $[\text{M}^{2+}] \gg [\text{H}^+] \approx 0$ there is observed almost exclusively sorption of metal cations in an equivalent ratio with anions having basic properties, therefore, the maximum sorption of Cu(II) by adsorbent is observed from neutral solutions:



At $[-\text{NH}_3]^+ = \text{const}$ and $[\text{H}^+] \gg [\text{M}^{2+}]$, metal cations are almost completely distributed in the water phase, since the main sorption sites in the presence of a large excess of protons are transferred to the inactive H-acid-salt form:



The obtained results are in agreement with the literature data,³² in which the complex character of the functional dependence of the sorption capacity of chitosan sorbents on the pH of the aqueous solution is indicated. All these studies provide a qualitative assessment of the complex dependence of heavy metal ions sorption on the pH of solution, due to the change in the state of metals in the aqueous phase. However, in the pH range of 1-7, the metal salts taken in the indicator quantities are in the dissociated, hydrated state in the aqueous phase, so the complex nature of the sorption process can be related with a change in the state of the sorption sites and with the state of the metal in the sorbent, depending on the pH of the aqueous phase.

Competitive and coordinated sorption equilibria are characterized by the coefficient of distribution. The K_D value of indicator quantities of metal ions in the heterophase "aqueous solution/sorbent" system can serve as an interphase indicator of the activity of free basic sorption and solvation reaction sites in phases capable of interacting with the formation of a donor-acceptor and coordination interaction with heavy metal ions and protons.

The sorption process usually can be described as an ordinary but a two-phase chemical reaction and the distribution law can be applied to sorption systems. It can be represented by a competitive, equivalent, consistent, interphase equilibrium distribution of $M^{2+}/2H^+$ ions in phases and by the equilibrium between the sorption sites in basic and bounded forms: the H-complex and the metal complex:

To shift the equilibrium and thereby to increase or decrease the K_D of the metal ions in phases, it is necessary to change the concentration of hydrated protons in the aqueous phase, at practically constant ratio of the anion concentration in phases.³³

In accordance with the experimental conditions the sorbent/solution module doesn't change with pH, and the concentration of metal ions in the heterophase system also remains constant at the level of indicator quantities.

In the case of ion-exchange proton-desorption in dilute aqueous solutions, the expression for the concentration constant K is:

$$K = K_{DM^{2+}}/K_{D2H^+} = \{[M^{2+}]_{\text{sorb}} \cdot [H^+]_{\text{sol}}^2\} / \{[M^{2+}]_{\text{sol}} \cdot [H^+]_{\text{sorb}}^2\} \quad (7)$$

Taking into account the adopted limitations and assumptions, the dependence $K_{DM^{2+}} = ([M^{2+}]_{\text{sorb}}/[M^{2+}]_{\text{sol}}) = f(\text{pH})$ in logarithmic form is:

$$\log K_{DM^{2+}} \approx \text{const} + n(\text{pH}). \quad (8)$$

Expressions (7) and (8) are valid if the concentration of sorption sites in a heterophase system is kept constant or if the amount of the chitosan sorption sites is much larger than the amount of the substance being distributed.

For the studied heterophase system, $[CS-NH_2]/[M^{n+}] = 0.2/(1.5 \cdot 10^{-4}) \gg 1$ (module=100, i.e. $C_{\text{sorb}} = 10$ g/L; 10 g of the sorbent contain ≈ 0.2 mol of $CS-NH_2$, and $C_{M^{2+}} = 1.5 \cdot 10^{-4}$ mol/L). The experimental data were presented in coordinates $\log K_D - \text{pH}$ (Fig. 5), the results of processing of the plot by the least-squares method are presented in Table. 3.

The parameter n of equation (8) for the sorption of Cu^{2+} within the pH range 1-7 shows the tangent of the slope angle close to $\text{tg} \alpha \approx 0.5$, with the constant of the equation 0.53 and a correlation coefficient is close to unity (Table 3). This reliably fixes the ratio of competitive interphase

distribution of metal cations with respect to the proton $(\text{Cu}^{2+})_{0,5}/(\text{H}^+)_{1}$ or proton to the metal cation $(2\text{H}^+)/(\text{Cu}^{2+})$.

To specify the mechanism of sorption and proton-desorption of heavy metal ions from water-acid media using chitosan, it is necessary to clarify the equivalence of the of anions and protons participation in such interphase exchange processes. Several basic structures of chitosan sorption sites are used to explain the mechanism of metals sorption from aqueous acid media: $\text{CS}[(\text{O}^-)\text{-NH}_2]$, $\text{CS}[(\text{-OH})\text{-NH}_2]$, $\text{CS}[\text{-NH}_2\cdot\text{H}_2\text{O}]$, $\text{CS}[\text{-NH}_2]$, and the most commonly used structure of sorption centers is: $\text{CS}(\text{-OH})\text{-NH}_2$.

Swollen chitosan, due to the presence of amino groups, exhibits stronger basic properties than the aqueous phase. Distributing substances (strong acids HX and their salts MX_2) are strong electrolytes and completely decompose into water to hydrated ions. Their cations $([\text{H}^+]_{\text{aq}}$ and $[\text{M}^{2+}]_{\text{aq}}$) act as strong electron acceptors, which are capable of forming chelate complexes in the sorbent phase and hydrate complexes in the aqueous phase.

d-Metals form stable hydrate complexes in water, the coordination number of which depends on the metal nature. The Cu^{2+} usually forms complexes with a coordination number of 4, thus probable structure of its hydrated cationic complex in the aqueous phase is: $[(\text{H}_2\text{O})_2\cdot\text{Cu}^{2+}\cdot(\text{H}_2\text{O})_2]$.

In contrast to the metal cations, the proton in the aqueous phase is capable of forming a number of hydrate complexes: $[\text{H}(\text{H}_2\text{O})]^+$ — hydroxonium ion, $[\text{H}(\text{H}_2\text{O})_2]^+$ — Cundel ion, $[\text{H}(\text{H}_2\text{O})_4]^+$ — Eigen ion, $[\text{H}(\text{H}_2\text{O})_6]^+$ — Stoyanov ion.³⁴ The mechanism of dissociation of strong acids in water is connected with the formation of H^+_{aq} with a distributed positive charge along its periphery, while the anion is then displaced to the periphery. In water H_3O^+ is unstable and immediately turns into the strongest, twice hydrated and most stable structure with a strong symmetric hydrogen bond $[\text{H}_2\text{O}\cdot\text{H}^+\cdot\text{OH}_2]$, which is usually used for interpretation of kinetics and thermodynamics involving the hydrated proton in aqua acid media. The metal cation also forms a similar hydrate complex in water.

Chitosan is a polysaccharide, built from hydrophilic units of glucosamine having an affinity for water $[\text{C}_6\text{H}_7\text{O}_2(\text{-OH})_2(\text{-NH}_2)]_n^-$, so it is completely soluble in slightly acidic aqueous media. Organic substances, including simple and complex sugars, have a smaller dielectric constant by an order of magnitude ($\epsilon(\text{-C}_6\text{H}_7\text{O}_2[\text{NH}_2(\text{OH})_2])\leq 8$) than water ($\epsilon(\text{H}_2\text{O})\approx 80$.) Therefore, dissociation of even strong acids and salts in such a gel phase of chitosan will terminate at the stage of formation of contact ion pairs at electron-donating neutral sorption sites of chitosan.

Introduction into heterophase “chitosan-water” system of acids and salts capable of completely or partially dissociating into ions will be accompanied by a different distribution

mechanism between the phases of acidic particles with electron-accepting properties (H^+ , M^{2+}) and basic electron-donating properties (X^-).

Water can't form hydrate complexes in the sorbent phase, since amines show more basic properties and water doesn't have an excessive negative charge, so it can't remove the positive charge from the amine complex of the metal in the electroneutral phase of the sorbent.

Since the chitosan fragments, including alcohol- and aminogroups (with a vicinal arrangement) and a water molecule: $(-HCOH-HCNH_2 \cdot H_2O)$ connected by hydrogen bonds can be considered as its sorption sites, therefore ethanolamine ($CH_2OHCH_2-NH_2$) was taken as its model.

The assumption was done that the structure of salts and acids in the heterophase system "crosslinked chitosan – water" at the reaction site of the chitosan should be close to their state at the reaction site of ethanolamine in the presence of water and without it.

The computational quantum chemistry modeling method was performed on some modeled metal-complex structures having functional groups of the same type as that of the chitosan sorption sites. The strength of such modeled metal-complex structures increases in a such sequence: $[(CH_2OHCH_2-NH_2)_2Cu^{2+}(Cl^-)_2] < [(CH_2OHCH_2-NH_2)_2Cu^{2+}(OH^-)_2] < [(CH_2OHCH_2-NH_3^+Cl^-)_2]$

At the same time, the hydroxide-ion can't participate in the formation of stronger electrically neutral metal complexes in aqueous phase in comparison with the chloride-ion because of its low concentration: $[OH^-] < 10^{-7} mol/L$ in aqueous solutions of acids. The proton-donor acidity of the particles of the dissolving medium increases in the series $RNH_2 < ROH < HOH < RCOOH$, and their basicity, the electron-donor capacity increases in the reverse order. Thus very weak acids (alcohols and amines) in the anionic form (RO^- , RNH^-) can exist only in alkaline media, and in the region of pH 1-7 their existence is almost impossible.

Organic solid phase, due to low dielectric permeability, small water content and the presence of amino groups, will form complexes with Cu^{2+} and H^+ (electron acceptors) as contact ion pairs. The chelate structures with H- and metal complexes on chitosan sorption sites were computed with the methods of quantum chemistry on modeled compounds, by adhering to chemistry's best practices. (Supplementary material).

The competitive distribution of salts and acids in the heterophase system "aqueous solution/chitosan" taking place at electroneutrality of phases causes an increase in the sorption of protons in the sorbent phase and an equivalent decrease in metal cations on the basic sorption sites of chitosan with simultaneous increase of M^{2+} in the aqueous phase.

The acid-base properties of mutually saturated phases during interphase equilibrium are adjusted to each other. With the change in the acidity of the aqueous phase, the acidity of the solid phase, being in equilibrium with it, also changes. The ion exchange mechanism in aqueous solutions of salts and acids under the following conditions: $CS[-NH_2] > H^+$, constant module, an

indicator and constant amount of metal cations in the system, should be described by a logarithmic relationship $\lg K_{DM^{2+}} \approx f(\text{pH})$ close to linear.

The equivalent ratio of electron acceptors ($\text{Cu}^{2+}/2\text{H}^+$) in competitive equilibrium for the electron-donating, basic sorption centers $\text{CS}[-\text{NH}_2]$ in the sorbent is confirmed by means of the experimental results (Fig. 5, Table 3). The competitive sorption of copper and a proton takes place on the amino groups of chitosan in an equivalent ratios with participation of anions.

The elemental composition of the sorbent, analyzed at equilibrium in the system «aqueous CuCl_2 solution/sorbent», confirms that the sorption of Cu^{2+} is accompanied by a consistent sorption of the Cl^- ions.

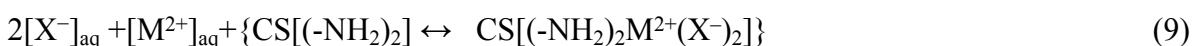
However, elemental analysis shows that sorption of the Cl^- ions occurs not in equivalent quantities towards to Cu^{2+} ions, but to the less extent.

The deficit of negative charges (inherent to Cl^- ions) in the sorption process towards to positive charges (carried by Cu^{2+} ions) on chitosan is covered by multiply charged anions (phosphates) included in the sorbent structure during its ionic crosslinking in the process of forming of chitosan beads in the solution of sodium tripolyphosphate.

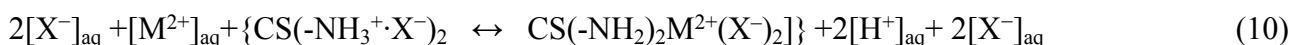
Thus, the mechanism of interphase distribution of heavy metals in a two-phase system “an aqueous solution of salts – chitosan” includes two interrelated processes. The spontaneous, equilibrium transition of the metal cations from the aqueous phase with less basicity is accompanied by a change in the intraspheric hydrate shell of the cationic metal complex $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ to the intraspheric solvate shell in the gel phase of chitosan with a greater basicity of $\text{CS}[(-\text{NH}_2)\text{Cu}(\text{H}_2\text{O})_2]^{2+}$. In a chitosan - substance with a low dielectric constant, the solvated ion pair transforms into the contact ion pair: $\text{CS}[(-\text{NH}_2)\text{Cu}(\text{X})_2]$.

In the presence of residual amounts of salt impurities (Na^+X_1^-) being immobilized in the gel phase they will participate in the compensation of the positive charge of the cation complex along with other mobile anions (X^-), passing from one phase to another. The participation of multiply charged ions in the formation of electrically neutral complexes on the amino groups of chitosan as crosslinking agents was noted by.³⁵ Therefore the mechanism of sorption/proton-desorption of heavy metals on chitosan from aqueous solutions of acids can be represented by the equilibria:

Salt sorption of M^{2+} by chitosan from solutions of salts in pure water:



Competitive, equivalent, coordinated, equilibrium mechanism of proton-desorption of M^{2+} in the two-phase system:

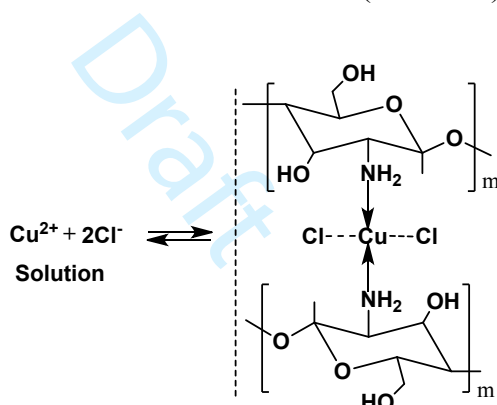


In aqueous solutions of acids and salts at $[\text{H}^+] > [\text{M}^{2+}]$ the sorption of the proton restricts the sorption of metal cations, which is accompanied by an increase in the pH of the aqueous phase

(Table 2). At electroneutrality of phases in the process of equivalent exchange of metal cations for protons, their anions participate in the same proportions in the interphase equilibria at the main sorption sites of chitosan ($\text{MX}_2/2\text{HX}$).

Anion of an acid with weak basic properties ($\text{X}^-=\text{Cl}^-$ and others) is involved in the formation of chelate complexes with the metal cation and the proton. At the same time, the joint participation of cations and anions ($2\text{H}^+/2\text{Cl}^-$ and $\text{Cu}^{2+}/2\text{Cl}^-$) on a competitive basis allows completely to remove the basic properties of the amine group of the sorbent due to its protonation and complexation, which allows such ions to participate in the alignment of excess acid-base interphase interactions.

As a result, the competitive mechanism of salt sorption of heavy metal ions and protons from electrically neutral aqueous solutions together with the participation of amine groups of the solid phase in the basic form of $\text{CS}[-\text{NH}_2]$ in the formation of electrically neutral complexes (H-salt, $\text{CS}[-\text{NH}_3^+\text{Cl}^-]$ and chelate metal complexes $\text{CS}[(\text{-NH}_2)_2\cdot\text{Cu}^{2+}\cdot(\text{Cl}^-)_2]$) is preferable in compare with all other hypotheses of the distribution of heavy metals and protons in the heterophase system an “aqueous solution of acids and salts of d-metals/chitosan” (scheme 1).



Scheme 1. Diamine-dichloride Cu(II) complex of chitosan

3.4. FTIR spectra

The FTIR spectra of crosslinked chitosan before and after adsorption of Cu^{2+} ions are shown in Fig. 6. The main FTIR peaks of the CS beads include the overlapped O-H and N-H stretching vibrations ($\nu_{\text{N-H/O-H}}$) at 3444 cm^{-1} , asymmetric C-H stretching vibration ($\nu_{\text{asC-H}}$) at 2847 cm^{-1} , the bending vibration of N-H ($\delta_{\text{N-H}}$) at 1647 cm^{-1} , and the C-O stretching vibrations ($\nu_{\text{C-O}}$) derived from glycosidic bonds (characteristic bands of polysaccharide) at 1073 and 1067 cm^{-1} . After Cu^{2+} ions sorption on chitosan, a shift of adsorption bands corresponds to $-\text{NH}$ and $-\text{CO}-$ stretching frequencies indicate that the $-\text{NH}_2$ group is involved in chemisorption of Cu(II) and subsequent complexation process. Appearance of a multiple peak in the region $500\text{-}600\text{ cm}^{-1}$ is assigned to the stretching vibration of N-Cu bond formed during complexation process.

3.5. SEM imaging

The change in surface morphology of the chitosan flakes and beads is characterized by SEM imaging. Fig. 7 shows the surface of CS flakes and beads crosslinked with epichlorohydrin and treated with sodium tripolyphosphate and also the bead intrinsic site in section. SEM images show that the intrinsic surface of the crosslinked sample is smooth and the outer surface is slightly rough and uniform (Figure 7b) in compare with CS-flakes (Figure 7a) having a number of bumps. The Figure 7(c-d) demonstrates the elemental composition of the chitosan flakes after Cd^{2+} and Cu^{2+} ions sorption.

The A_{∞} values for various metals are represented in the Table 4.

Conclusions

For dilute solutions of salts, a linear dependence of the distribution coefficient of heavy metal ions on the acidity of the aqueous phase in the logarithmic coordinates $\log K_{\text{DM}^{2+}} = f(\text{pH})$ with a slope of tangent angle (1/2) and with a correlation coefficient of 0.99 is established.

The solvation mechanism of sorption/protodesorption of Cu^{2+} cations by chitosan from/in aqueous-acid media is substantiated, which is based on a competitive, equivalent, coordinated, interphase equilibrium of the distributed cations in phases ($\text{M}^{2+}/2\text{H}^{+}$), on an equilibrium between the basic and bound forms devoid of basic properties, sorption sites of the sorbent ($[-\text{NH}_2]/[-\text{NH}_3^+]$ and $[-\text{NH}_2]_2/[(-\text{NH}_2)_2\text{Cu}^{2+}]$), on the formation in the aqueous phase of the hydrate complexes of the proton and the metal cation.

In the sorption process, a formation of chelate complexes of the compositions: diamine dichloride metal complex of chitosan $\text{CS}[(-\text{NH}_2)_2\text{MCl}_2]$ and aminohydrochloride complex of chitosan $\text{CS}[-\text{NH}_2\cdot\text{HCl}]$ occurred on amino groups of the sorbent with equivalent coordinated participation of metal cations, protons and anions.

The mechanism of the influence of protons during protodesorption is connected with the transfer of an equivalent amount of amino groups $\text{CS}[(-\text{NH}_2)_2]$ - the basic sorption sites into the inactive H-salt form of $\text{CS}[(-\text{NH}_3^+\text{Cl}^-)_2]$ and thereby the d-metal cations are displaced from their electrically neutral, chelate metal complexes $\text{CS}[(-\text{NH}_2)_2\text{Cu}(\text{Cl})_2]$ on the sorbent to the aqueous phase with a decrease in the equilibrium sorption capacity of the sorbent.

The maximum sorption of metal ions is observed in the neutral region, at pH 5-7. The convex isotherms of the Cu^{2+} ions sorption on chitosan are well described by a linear dependence in

the coordinates $C_{M2+}/A = f(C_{M2+})$. The limiting sorption obtained using the Langmuir model is in agree with the experimental data.

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Table 1. Parameters of the Langmuir equation

Sorbent	$1/A_{\infty} \cdot K$	$1/A_{\infty}$	A_{∞} , mol/kg	Correlation coefficient
CS-flakes	$3,4 \pm 4 \cdot 10^{-4}$	$1,28 \pm 1 \cdot 10^{-4}$	0,78	0,99
Modified CS	$1,9 \pm 4 \cdot 10^{-4}$	$0,6 \pm 1 \cdot 10^{-4}$	1,6	0,99

Table 2. pH-values of initial and equilibrium solutions of Cu(II)

pH _{initial}	pH _{equilibrium}
1,24	1,30
2,08	2,27
3,02	4,34
4,03	5,71
4,85	6,18
5,41	6,40

Table 3. Parameters of the equation: $\lg K_D = \text{const} + n \cdot (\text{pH})$

Parameter	constant	n	Correlation coefficient
	$0,53 \pm 0,005$	$0,42 \pm 0,046$	0,99

Table 4. Sorption capacity of chitosan

Metal ion	A_{∞} , mol/kg				
	Cd^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}
Chitosan flakes	0,49	0,65	0,58	0,78	0,73
Crosslinked chitosan	1,05	1,33	1,21	1,60	1,42

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Table 4. Sorption capacity of chitosan

Fig. 1. Kinetic sorption curve of Cu(II) ions by cross-linked chitosan (1) and by chitosan flakes

Fig. 2. Pseudo second-order sorption kinetics of Cu(II) by cross-linked chitosan (2) and by chitosan flakes (1)

Fig. 3. Sorption isotherm of copper ions by cross-linked chitosan (1) and by chitosan flakes (2)

Fig. 4. Effect of pH on the sorption degree (α) of copper ions by crosslinked chitosan

Fig. 5. Effect of pH of aqueous solution on the distribution of copper ions in heterophase system "HCl-H₂O-CuCl₂-chitosan"

Fig. 6. FTIR spectra of crosslinked chitosan before (1)

and after (2) Cu²⁺ ions sorption: (a) The surface of CS-flakes (b) The surface and intrinsic site in section of CS-bead

Fig. 7. SEM-images and elemental composition of the chitosan flakes and cross-linked beads

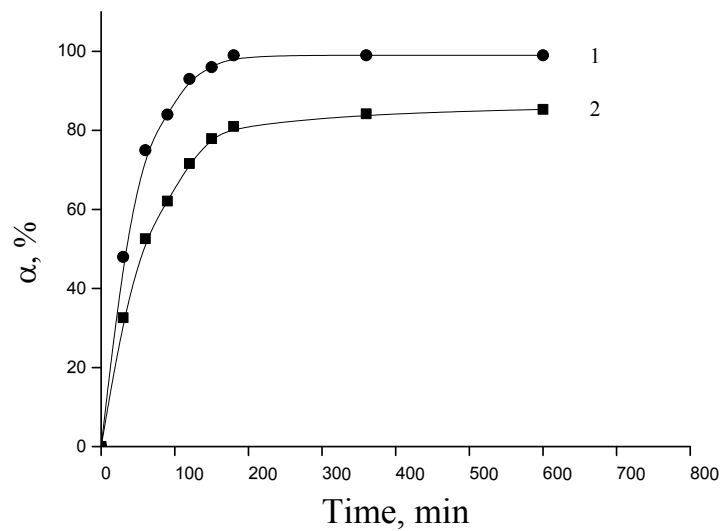


Fig. 1. Kinetic sorption curve of Cu(II) ions by cross-linked chitosan (1) and by chitosan flakes

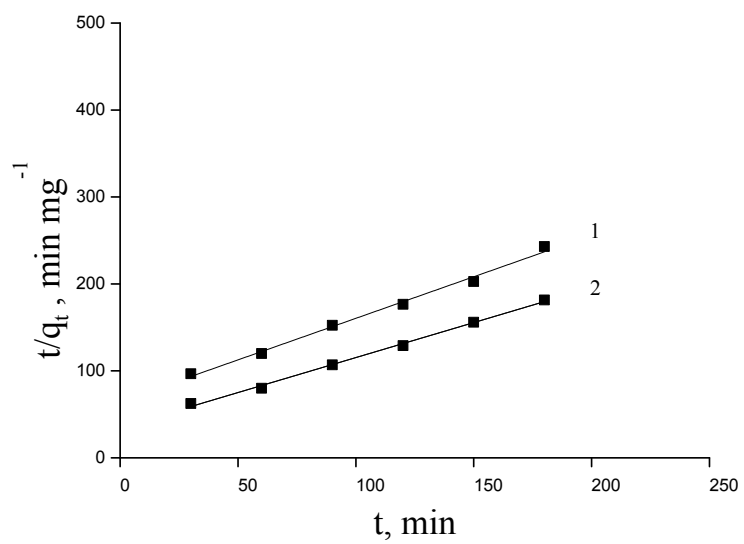


Fig. 2. Pseudo second-order sorption kinetics of Cu(II) by cross-linked chitosan (2) and by chitosan flakes (1)

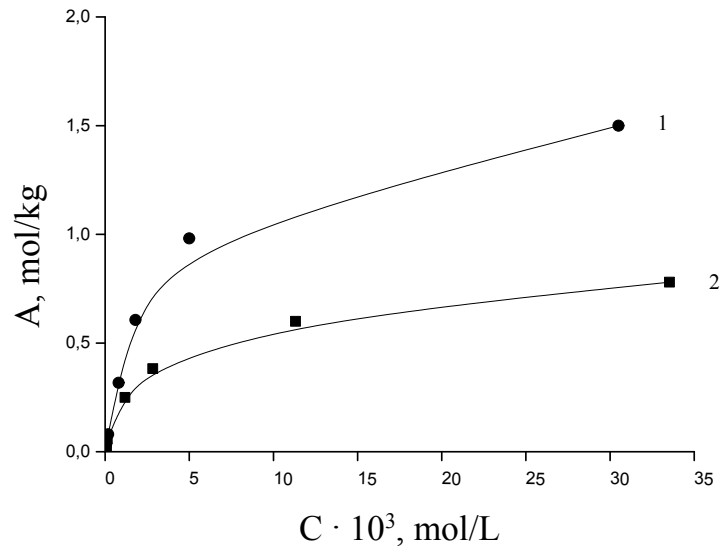


Fig. 3. Sorption isotherm of copper ions by cross-linked chitosan (1) and by chitosan flakes (2)

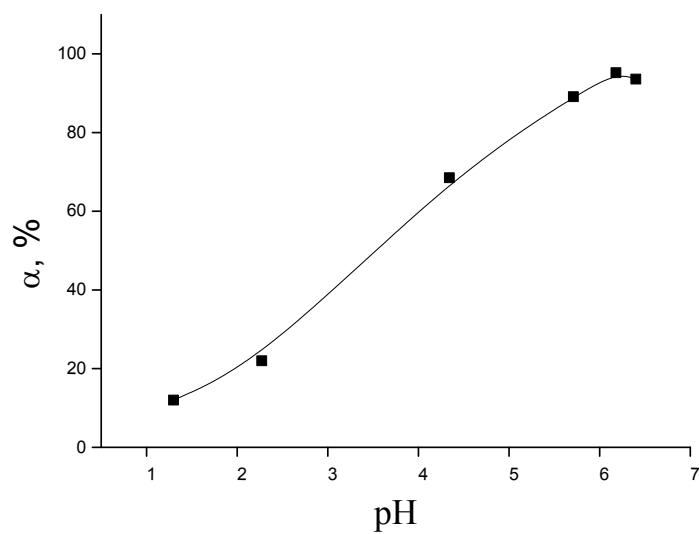


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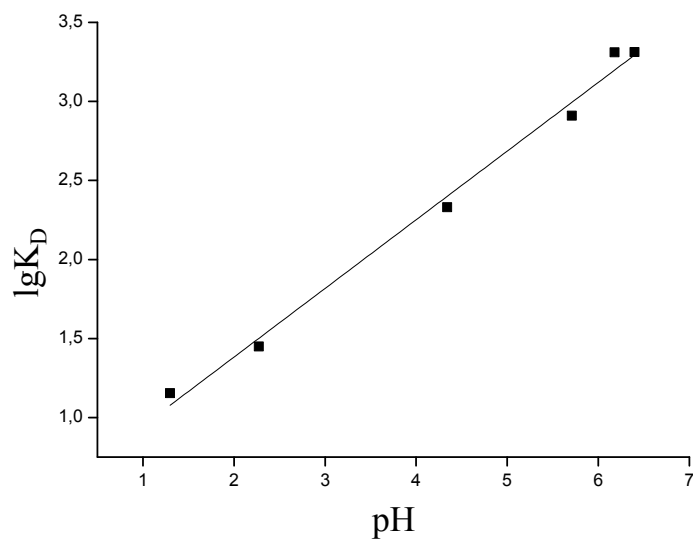


Fig. 5 – Effect of pH of aqueous solution on the distribution of copper ions in heterophase system “HCl–H₂O–CuCl₂–chitosan”

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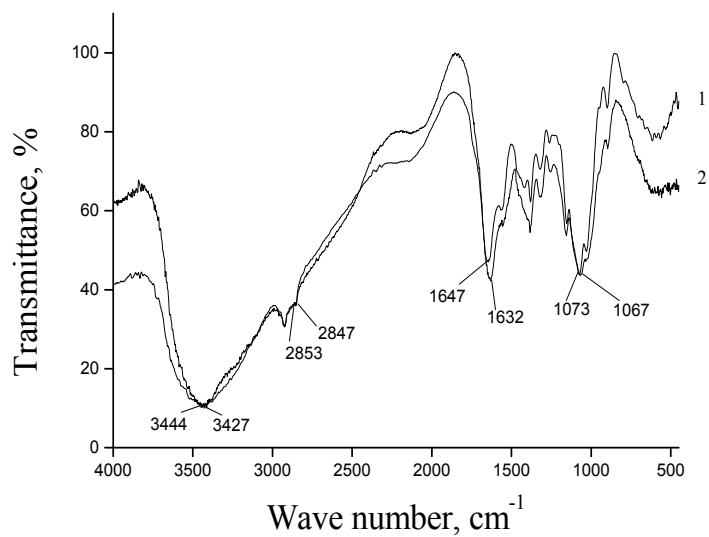


Fig. 6. FTIR spectra of crosslinked chitosan before (1) and after (2) Cu²⁺ ions sorption

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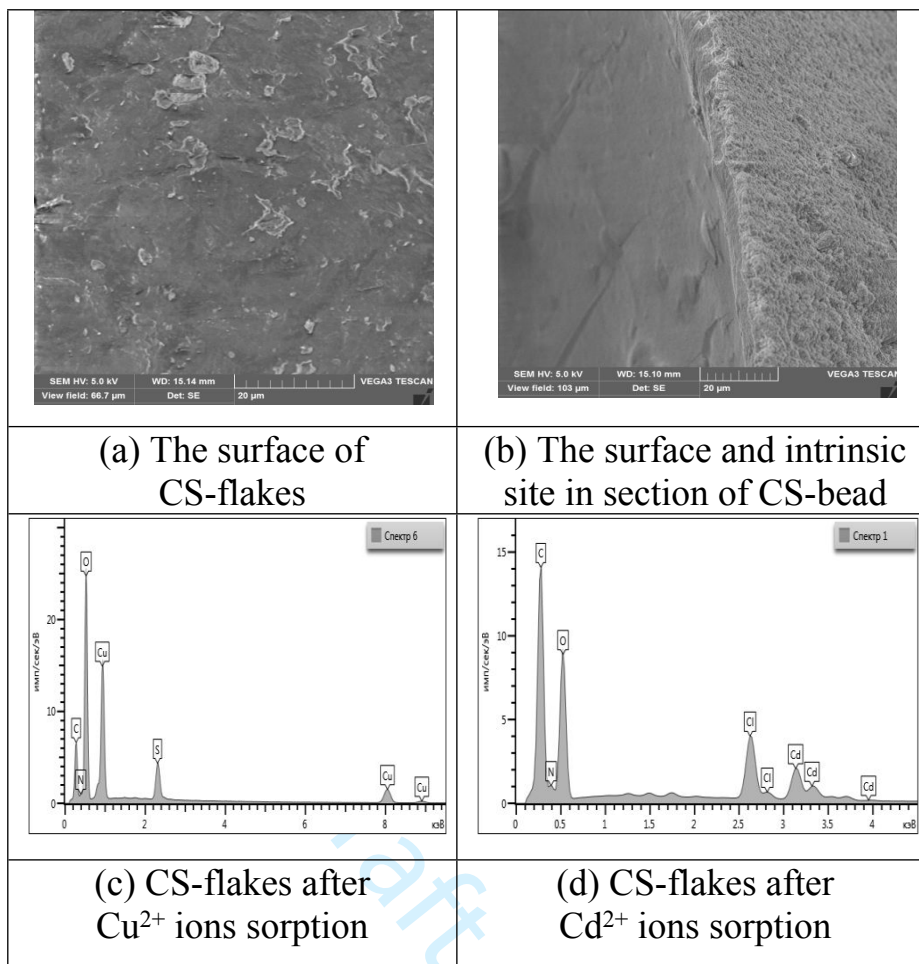


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