Sorption of Cu(II) complexes with ligands tartrate, glycine and quadrol by chitosan

Ona Gylienė *, Rima Binkienė, Rita Butkienė

Institute of Chemistry, A. Goštauto 9, Vilnius LT 01108, Lithuania

ARTICLE INFO

ABSTRACT

The sorption by chitosan in Cu(II) solutions containing tartrate, glycine (amino acetic acid) and quadrol (N,N,N′,N′-tetrakis(2-hydroxypropyl)ethylenediamine) as ligands has been investigated. The degree of sorbate removal strongly depends on pH. In solutions containing tartrate almost complete sorption of both Cu(II) and tartrate proceeds in mildly acidic and neutral solutions. The sorption of Cu(II) is also complete in alkaline solutions containing glycine; meanwhile a substantial sorption of glycine proceeds at pH ~6. The Cu(II) sorption in solutions containing quadrol is insignificant. Any sorption of quadrol does not proceed in the whole range of pH investigated. The investigations under equilibrium conditions showed that the Cu(II) sorption from tartrate containing solutions obeys Freundlich equation and in solutions containing glycine and quadrol it fits Langmuir equation.

Supposedly, Cu(II) sorption onto chitosan proceeds with formation of amino complexes onto the surface of chitosan; the sorption of tartrate proceeds as electrostatic as well as with formation of amide bonds.

Applying of electrolysis enables a complete removal of sorbed Cu(II) and ligands without changes in physical and chemical properties of chitosan. This is confirmed by sorption ability of regenerated chitosan, measurements of its molecular weight, the deacetylation degree and FT-IR spectra.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Due to the intensive agricultural and industrial activities, pollution of the environment steadily increases. Among the anthropogenic pollutants, the heavy metals make up the significant part. Differently from organic pollutants, which may be destroyed to harmless substances, heavy metals are indestructible. Their toxicity depends on the chemical species. The soluble metal compounds are most dangerous for the environment. The heavy metal compounds with complexing agents (ligands) are numbered among the most easily soluble ones [1–4]. Heavy metal ligands are widely used in different branches of industry such as metal finishing, electroplating, painting, dying, photography, surface treatment industry, in the fabrication of semiconductor devices, catalysts, in remediation of soils polluted with heavy metals, etc. in order to enhance the metal solubility. However, such a peculiarity of ligands hinders the metal recovery in the form of insoluble compounds, which is most widely used for decontamination of effluents containing heavy metals. Usually, prior to application of practically reasonable methods for metal removal (precipitation, coagulations, sorption, etc.) the ligands are destroyed using different oxidizers [5,6].

Increasing amounts of metal complexes used in different branches of industry require cost effective treatment technologies. One of such technologies for wastewater treatment is the use of biosorbents [7–9].

Differently from synthetic ion exchangers, which are used for wastewater treatment, biosorbents are biodegradable and rather cheap; their sources are bio-renewable. Chitin-containing sorbents show selective sorption for heavy metal ions. Chitin is one of the most abundant natural biopolymers. Chitosan (copolymer of β-[1 → 4]-linked 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose), which is obtained from chitin (β-[1 → 4]-linked 2-acetamido-2-deoxy-D-glucopyranose) by its deacetylation, is able to sorb both heavy metals and organic compounds [10–13]. An amide linkage of chitin is kinetically stable. It can be hydrolyzed to amine in boiling alkali [14]. However, the production of chitosan from chitin-containing wastes raises the price and limits the industrial application of chitosan. The sorption of heavy metal ions, which act as biocides for many microorganisms, aggravates chitosan biodegradability under natural conditions [15,16]. The use of peculiar microorganisms for destruction of chitosan after sorption adds also to the limited use of chitosan in practice. The regeneration of chitosan and its reuse could solve the problem of disposal of the spent sorbent.

In case of using the polycarboxylic acids as heavy metal ion ligands, their sorption mechanism onto chitosan could be rather complicated. Along with electrostatic interactions, which may pro-

---

* Corresponding author. Tel.: +370 5 2729127 fax: +370 5 2649774.
E-mail address: gyliene@ktl.mii.lt (O. Gylienė).

ceed between COO⁻ ions of carboxylic acids and amino groups of chitosan, the chemical interactions between the undissociated –COOH groups of acids and the –NH₂ groups of chitosan with formation of amide groups could take place [17–19]. The formation of amide bonds during interaction of chitosan with di- and tricarboxylic acids at room temperature has also been shown in the case of cross-linking of chitosan [20].

The sorption of free heavy metal ions onto chitosan is widely investigated. The sorption proceeds due to interaction of chitosan hydroxyl and amine groups with metal ions giving metal complexes. The sorption of heavy metal complexes onto chitosan is poorly investigated. A few investigations carried out in this field indicate that the presence of ligands in solutions hinders the heavy metal recovery [17,21–25]. The reasons of hindrance effects of ligands are also poorly investigated. This effect depends mostly on ligand concentration and pH. Our investigations showed [17,18,23] that the main reason of decrease in heavy metal sorption onto chitosan in solutions is the sorption of ligands. The sorption of ligands proceeds partly due to electrostatic interactions [16]. In case of ligands containing carboxylic groups the sorption proceeds partly also with formation of covalent bonds between the functional groups of chitosan and the ligands [17,18]. This assumption is also supported by the fact that the complete desorption of carboxylic acids does not proceed by changing of pH value. The formation of these bonds has been proved also by the authors of [19,20], when interactions of carboxylic acids and chitosan proceeded. The conversion of amide groups into amine groups can be performed applying electrolysis [17,18].

The aim of this study was to investigate possibilities to apply the sorption onto chitosan for treatment of the wastewaters of electroless copper plating solutions. These solutions contain copper ions and complexing agents along with other components necessary to obtain copper deposits. Recently, as alternative to environmentally dangerous ligand EDTA, the biodegradable copper ligands such as tartrate and quadrol (N,N,N′,N′-tetrakis(2-hydroxypropyl)ethylenediamine) have been investigated very intensively. In order to increase the stability of solutions and to improve the quality of deposition the additive of glycine (amino acetic acid), which also makes strong complexes with copper ions, is used [26–29]. In this work the investigations were carried out with the model solutions containing Cu(II) and ligands tartrate, glycine and quadrol in concentrations comparable with those present in a spent electroless copper plating solution. The attempts have also been made to regenerate the chitosan after sorption applying electrolysis in order to reuse it anew.

2. Experimental

2.1. Sorption experiments

Chitosan flakes (deacetylation degree about 80%) produced by JSC "Sonat" (Russia) from crab shells were used for experiments. The chitosan after keeping 1 day in distilled water for swelling was put on a glass filter for water removal. So prepared it was used for sorption experiments.

All sorption experiments were carried out under batch conditions with solutions containing ~10 mmol L⁻¹ CuSO₄ and ligands tartrate, glycine and quadrol in concentrations up to 20, 25 and 50 mmol L⁻¹. These concentrations are comparable to the concentrations in rinsing water after electroless copper plating in manufacture of printed circuit boards, when the tartrate- or quadrol-containing solutions are used. Adsorption was investigated at room temperature (20 ± 2 °C) by pouring ligand-containing solutions onto chitosan and occasional mixing. pH was checked and adjusted with NaOH or H₂SO₄ solutions 5 times a day so long as

the equilibrium concentrations (pH, Cu(II), ligand) were achieved. The sorbed quantities of Cu(II) and ligands were determined from the changes in the concentrations of solutions. After sorption, chitosan was filtered and rinsed with cold deionized water and dried at 70 °C.

2.2. Analysis of solutions

Cu(II) was determined after its reduction to Cu(I) by means of iodide in acidic solutions. The concentration of the iodine formed was determined by titration with a $Na_2S_2O_3$ solution. Low concentrations of Cu(II) were determined photometrically using diethylditiocarbamate as an indicator [30]. The latter method allows determination of Cu(II) in solution under our experimental conditions in concentrations up to 0.5 mg L⁻¹.

The concentration of ligands in the solutions was determined after oxidation in alkaline solutions with $KMnO_4$, its excess being retitrated in acidic solutions with oxalic acid. In calculations it has been assumed that the oxidation numbers for tartrate, glycine and quadrol are 10, 6 and 40, respectively. The accuracy of these determinations is ±5%.

2.3. Electrochemical measurements and regeneration of chitosan

Electrochemical investigations were carried out using a ПИ-51 potentiostat (Russia). Voltammetric measurements were carried out in a three-compartment cell at 20 ± 1 °C. A Pt plate was used as a working electrode; a saturated Ag/AgCl/KCl electrode was used as reference and platinum foil served as a counter electrode. The potential sweep rate was 20 mV s⁻¹.

Regeneration of chitosan was carried out under galvanostatic conditions and a two-compartment cell–cathodic with a volume of 100 mL and anodic with 10 mL, separated by a glass filter was used. Chitosan (1 g of dry weight before sorption) was loaded in the cathodic compartment. Pt wires were used as a cathode and as an anode. The electrochemical cell was filled with 0.1 mol L⁻¹ Na_2SO_4 solution. The solution with chitosan was mixed with a magnetic stirrer during electrolysis.

2.4. Investigations of physical and chemical properties of chitosan

The quality of regenerated chitosan was evaluated by assessment of IR-spectra, determination of molecular weight and deacetylation degree. The infrared spectra of chitosan were recorded in KBr pellets on a Fourier transformation infrared spectrometer (Hartman & Braun, Canada) with 2 cm⁻¹ scale resolutions. The spectra were recorded in the wave number region between 4000 and 500 cm⁻¹.

The molecular weight of chitosan (M) was determined by measurement flow rate of 0.05–0.15% chitosan dissolved in 0.5 mol L⁻¹ acetic acid and 0.5 mol L⁻¹ sodium acetate solution at 25 °C using Ostwald viscometer (ВЛЖ-2, Russia) with a capillary diameter of 0.99 mm. The molecular weight (M) was calculated according to Mark–Houwink's equation:

$$\eta = K_m M^{\alpha},$$

where η is the intrinsic viscosity estimated on the measurements of flow rate; K_m and α are constants the values of which depend on the nature of the polymer and solvent as well as on temperature. In this particular case $K_m = 3.5 \times 10^{-4}$ and $\alpha = 0.76$ [31].

The deacetylation degree was evaluated by means of titration with HCl. The length of plateau at pH ~6, which coincides with the protonation of the –NH₂ group of chitosan, corresponds to its deacetylation degree.
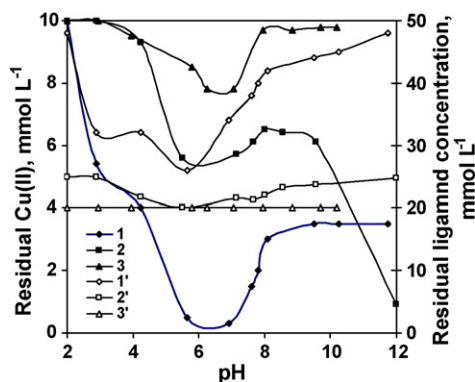
Fig. 1. Residual Cu(II) (1, 2 and 3) and ligand (1′, 2′ and 3′) concentrations after sorption from solutions containing 10 mmol L^{-1} Cu(II) and 50 mmol L^{-1} tartrate (1 and 1′); 10 mmol L^{-1} Cu(II) and 25 mmol L^{-1} glycine (2 and 2′); 10 mmol L^{-1} Cu(II) and 20 mmol L^{-1} quadrol (3 and 3′). Load 5 g L^{-1}; temperature 20 °C.

3. Results and discussion

3.1. Sorption experiments

The investigations were carried out with ligands containing different functional groups—tartrate: two carboxylis groups (pK_1 ∼3.2; pK_2 ∼4.8), glycine: amine and carboxylic groups (pK_1 ∼2.3; pK_2 ∼9.7) and quadrol: four hydroxylic groups (pK_1 ∼6.9; pK_2 ∼8.8). Cu(II) with all these ligands form complexes with ratio 1:2. Thus, in pH range close to neutral Cu(II) the complexes with tartrate and glycine are not charged, and the complex with quadrol is positively charged.

The sorption of Cu(II) as well as ligands strongly depends on nature of ligands and pH (Fig. 1). In acidic solutions any sorption of Cu(II) or ligands does not proceed. With increase in pH the sorption increases. For Cu(II) and tartrate it is the highest at pH ∼6. In alkaline solutions the sorption of tartrate rapidly decreases with increase in pH, meanwhile the sorption of Cu(II) remains almost constant (Fig. 1, curves 1 and 1′).

The glycine is sorbed only in the pH range 6–8 and makes up 15–20% of the initial its concentration. The sorption of Cu(II) ions from glycine-containing solutions increases with increase in pH and is the highest at pH 12 (Fig. 1, curves 2 and 2′).

It is usually assumed [13] that the interaction of carboxylic acids with chitosan is the interaction between a weak acid and a weak base which can be described by the equation:

Chit–NH$_2$ + HOOC–R → Chit–NH$_3^+$ + RCOO$^-$
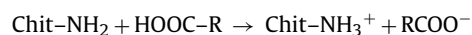
The protonation of –NH$_2$ groups of chitosan proceeds at pH < 6.3.

The reason why the sorption of Cu(II) complex prevails in acidic solutions, when compared with that in neutral and weakly alkaline solutions can be explained on the ground of electrostatic interaction of a complex with protonated amino groups of chitosan. This mechanism proposed in [32] is supported by changes in pH.

The thorough investigations of sorption of Cu–EDTA and other carboxylic ligands onto chitosan [17,18,22,24] showed that these interactions are more complicated. The chemical interactions between the ligand and chitosan with formed covalent bonds could proceed along with electrostatic interactions. The functional groups of ligands are responsible for sorption onto chitosan, i.e. for interaction with chitosan functional groups—amine and hydroxyl. The tartrate carboxylic groups, which are able to form amide bonds with amine groups of chitosan, are sorbed best. Despite the possible electrostatic interactions of chitosan amino groups with carboxylic groups of glycine its sorption is weak. Remarkable is the fact that the sorption of tartrate and glycine ligands proceeds at pH > 6.3 where chitosan is not protonated, though the sorption ability at
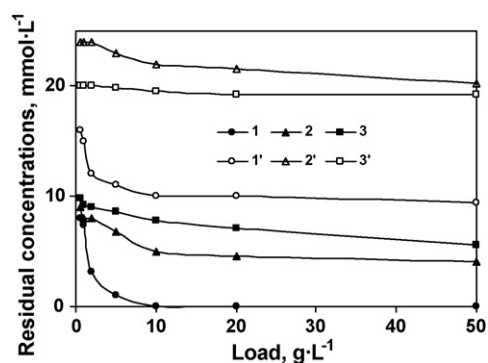
these pH values is lower. Anyway, the highest sorption ability for ligands is achieved at such pH values where chitosan is protonated and ligands are partly dissociated.

The complexes formed with Cu^{2+} and quadrol have positive charge. As it can be expected, any electrostatic or chemical interactions between the hydroxyl groups of quadrol and amine groups of chitosan should not proceed. Actually, the sorption of quadrol onto chitosan did not proceed in the whole pH-range investigated. The sorption of Cu(II) in quadrol-containing solutions proceeds only in pH range 6–8, which is very low as compared with that in other ligand-containing solutions.

Such peculiarities of Cu(II) complex sorption onto chitosan in mildly acidic and neutral solutions also reflects the importance of the stability of the Cu(II) complexes with the ligands investigated. The degree of Cu(II) removal, apparently, is related to the stability of Cu(II) complexes, which could be arranged in the following order: quadrol (p$K_{1,2}$ ∼10) > glycine (p$K_{1,2}$ ∼8) > tartrate (p$K_{1,2}$ 6) [26,28,32]. When the stability of Cu(II) complex is lower, the removal of Cu(II) is more complete. Therefore the most complete sorption of Cu(II) proceeds in tartrate-containing solutions. From glycine-containing solutions Cu(II) is sorbed in a considerably lower degree at pH values close to neutral. On the other hand, the increased sorption of Cu(II) from glycine-containing solutions with increase in pH, when the stability of glycine complex increases points to on the possible changes in the sorption mechanism with change in pH. Taking into account the possible donor–acceptor interaction between the metals and ligands and metals and amine or hydroxyl groups of chitosan and the competitive adsorption between Cu^{2+} and ligands onto chitosan, the sorption mechanism should be even more complicated.

The influence of chitosan dose onto its sorption ability in different ligands containing solutions indicates also the complexity of the process (Fig. 2). The low portions of chitosan only have a remarkable influence on the sorbed quantities of Cu(II) and ligands from solutions. The chitosan doses higher than 10 g L^{-1} do not have any considerable influence on sorption ability.

The investigations at equilibrium conditions (Fig. 3) showed an increasing sorption of Cu(II) with increase in its concentration in solutions. The sorption of tartrate increases as well. The sorption of other two ligands – glycine and quadrol – was not determined due to their low sorbed quantities.

The Cu(II) sorption peculiarities were evaluated by testing the experimental data according to Langmuir and Freundlich isotherms [33]. Langmuir isotherm describes the sorption process in the case of monolayer coverage. Its linear expression is:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{C_e}{q_m}$$

Fig. 2. Influence of chitosan amount on Cu(II) (1, 2 and 3) and ligand (1′, 2′ and 3′) sorption from solutions containing 10 mmol L^{-1} Cu(II) and 25 mmol L^{-1} tartrate at pH 6 (1 and 1′); 10 mmol L^{-1} Cu(II) and 25 mmol L^{-1} glycine (2 and 2′) at pH 11; 10 mmol L^{-1} Cu(II) and 20 mmol L^{-1} quadrol at pH 6 (3 and 3′). Temperature 20 °C.
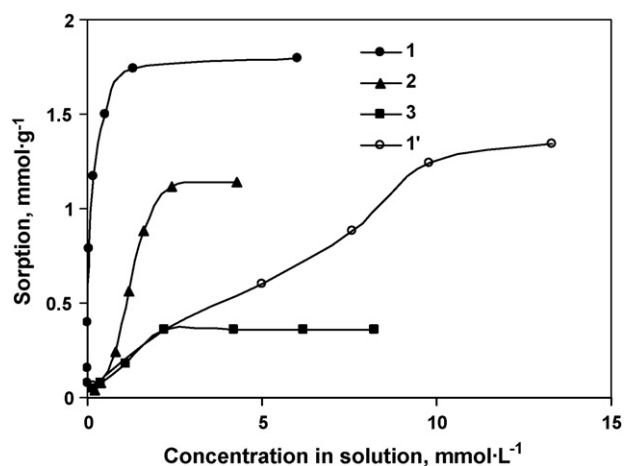
Fig. 3. Sorption isotherm for Cu(II) (1, 2 and 3) and tartrate (1′) at concentration ratios between Cu(II) and ligands 2.5 from solutions containing Cu(II) and tartrate at pH 6 (1 and 1′); Cu(II) and glycine (2) at pH 11; Cu(II) and quadrol at pH 6 (3). Temperature 20 °C; load of chitosan 5 g L^{-1}.

Table 1
Parameters of Langmuir and Freundlich equations for Cu(II) sorption onto chitosan.

Ligand	Langmuir equation			Freundlich equation		
	K_a, L mmol^{-1}	q_m, mmol g^{-1}	R^2	K_F, L g^{-1}	$1/n$	R^2
Tartrate	0.12	1.99	0.8024	4.83	0.726	0.9967
Glycine	2.04	1.8	0.9998	1.64	0.3468	0.9382
Quadrol	0.86	0.42	0.978	6.56	0.5381	0.9202

where K_a is the Langmuir constant, q_m is the maximum sorption corresponding to the monolayer coverage, and C_e and q_e are the equilibrium concentrations of adsorbate in solution and in sorbent, respectively. The plotting C_e/q_e versus C_e enables to determine K_a and q_m.

The linear form of Freundlich isotherm is as follows:

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e)$$

According to the adsorption theory, constant K_F indicates the chitosan sorption capacity when the concentration of adsorbate in solution is equal to 1 mol L^{-1}. The coefficient $1/n$ represents the sorption intensity and adsorbent heterogeneity.

These parameters are presented in Table 1.

The high values of regression coefficients R^2 indicate that the sorption obeys Langmuir or Freundlich equation. In case of Cu(II) sorption from tartrate solutions, when the intense sorption of ligand proceeds, it is not likely that the sorption could fit the Langmuir model, i.e. Cu(II) should make the monolayer on the surface of chitosan. In this case the Freundlich model better describes the sorption process; although the fit of this equation could be rather

coincidental than indicating the sorbent heterogeneity. On the other hand, the surface heterogeneity for Cu(II) sorption could be assumed as the partial its coverage with tartrate. In case of Cu(II) sorption from glycine and quadrol solutions, when the ligand sorption does not proceed, the Langmuir equation better describes the sorption process.

From a practical viewpoint, the sorption in alkaline solutions containing an additive glycine is most interesting. Such a composition of solutions coincides with that of the wastewaters of electroless copper plating. The results of sorption experiments are presented in Table 2. As it can be expected, significant sorption of ligands does not proceed in alkaline solutions. Tartrate and glycine are sorbed best in neutral solutions. These ligands in alkaline solutions are sorbed in a considerably lower degree.

Cu(II) ions from glycine as well as from the mixture of glycine- and tartrate-containing solutions are removed best in alkaline solutions. The remarkable decrease in residual Cu(II) concentration in the case of addition of glycine to tartrate containing alkaline solutions in comparison with solutions containing only glycine or tartrate is unexpected and hardly could be explained by complex formation in relation to their stability. In this case the chemical interactions could play an important role. It is worth noting that the addition of glycine to quadrol solutions has no influence on sorption.

FT-IR spectra of pure chitosan and these after sorption of Cu(II) complexes are presented in Fig. 4. The peak 1560 cm^{-1}, which appears in the spectrum of pure chitosan, is attributed to the –NH$_2$ group due to N–H deformation vibration. It is shifted to a higher wavenumber (~1600 cm^{-1}) in the spectra of chitosan after sorption of Cu(II) complexes. This indicates that H atom in the N–H bond has been substituted by Cu(II) ions, apparently, with formation of Cu(II)–amino surface complexes. The peaks at 1660 cm^{-1} which may also belong to amide I band and 1600 cm^{-1}, which is attributed to amide II, may be overlapped by both N–H deformation and C–N stretching vibrations (1630 cm^{-1}). In the case of Cu(II)–tartrate complex sorption, the increased intensity of both peaks at 1660 and 1600 cm^{-1}, indicates the formation of amide bonds between –COOH groups of tartrate and –NH$_2$ groups of chitosan.

3.2. Regeneration of chitosan

Desorption of Cu(II) and ligands from chitosan, i.e. its regeneration depends mainly on the chemical composition of ligand. The acidic treatment enables to regenerate chitosan with sorbed Cu(II) ions only, viz. when the Cu(II) sorption proceeds in glycine-containing solutions at pH ~12 or in quadrol-containing solutions. However, in the case of sorption of ligands the chitosan cannot be regenerated by changing pH. Electrolysis is proposed for chitosan regeneration after carboxylic acid sorption [18].

In this case electrolysis was also applied for regeneration of chitosan after sorption of Cu(II) complexes with the purpose to reuse
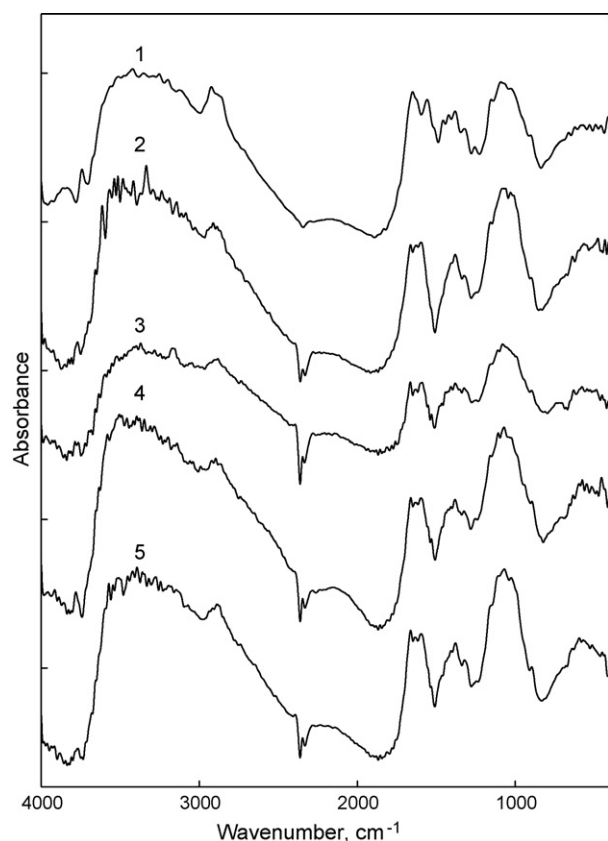
Table 2
Cu(II) and ligand sorption onto chitosan in mixture of ligands at chitosan dose of 5 g L^{-1}.

Composition of solutions, mmol L^{-1}	pH	Degree of removal, %		Residual concentrations, mmol L^{-1}	
		Cu(II)	Ligand	Cu(II)	Ligands
Cu(II) 10; tartrate 40	7	95	35	0.5	26
Cu(II) 10; tartrate 40	12	65	~0	3.5	40
Cu(II) 10; glycine 25	5	44	20	5.6	20
Cu(II) 10; glycine 25	12	97	~0	0.3	25
Cu(II) 10; quadrol 20	7	22	0	7.8	20
Cu(II) 10; tartrate 40; glycine 25	7	21	50	5.9	≪40 mmol L^{-1} tartrate + 25 mmol L^{-1} glycine
Cu(II) 10; tartrate 40; glycine 25	12	99.9	13	0.01	<40 mmol L^{-1} tartrate + 25 mmol L^{-1} glycine
Cu(II) 10; quadrol 20; glycine 25	7	22	~0	7.8	≈20 mmol L^{-1} quadrol + 25 mmol L^{-1} glycine
Cu(II) 10; quadrol 20; glycine 25	12	~0	~	10	≈20 mmol L^{-1} quadrol + 25 mmol L^{-1} glycine

Fig. 4. FT-IR spectra of pure chitosan (1) and after sorption in Cu(II)-complex solutions, containing tartrate (2) at pH 6; glycine and tartrate at pH 11 (3); quadrol at pH 6 (4); glycine at pH 6 (5).
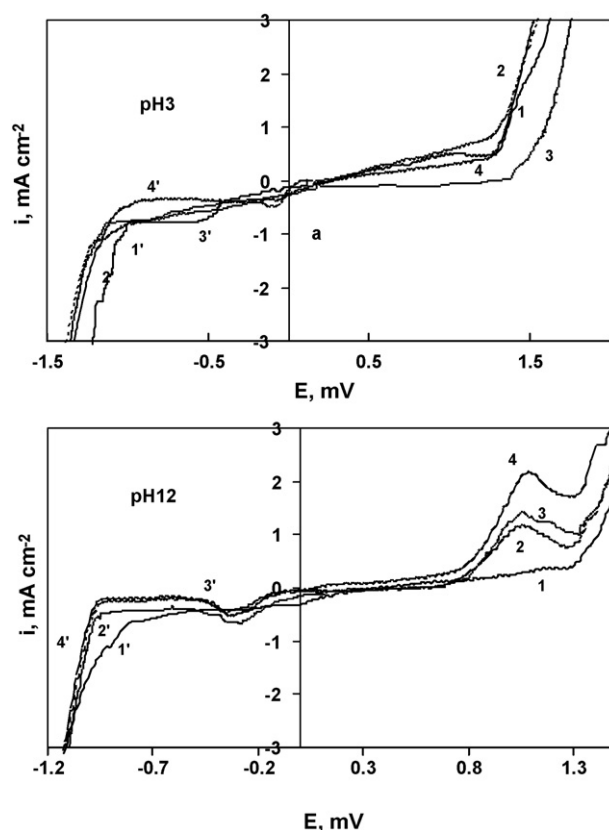

Fig. 5. Anodic (1, 2, 3 and 4) and cathodic (1′, 2′, 3′ and 4′) voltammograms of Pt electrode in 0.1 mol L^{-1} Na$_2$SO$_4$ solutions; 1 and 1′: without chitosan and containing 1 g L^{-1} chitosan sorbed Cu(II) 098 mmol and tartrate 2.5 mmol (2 and 2′), Cu(II) 0.5 and glycine 0.3 (3 and 3′) and Cu(II) 0.4 mmol, tartrate 0.44 and glycine 0.05 mmol (4 and 4′).

it anew. Cathodic and anodic voltammograms recorded in acidic solutions at pH 3 and alkaline solutions at pH 12 (Fig. 5) showed different behavior of Pt electrode in Na$_2$SO$_4$ solutions containing chitosan sorbed Cu(II) and ligands. In diluted solutions the evolution of hydrogen is the main cathodic reaction, and the evolution of oxygen is the main anodic reaction. The voltammetric investigations showed that at pH 3 remarkable polarization of Pt electrode proceeds in the cathodic process in all the cases investigated, meanwhile some retarding effect in the anodic process is observed only in the case of sorption in glycine-containing solutions. The reason could be a high inhibition action of glycine [34]. At pH 12 (Fig. 5) the anodic process is more intensive at potentials more negative than the potentials of oxygen evolution. Thus, the voltammetric investigations show that the cathodic deposition of copper proceeds best in acidic solutions and the anodic oxidation of organic ligands—in alkaline solutions. However, during electrolysis the pH value in the cathodic department increases while in the anodic one—decreases.

Thus, the regeneration of chitosan applying electrolysis requires regular pH adjustment.

The parameters of electrochemical regeneration of chitosan and its properties are presented in Table 3. The data show that the appropriate conditions of electrolysis enable successful regeneration of chitosan. The best results are obtained at a lower current strength and more prolonged electrolysis, meanwhile high current strengths lead to destruction of chitosan. A lower deacetylation degree indicates an insufficient current quantity applied to regeneration. In this case some increase in molecular weight also is observed. This could happen due to cross-linking of chitosan chains, if the sorption of tartrate proceeded with formation of covalent bonds. The imperfect electrolysis leads also to insufficient removal of sorbed copper complexes from chitosan. High current strengths applied to regeneration lead to destruction of chitosan molecules. This was confirmed by the decreased molecular weights measured.
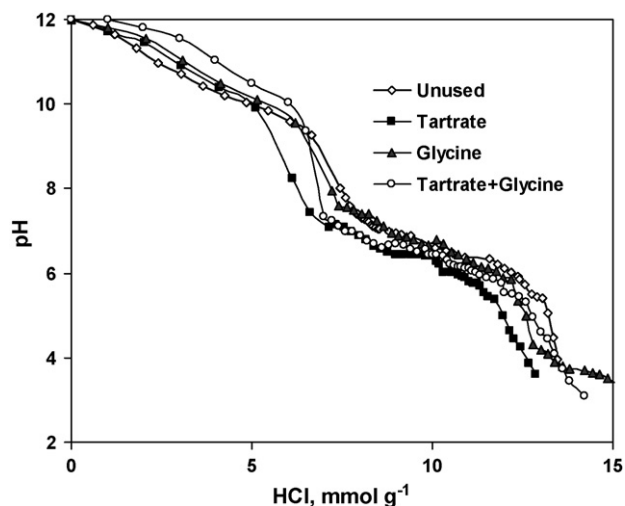
Table 3
The parameters of electrochemical regeneration of chitosan and its properties.

Sorbed quantity, mmol g^{-1}	Conditions of electrolysis		Properties of regenerated chitosan		Sorption ability after electrolysis, mmol g^{-1}	
	Current intensity, mA	Duration of electrolysis, h	Molecular weight	Deacetylation degree, %	Cu(II)	Ligand
Initial chitosan			150,000	80		
Cu(II) 098; tartrate 2.5	50	4	18,000	70	1	1
	100	4	160,000	80	1	2.6
	200	8	60,000	85	1.2	1.9
Cu(II) 0.5; glycine 0.3	50	4	145,000	80	0.6	0.4
	100	4	120,000	85	0.8	0.4
	200	4	60,000	85	0.7	0.5

Fig. 6. pH-Metric titration curves of unused chitosan and regenerated ones after sorption of Cu complexes with tartrate and glycine.

However, the electrochemical regeneration of chitosan enables to choose the conditions, when a complete removal of sorbed Cu(II) complexes can be achieved without any remarkable change in the physicochemical properties of chitosan. This was confirmed by pH-metric titration curves (Fig. 6) and FT-IR investigations (Fig. 7). The chitosan titration curves are very similar to those of pure chitosan. The spectra of regenerated chitosan exhibit a distinct peak at 1560 cm^{-1}, which is attributed to the –NH$_2$ group of chitosan. Under the optimal conditions of electrolysis the FT-IR spectra of regenerated chitosan after sorption of Cu(II) complexes with tar-
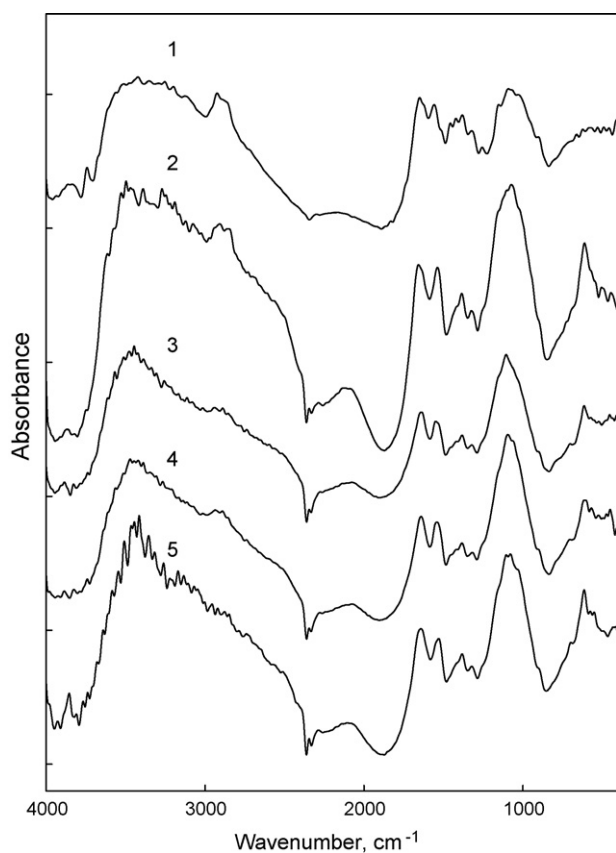
trate and glycine are identical to the spectra of pure chitosan. The sorption ability of chitosan regenerated under optimal conditions is similar to that of initial chitosan. It is worth noting that even when the physicochemical properties of chitosan are changed by applying electrolysis, its sorption ability remains high.

The comparison of the results obtained earlier for chitosan regeneration after sorption of tartrate [18] and Cu(II)–tartrate complex indicates, that in the latter case chitosan is regenerated more easily, i.e. the regeneration takes less current quantities for desorption of the same quantity of tartrate. The reason of such an effect could be different sorption mechanisms. In the case of Cu(II)–tartrate sorption, the –NH$_2$ groups of chitosan could interact both with Cu(II) ions forming amino complexes and with tartrate forming amide bonds.

On the whole, among the Cu(II) complexes investigated, only tartrate-containing solutions can be effectively decontaminated by chitosan. After the sorption chitosan can be regenerated applying electrolysis and reused anew. Usually electrolysis is assumed as a cost-effective treatment technology for wastewaters containing the heavy metals (cathodic deposition) and organic compounds (anodic oxidation) [35]. However, its efficiency decreases with decrease in concentration of pollutants in wastewaters. On the contrary, sorption is applied for concentration of pollutants in diluted solutions. The subsequent application of these two methods, sorption onto chitosan and its electrochemical regeneration, enables to solve problems of wastewater treatment in manufacture of printed circuit boards and other branches of industry, where the electrochemical equipment is used.

4. Conclusions

Cu(II) sorption onto chitosan from solutions containing ligands depends on the nature of ligands and pH of solutions. Cu(II) is sorbed best from tartrate-containing solutions in mildly acidic and neutral solutions. This sorption obeys Freundlich isotherm. Tartrate is also sorbed simultaneously with Cu(II) by chitosan. A complete sorption of Cu(II) proceeds in alkaline glycine-containing solutions. The sorption of glycine by chitosan is insignificant. The lowest sorption of Cu(II) proceeds in quadrol-containing solutions. Quadrol is not sorbed by chitosan.

Applying electrolysis enables to remove sorbed Cu(II) and ligands from chitosan. The regeneration efficiency depends on the current strength and duration of electrolysis.

Fig. 7. FT-IR spectra of pure chitosan (1) and after regeneration of sorbed Cu(II)-complexes with: tartrate (2) at pH 6; glycine and tartrate at pH 11 (3); quadrol at pH 6 (4); glycine at pH 6 (5).

References

[1] B. Nowack, Environmental chemistry of aminopolycarboxylate chelating agents, Environ. Sci. Technol. 36 (2002) 4009–4016.

[2] L.H. Wu, Y.M. Luo, P. Christie, Effects of EDTA and low molecular weight organic acids on soil solution properties of a heavy metal polluted soil, M. H. Wong, Chemosphere 50 (2003) 819–822.

[3] G. Skodras, P. Grammelis, M. Prokopidou, E. Kakaras, G. Sakellaropoulo, Chemical, leaching and toxicity characteristics of CFB combustion residues, Fuel 88 (2009) 1201–1209.

[4] E. Marguí, V. Salvadó, I. Queralt, M. Hidalgo, Comparison of three-stage sequential extraction and toxicity characteristic leaching tests to evaluate metal mobility in mining wastes, Anal. Chim. Acta 524 (2004) 151–159.

[5] M.D. Tucker, L.L. Barton, B.M. Thomson, B.M. Wagener, A. Aragon, Treatment of waste containing EDTA by chemical oxidation, Waste Manage. 19 (1999) 477–482.

[6] M. Verhaege, G. Lissens, K. Van Hege, M. Verstracte, Elimination of organic pollutants from plating rinse solutions by electrochemical treatment, in: B. Bjorkman, C. Samuelsson, J.-O. Wirkstrom (Eds.), Recycling and Waste Treatment in Mineral and Metal Processing: Technical and Economic Aspects, vol. 1, Lulea, Sweden, 2002, pp. 541–550.

[7] X.S. Wang, Z.Z. Li, C. Sun, A comparative study of removal of Cu(II) from aqueous solutions by locally low-cost materials: marine macroalgae and agricultural by-products, Desalination 235 (2009) 146–159.

[8] B. Pejic, M. Vukcevic, M. Kostic, P. Skundric, Biosorption of heavy metal ions from aqueous solutions by short hemp fibers: effect of chemical composition, J. Hazard. Mater. 164 (2009) 146–153.

[9] M. Otero, F. Rozada, A. Morán, L.F. Calvo, A.I. García, Removal of heavy metals from aqueous solution by sewage sludge based sorbents: competitive effects, Desalination 239 (2009) 46–57.

[10] O. Gylienė, M. Šalkauskas, R. Rekertas, Removal of free and complexed heavy-metal ions by sorbents produced from fly (*Musca domestica*) larva shells, Water Res. 36 (2002) 4128–4136.

[11] I.G. Lalov, I. Guerginov, M.A. Krysteva, K. Farsov, Treatment of waste water from distilleries with chitosan, Water Res. 34 (2000) 1503–1506.

[12] F.-C. Wu, R.-L. Tseng, R.-S. Juang, Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan, Water Res. 35 (2001) 613–648.

[13] M.V. Shamov, S.Y. Bratskaya, V.A. Avramenko, Interaction of carboxylic acids with chitosan: effect of pK and hydrocarbon chain length, J. Coll. Interf. Sci. 249 (2002) 316–321.

[14] K.H. Chu, Removal of copper from aqueous solutions by chitosan in prawn shell: adsorption equilibrium and kinetics, J. Hazard. Mater. 90 (2002) 77–95.

[15] T.J. Beveridge, M.N. Hughes, H. Lee, K.T. Leung, R.K. Poole, I. Savvaidis, S. Silver, J.T. Trevors, Metal–microbe interactions: contemporary approaches, Adv. Microb. Physiol. 38 (1996) 177–243.

[16] M. He, G. Tian, X. Liang, Phytotoxicity and speciation of copper, zinc and lead during the aerobic composting of sewage sludge, J. Hazard. Mater. 163 (2009) 671–677.

[17] O. Gylienė, O. Nivinskienė, I. Razmutė, Copper(II)–EDTA sorption onto chitosan and its regeneration applying electrolysis, J. Hazard. Mater. 137 (2006) 1430–1437.

[18] O. Gylienė, O. Nivinskienė, T. Vengris, Sorption of tartrate, citrate, and EDTA onto chitosan and its regeneration applying electrolysis, Carbohyd. Res. 343 (2008) 1324–1332.

[19] G.C. Ritthidej, T. Phaechamud, T. Koizumi, Moist heat treatment on physicochemical change of chitosan salt films, Int. J. Pharm. 232 (2002) 11–22.

[20] M. Bodnar, J.F. Hartmann, J. Borbely, Preparation and characterization of chitosan-based nanoparticles, Biomacromolecules 6 (2005) 2521–2527.

[21] R.-S. Juang, F.-C. Wu, R.-L. Tseng, Adsorption removal of copper(II) using chitosan from simulated rinse solutions containing chelating agents, Water Res. 33 (1999) 2403–2409.

[22] F.-C. Wu, R.-L. Tseng, R.-S. Juang, Role of pH in metal adsorption from aqueous solutions containing chelating agents on chitosan, Ind. Eng. Chem. Res. 38 (1999) 270–275.

[23] O. Gylienė, R. Tarozaitė, O. Nivinskienė, Sorption of Ni(II)–citrate complex from electroless nickel plating solutions onto chitosan, Trans. Inst. Met. Finish. 82 (1–2) (2004) 38–42.

[24] J. Guzman, I. Saucedo, J. Revilla, R. Navarro, E. Guibal, Copper sorption by chitosan in the presence of citrate ions: influence of metal speciation on sorption mechanism and uptake capacities, Int. J. Biol. Macromol. 33 (2003) 57–65.

[25] K. Inoue, K. Yoshizuka, K. Ohto, Adsorptive separation of some metal ions by complexing agent types of chemically modified chitosan, Anal. Chim. Acta 388 (1999) 209–218.

[26] E. Norkus, A. Vaškelis, I. Žakaitė, J. Reklaitis, Polarographic investigation of Cu(II) complexes with N,N,N′,N′-tetrakis-(2-hydroxypropyl)-ethylenediamine, Talanta 42 (1995) 1701–1705.

[27] G. Orhan, S. Gurmen, S. Timur, The behaviour of organic components in copper recovery from electroless plating bath effluents using 3D electrode systems, J. Hazard. Mater. 112 (2004) 261–267.

[28] E. Norkus, A. Vaškelis, I. Stalnionienė, Mischpotential von Kupfer in Lösungen zur stromlosen Verkupferung unter Anwendung von Quadrol, L(+) und DL(+) Tartrat als Kupferionenliganden, Galvanotechnik 95 (2004) 2646–2655, (in German).

[29] A. Vaškelis, E. Norkus, I. Stalnionienė, G. Stalnionis, Effect of the Cu electrode formation conditions and surface nano-scale roughness on formaldehyde anodic oxidation, Electrochim. Acta 49 (2004) 1613–1621.

[30] F.J. Welcher, Industrial and natural products and noninstrumental methods, Part B, in: F.J. Welcher (Ed.), Standard Methods of Chemical Analysis, vol. 2, 6th ed., D. Van Nostrand Co., Inc., Toronto–New York–London, 1967.

[31] K.V. Harish, F.S. Prashanth, N. Kittur, R.R. Tharanathan, Solid state structure of chitosan prepared under different N-deacetylating conditions, Carbohyd. Polym. 50 (2002) 27–33.

[32] Stability constants. Metal Ion Complexes. Special publication No. 17, 1964, The Chemical Society, London.

[33] Y.S. Ho, C.C. Wang, Pseudo isotherms for the sorption of cadmium ion onto tree fern, Process Biochem. 39 (2004) 761–765.

[34] A.A. El-Shafei, M.N.H. Moussa, A.A. El-Far, Inhibitory effect of amino acids on Al pitting corrosion in 0.1 M NaCl, J. Appl. Electrochem. 27 (1997) 1075–1078.

[35] A.J. Chaudhary, J.D. Donaldson, S.M. Grimes, M. ul-Hassen, R.J. Spencer, Simultaneous recovery of heavy metals and degradation of organic species—copper and ethylendiaminetetra-acetic acid (EDTA), J. Chem. Technol. Biotechnol. 75 (2000) 353–357.