

# Copper(II)–EDTA sorption onto chitosan and its regeneration applying electrolysis

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## Abstract

Cu(II)–EDTA (ethylenediaminetetraacetate) complexes are widely used in the manufacture of printed circuit boards. In order to avoid the outlet into the environment the sorption of complexes onto chitosan is proposed. The uptake of both Cu(II) and EDTA proceeds in weakly acidic (pH 3–5) and strongly alkaline (pH > 12) solutions. In acidic solutions EDTA sorption prevails. FT-IR investigations have shown that in acidic solutions the amide bonds between –COOH groups of EDTA and –NH<sub>2</sub> groups of chitosan were formed. In alkaline solutions the single EDTA sorption does not proceed. In this media the sorption is enhanced by Cu(II) ions. The possible sorption mechanisms are discussed.

The uptake of both Cu(II) and EDTA by chitosan depends on the ratio between them in solutions. EDTA sorption in acidic solutions increases with increase in its concentration while that of Cu(II) decreases. In alkaline solutions the sorption of both Cu(II) and EDTA increases with increase in Cu(II) concentration.

The use of electrolysis enables to regenerate chitosan and to reuse it. During electrolysis copper is deposited onto the cathode and EDTA is oxidized onto the anode. The current efficiency depends on the current intensity, the load of chitosan and the pH of the background electrolyte. Electrolysis under the most favorable conditions ensures the 10-cycles regeneration without considerable changes in the sorption properties of chitosan. FT-IR spectra of the initial and regenerated chitosans are similar.

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**Keywords:** EDTA; Cu(II); Sorption; Chitosan; Regeneration

## 1. Introduction

Soluble heavy metal complexes are widely used in industry, agriculture and household. Cu(II)–EDTA complexes are used for electroless copper plating in manufacture of printed circuit boards. Though EDTA is considered as non-toxic, it is not biodegradable in the environment. Moreover, EDTA acts as a powerful complexing agent for soil metals such as Ca(II), Mg(II), Al(III), Fe(III) and changes their equilibrium concentrations in aquatic systems [1,2].

The recovery of metals from complex solutions is performed, as a rule, only after destruction of ligands. Commonly for ligand destruction chemical [3,4] and electrochemical [5–7] oxidation is used. Sorption is used mainly for metal recovery from dilute solutions. In practice the synthetic ion exchangers are used as

sorbents. However, the increasing wastewater volumes require new and cost effective technologies, one of which is the use of biosorbents. Usually, the agricultural and wood treatment wastes are used as biosorbents. Differently from synthetic sorbents the biosorbents are bio-renewable, biodegradable and cost-effective. However, the sorption ability of biosorbents usually is lower; their regeneration in many cases is not a solved task. Chitin containing biosorbents is distinguished for its high sorption ability and selectivity for heavy metals. Chitosan, the deacetylated chitin, is able to sorb both heavy metals and organic compounds. The sorption ability of chitosan in many cases exceeds that of synthetic sorbents.

The regularities of heavy metal sorption by chitosan are widely studied. The chitosan sorption ability depends on its physical and chemical properties. The deacetylation degree (the number of amino groups in polymer molecule) has the decisive influence. The amino groups interact with heavy metal ions forming the complexes on the sorbent surface. Metal ions may be bound with several nitrogen atoms from the same or from

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different chains of chitosan (“bridge model”) or with the single amino group (“pendant model”). The residual sites could be occupied by –OH group of chitosan or by H<sub>2</sub>O or hydroxyl group [8,9].

The sorption ability of chitosan for heavy metal complexes is poorly investigated [10–14]. As a rule, it is lower for heavy metals as compared to that of free metal ions. Carboxylic acids, which act as the ligands for heavy metal ions, interact with the amino group of chitosan forming amide bonds [15,16]. The amide group forms weaker complexes with metals as compared to those formed by the amino group. On the other hand, the emerged new functional groups from carboxylic acids can act as ligands for heavy metal ions [16,17].

Desorption of heavy metal complexes from chitosan remains poorly investigated. In the case of free metal ions such as Cu(II), Ni(II), Zn(II), UO<sup>2+</sup>, desorption proceeds only in strong acidic solutions. However, in such a medium the dissolution of chitosan proceeds, except for sulfuric acid solutions, where chitosan is insoluble. In the case of ligand sorption the amide groups formed are stable and their conversion into amine groups requires special treatment (deacetylation). It is usually carried out in alkaline solutions at high temperatures [18].

The aim of this study was to investigate the regularities of Cu(II)–EDTA sorption by chitosan and chitosan regeneration after sorption using electrolysis.

## 2. Experimental

Chitosan (with 85% deacetylation) was used as purchased from “Reagent” (Russia) in the form of flakes.

The deacetylation degree (DD) of chitosan was determined after dissolution in HCl and titration with NaOH. The volume of alkali needed to neutralize the protonated amino groups was calculated from the points corresponding to the sharp change in the slope of the titration curve.

The average molecular weight ( $M$ ) of chitosan was calculated by Mark–Houwink equation  $\eta = K_m M^\alpha$  ( $M = (\eta/K_m)^{1/\alpha}$ ), where  $\eta$  is the relative viscosity, constants  $K_m = 3.5 \times 10^{-4}$  and  $\alpha = 0.76$  [19]. The viscosity measurements in 0.5 mol/l acetic acid and 0.2 mol/l sodium acetate buffer were performed using Ostwald viscometer and recording the efflux time of solution at 25 °C.

All sorption and desorption experiments were carried out under batch conditions. The load was 10 g of dry sorbent per litre of solution in sorption experiments. The adsorption was investigated at room temperature by pouring CuSO<sub>4</sub> and Na<sub>2</sub>EDTA containing solutions onto chitosan. pH was adjusted with NaOH or H<sub>2</sub>SO<sub>4</sub> solutions. Desorption experiments followed the adsorption experiments. After sorption, chitosan was filtered and rinsed with cold deionized water and dried at 70 °C. Desorption was carried out by pouring it with 0.1 mmol l<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> solutions. Analysis and electrolysis were carried out after 1 day at least, when the equilibrium concentrations were reached. The sorbed and desorbed quantities of Cu(II) and EDTA were determined from the changes in their concentrations in solutions.

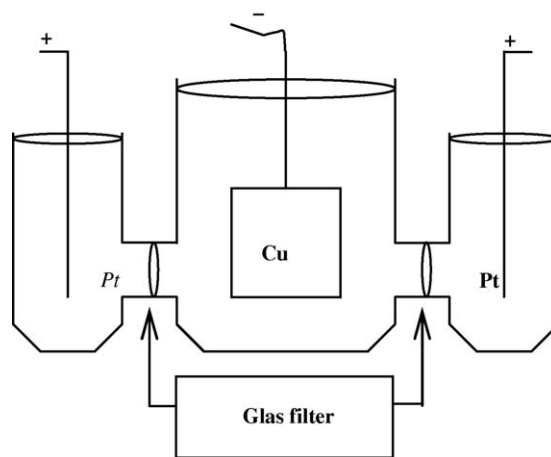


Fig. 1. Electrochemical cell for galvanostatic investigations.

Regeneration of chitosan was carried out electrochemically under galvanostatic conditions using a ПИ-51 potentiostat (Russia) and three camera cells – cathodic with a volume of 80 ml and two anodic with a volume of 10 ml each separated by a glass filter (Fig. 1).

Chitosan containing Cu(II)–EDTA was loaded in the cathodic compartment. The copper sheet of 40 cm<sup>2</sup> was used as a cathode and Pt wires of 0.5 cm<sup>2</sup> each as anodes. The electrochemical cell was filled with a 0.1 mol l<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> solution. The solution with chitosan was mixed using a magnetic stirrer during electrolysis. In long term experiments, when electrolysis was off, the catholyte and anolyte were poured out separately from the cells.

The content of Cu(II) in chitosan was determined after treatment of 0.02–0.05 g of dried samples with a mixture of H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> at high temperatures according to [20].

The current efficiency for Cu(II) and EDTA was determined from the ratio between the Cu(II) or EDTA removed during regeneration and the theoretically calculated copper deposition or EDTA oxidation mass ( $m$ ) according to Faraday’s law:

$$m = \frac{M}{nF} It,$$

where  $M$  is the molar mass of substances,  $I$  the current intensity (A),  $t$  the time (s),  $n$  the equivalent of substances, for Cu(II) it is equal to 2, and for EDTA – 32, and  $F$  is the Faraday’s number equal to 96,500 °C.

EDTA in solutions was determined complexometrically by titration with Bi(III) in acidic solutions (pH ~3 adjusted with HNO<sub>3</sub>). In electrochemical experiments EDTA was determined by oxidation with the excess of KMnO<sub>4</sub> in alkaline solutions and retitrated with oxalic acid in acidic solutions [21].

Cu(II) was determined after its reduction to Cu(I) by means of iodide in acidic solutions. The concentration of iodine formed was determined by titration with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. Low concentrations of Cu(II) were determined photometrically using diethylditiocarbamate as an indicator [21]. The infrared spectra of chitosan were recorded in KBr pallets on a Fourier transformation infrared spectrometer (Hartman & Braun, Canada) with 2 cm<sup>-1</sup> scale resolutions.

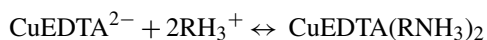
Table 1  
pH influence on Cu(II) and EDTA uptake by chitosan from solution containing 10 mmol l<sup>-1</sup> CuSO<sub>4</sub> and 12 mmol l<sup>-1</sup> EDTA

pH	Cu(II) (mmol g <sup>-1</sup> )	EDTA (mmol g <sup>-1</sup> )
2	0.4	0.47
3	0.45	0.35
4	0.35	0.33
5	0.25	0.17
6	0.15	0.17
7	0.15	0.05
8	0.01	0.05
9	0.01	0.02
10	0.01	0.01
11	0.05	0.03
12	0.1	0.06
12.5	0.35	0.25
13	0.4	0.4

### 3. Results and discussion

The retarding effect of EDTA on Cu(II) sorption by chitosan is described in Refs. [10,11]. It is explained by competition between coordination of Cu(II) with unprotonated chitosan and electrostatic interaction of Cu(II) chelate with protonated amino groups. However, the uptake of EDTA by chitosan has not been investigated. Our experiments were carried out in a wide range of pH and EDTA concentrations with the purpose to find the maximum sorption of both Cu(II) and EDTA.

Experiments have shown (Table 1) that the best sorption of both Cu(II) and EDTA proceeds in acidic (pH 3–4) and alkaline solutions (pH 12–13). In the close to neutral media the sorption is negligible. The reason of prevailing Cu(II)–EDTA sorption in acidic solutions, when comparing with that in neutral and weakly alkaline solutions, could be electrostatic interaction of an anionic complex with protonated amino groups of chitosan [11] according to the equation:



This mechanism proposed by Wu et al. is supported by changes in pH. During the complex sorption the pH increases and to maintain the pH value constant the acid is added to the solutions.

Our investigations have shown that during sorption of single EDTA the pH increases as well (Table 2). The quantities of acid required maintaining the pH value constant increase with increase in the quantities of EDTA sorbed, though they are not

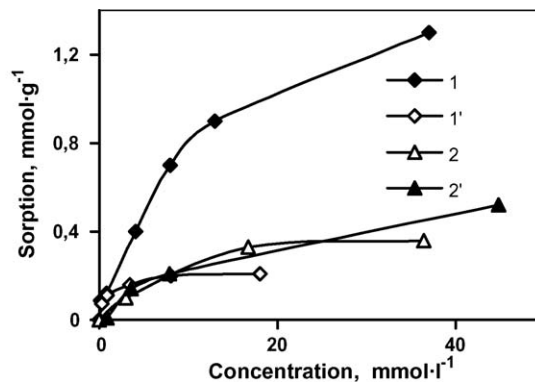


Fig. 2. Sorption isotherms for Cu(II) (1 and 1') and EDTA (2 and 2') at pH 3; single Cu(II) and EDTA (1 and 2) and [Cu(II)]:[EDTA] = 1:2 (1' and 2').

strictly equivalent to them. The Cu(II) uptake depends on the quantity of EDTA sorbed prior to the procedure. Cu(II) uptake decreases with increase in the amounts of EDTA sorbed. The Cu(II) uptake requires again the addition of acid for maintenance of pH 3. It is worth noting that during the sorption of Cu(II) by chitosan containing greater quantities of sorbed EDTA, the maintenance of constant pH-value requires addition of acid immediately after treatment with Cu(II) solution. The Cu(II) uptake is slow. The equilibrium is achieved after 3–5 days by occasional mixing. During the sorption pH decreases, therefore, NaOH is added in order to maintain the pH constant. Obviously, when the large quantity of EDTA is sorbed the interaction of Cu(II) with functional groups of EDTA proceeds. In the pH range 2–6 H<sub>2</sub>EDTA<sup>2-</sup> is the prevailing form of EDTA. Cu(II) ions form complexes substituting the H<sup>+</sup> ions, therefore, solutions become more acidic. In this case to maintain the pH values constant NaOH is added. When the low quantities of EDTA are sorbed, the Cu(II) sorption proceeds probably through chitosan free functional groups.

When experiments were performed in solutions containing approximately equal concentrations of Cu(II) and EDTA the adsorbed quantities were nearly equal (Table 1). However, at different concentrations of Cu(II) and EDTA, the differences in the sorbed quantities revealed themselves. The sorption isotherms (Fig. 2) obtained at pH 3 show that the retarding effect of EDTA on Cu(II) sorption increases with increase in its equilibrium concentrations in solutions. In Cu(II)–EDTA solutions the Cu(II) uptake by chitosan is several times lower than that in solutions without EDTA (curves 1 and 1'). However, the sorption of both

Table 2  
EDTA uptake by chitosan at pH 3 and subsequent Cu(II) uptake from 10 mmol l<sup>-1</sup> CuSO<sub>4</sub>·5H<sub>2</sub>O at pH 3 after EDTA sorption and quantities of H<sub>2</sub>SO<sub>4</sub> and NaOH used for maintaining the constant value of pH

EDTA sorption			Cu(II) sorption		
Initial EDTA concentration (mmol l <sup>-1</sup> )	EDTA sorbed (mmol l <sup>-1</sup> )	H <sub>2</sub> SO <sub>4</sub> used (mmol l <sup>-1</sup> )	Cu(II) sorbed (mmol l <sup>-1</sup> )	H <sub>2</sub> SO <sub>4</sub> used (mmol l <sup>-1</sup> )	NaOH used (mmol l <sup>-1</sup> )
2	0.11	0.16	0.98	0.44	
5	0.2	0.26	0.96	0.46	
20	0.4	0.35	0.8	0.39	0.05
50	1.1	0.38	0.42	0.1	0.025
100	1.5	0.51	0.02	0.05	0.001

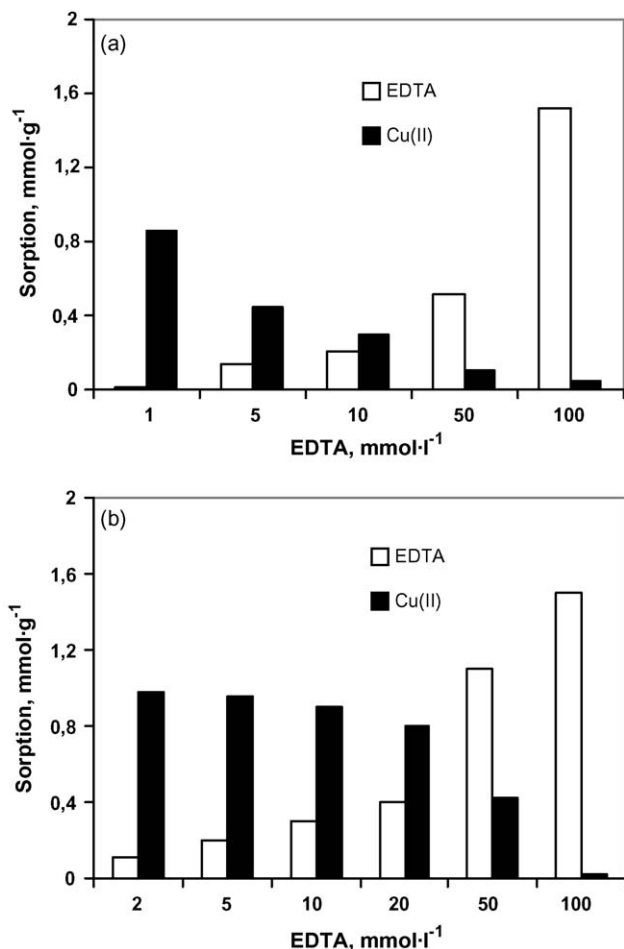


Fig. 3. Influence of EDTA concentration on Cu(II) and EDTA uptake by chitosan: (a) sorption in Cu(II)–EDTA solutions, containing 10 mmol l<sup>-1</sup> Cu(II) and (b) sorption in EDTA solutions and subsequent sorption in 10 mmol l<sup>-1</sup> Cu(II) solutions. pH 3.

free EDTA and from Cu(II)–EDTA solution is similar and the participation of Cu(II) ions in solution has not visible influence on EDTA sorption (Fig. 2, curves 2 and 2'). The prevailing EDTA sorption and its retarding effect on Cu(II) sorption develops only at high EDTA concentrations. At low EDTA concentrations its influence on the Cu(II) uptake is insignificant (Fig. 3). This effect is more evident in Cu(II)–EDTA solutions. When comparing the EDTA sorption in Cu(II)–EDTA solutions (Fig. 3a) and in solutions without Cu(II) ions (Fig. 3b), it is equal in both cases. However, the Cu(II) sorption remarkably differs. In integrated solution the Cu(II) uptake is considerably lower than that in the case of sorption of EDTA alone and the subsequent sorption of Cu(II).

The prevailing EDTA sorption onto chitosan hardly can be explained by electrostatic interactions between them. It is known [22] that in acidic solutions the complexing agent EDTA is covalently bound to the primary amino groups of chitosan with formation of amide bonds. However, the sorption of Cu(II)–EDTA complex in alkaline solutions is even more incomprehensible. We failed to find any literature sources dealing with sorption in strong alkaline solutions, with exception of the work of Juang et al. [10], where the enhanced effect of NaOH on

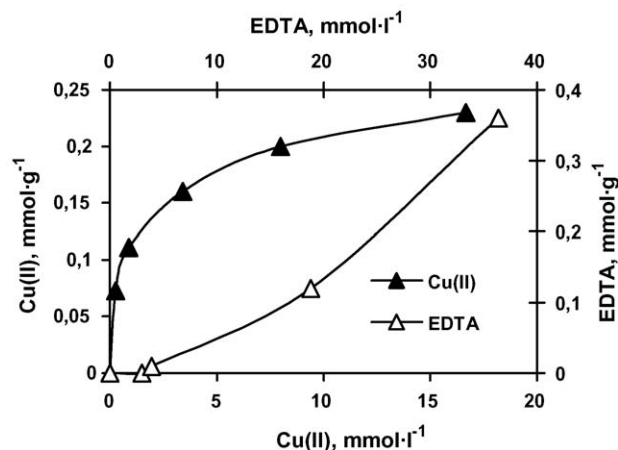


Fig. 4. Sorption isotherms for Cu(II) and EDTA at pH 12.5 and [Cu(II)]:[EDTA]=1:2.

the Cu(II) uptake by chitosan in the presence of EDTA is described.

The electroless copper plating solutions containing a Cu(II)–EDTA complex are alkaline (the reducing agent formaldehyde is sufficiently strong only in alkaline solutions), therefore, the investigations of sorption in alkaline solutions are important from the practical point of view. In strongly alkaline solutions (pH above 12) the hydroxocomplex of CuEDTA(OH)<sup>3-</sup> is formed [23,24]. The logarithm of the stability constant of this complex ( $\text{Cu}^{2+} + \text{EDTA}^{4-} + \text{OH}^- \leftrightarrow \text{CuEDTA}(\text{OH})^{3-}$ ) is equal to 21.1 and it exceeds that of CuEDTA<sup>2-</sup>, which is equal to 18.2. Obviously the most stable complex, hydroxocomplex, is sorbed by chitosan. It is worth noting that the colors of the sorbed onto chitosan complexes are different. Chitosan after sorption in acidic solutions turns blue and in alkaline solutions it turns violet. The reason could be the different composition of the complexes formed in acidic and alkaline solutions.

In contrast to acidic solutions, the EDTA alone sorption in alkaline solutions does not proceed. Under these conditions the Cu(II)–EDTA complex is sorbed. The sorption isotherm (Fig. 4)

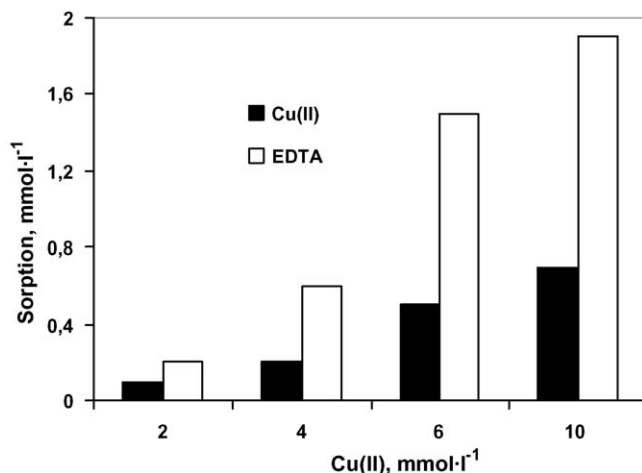


Fig. 5. Influence of Cu(II) concentration on Cu(II) and EDTA sorption at pH 12.5 from solutions containing 100 mmol l<sup>-1</sup> EDTA.



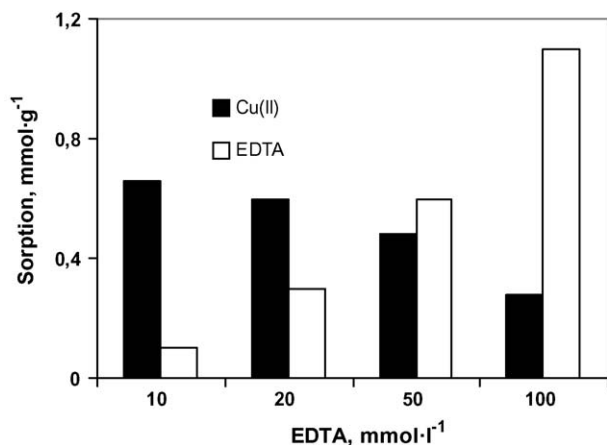


Fig. 6. Influence of initial EDTA concentration on Cu(II) and EDTA sorption at pH 12.5 from solutions containing 10 mmol l<sup>-1</sup> Cu(II).

shows that with increase in the complex concentration, the sorption of Cu(II), along with that of EDTA, increases. The sorbed quantities are similar to those in acidic solutions. When the concentration of EDTA is maintained constant (Fig. 5), the uptake of both EDTA and Cu(II) increases with increase in Cu(II) concentration. When the concentration of Cu(II) is maintained constant, the uptake of both Cu(II) and EDTA increases with increase in EDTA concentration, as well (Fig. 6). The retarding effect of EDTA on Cu(II) sorption in alkaline solutions is not so distinct as that in acidic solutions (Figs. 3a and 6).

The sorption mechanism of Cu(II)–EDTA complex onto chitosan in alkaline solutions is difficult to understand as in alkaline solutions the undissociated –COOH groups cannot be formed and they cannot interact with the –NH<sub>2</sub> groups of chitosan. The negligible sorption of EDTA alone in alkaline solutions confirms this assumption. Apparently, in alkaline solutions the complexing ability of chitosan –NH<sub>2</sub> group increases and its lone nitrogen electron pair makes up an additional complex bond with Cu(II) ion.

FT-IR spectra of free chitosan, Cu(II)–EDTA complex absorbed onto free chitosan and chitosan after regeneration were recorded over a frequency region of 400–4000 cm<sup>-1</sup>. The sorption of EDTA and Cu(II) in acidic solution proceeds via formation of amide bonds between the amino group in chitosan and the carboxyl group in EDTA as indicated by absorption at 1655 and 1550 cm<sup>-1</sup> bands in the FT-IR spectrum (Fig. 7b). When the Cu(II)–EDTA complex was sorbed from solution at pH 3, a strong absorption band at 1629 cm<sup>-1</sup> characteristic of Cu(II)–EDTA complexes overlapped with the amide II band at 1655 cm<sup>-1</sup> giving a very strong peak (Fig. 7c). After sorption of EDTA and Cu(II) in alkaline solution (pH 12.5), the FT-IR spectra showed strong intensity bands at 1660 and 1599 cm<sup>-1</sup> (Fig. 7d and e). Exact assignment of the bands in this spectrum is complicated because Cu<sup>2+</sup> may be absorbed as a chelate coordinated by the amino and/or hydroxyl groups of chitosan.

The sorption of Cu(II)–EDTA is an irreversible process. Desorption cannot be performed in weakly alkaline or neutral solutions where the sorption is negligible. The investigations of desorption are important not only from the practical point of

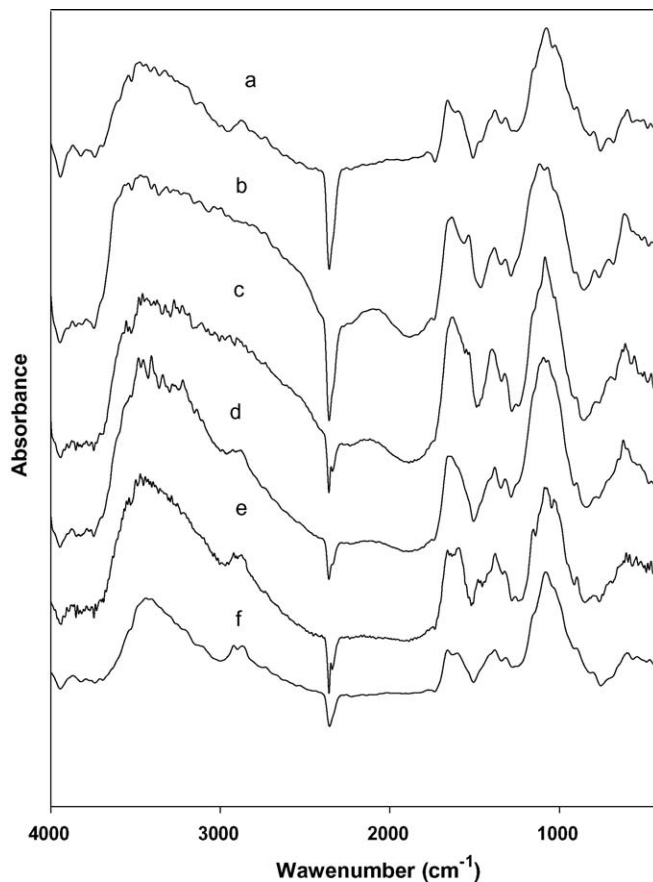


Fig. 7. FT-IR spectra of chitosan: (a) unexploited, (b) after sorption EDTA and Cu(II) from acidic solution at pH 3, (c) after sorption Cu(II)–EDTA complex from acidic solution at pH 3, (d) after sorption EDTA and Cu(II) from alkaline solution at pH 12, (e) after sorption Cu(II)–EDTA complex from alkaline solution at pH 12 and (f) regenerated.

view. These investigations can provide a significant contribution to evaluation of sorption mechanisms.

Detailed investigations of desorption were carried out in the pH range 3–12 in solutions containing 0.1 mol l<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> (Fig. 8). Cu(II) and EDTA desorption depended on sorption conditions and varied with pH. In acidic solutions, Cu(II) desorption weakly depends on pH, meanwhile the EDTA desorption increases with increase in pH. When the sorption is carried out in alkaline solutions, the highest degree of desorption of both Cu(II) and EDTA can be reached in acidic solutions. Desorbed quantities in the best cases did not exceed 10% for EDTA and 3% for Cu(II). Such a negligible desorption at various values of pH indicates that strong bonds between the sorbate and the sorbent exist. On the other hand, the increasing desorption of EDTA with increase in pH (Fig. 8a) could proceed in the case when EDTA was bound with chitosan by electrostatic interaction.

Desorption experiments have shown that the regeneration of sorbent cannot be achieved by acidic or alkaline treatment. It assures at most only a 5–10% desorption. Therefore, attempts were made to regenerate chitosan by using electrolysis, which enables to deposit copper onto the cathode and to oxidize EDTA onto the anode. Na<sub>2</sub>SO<sub>4</sub> was used as the background electrolyte in order to avoid the proceeding of side-electrochemical reac-

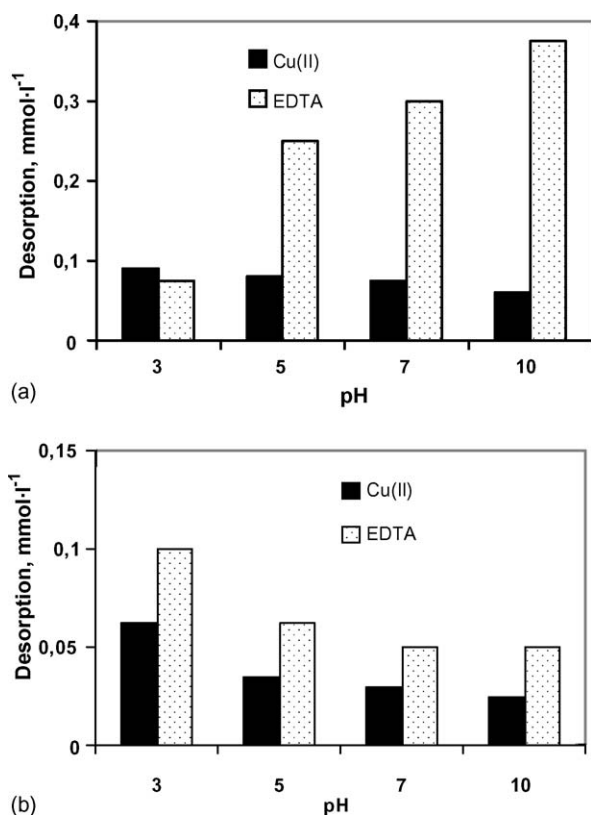


Fig. 8. Influence of pH on Cu(II)-EDTA desorption in  $100 \text{ mmol l}^{-1} \text{ Na}_2\text{SO}_4$  solution after sorption at pH 3 (a) and pH 12.5 (b). Sorbed quantities: Cu(II),  $0.35 \text{ mmol g}^{-1}$  and EDTA,  $0.3 \text{ mmol g}^{-1}$  (a) and Cu(II),  $0.45 \text{ mmol g}^{-1}$  and EDTA,  $0.5 \text{ mmol g}^{-1}$  (b). Load  $10 \text{ g l}^{-1}$ .

tions. During electrolysis, hydrogen evolution along with copper deposition proceeds onto the cathode and oxygen formation along with EDTA oxidation proceeds onto the anode. As a result, the catholyte went alkaline and the anolyte went acidic. Therefore, the pH value in the cathodic part was maintained constant by addition of acids.

The electrolysis data obtained under galvanostatic conditions at pH 3 and a current intensity of  $100 \text{ mA}$  for  $36 \text{ h}$  are tabulated in Table 3. The major part of Cu(II) and EDTA was removed during the first  $16 \text{ h}$ . However, the sorption properties of chi-

Table 3

Electrochemical regeneration of chitosan after sorption (sorption carried out at pH 3) containing  $0.30 \text{ mmol g}^{-1}$  Cu(II) and  $0.63 \text{ mmol g}^{-1}$  EDTA

Duration of electrolysis (h)	Concentrations in solution ( $\text{mmol l}^{-1}$ )			
	Catholyte		Anolyte	
	Cu(II)	EDTA	Cu(II)	EDTA
0	0.3	1.1	0.3	1.1
4	0.1	1.3	0.1	3.3
8	<0.01	2.9	0.1	2.9
16	<0.01	1.5	0.1	1.3
24	<0.01	0.9	0.05	0.8
30	<0.01	0.25	0.01	0.2
36	<0.01	0.2	<0.01	0.2

$I = 100 \text{ mA}$  ( $i_k = 2.5 \text{ mA cm}^{-2}$ ;  $i_a = 100 \text{ mA cm}^{-2}$ ;  $E = 4-5 \text{ V}$ ), pH  $\sim 3$  (catholyte), load  $10 \text{ g l}^{-1}$ .

Table 4

Electrochemical regeneration of chitosan after sorption (sorption carried out at pH 3) containing  $0.45 \text{ mmol g}^{-1}$  Cu(II) and  $1.35 \text{ mmol g}^{-1}$  EDTA without adjusting of pH

Duration of electrolysis (h)	Concentrations in solution ( $\text{mmol l}^{-1}$ )			
	Catholyte		Anolyte	
	Cu(II)	EDTA	Cu(II)	EDTA
0	1.8	5.8	1.8	5.8
1	0.8	7.7	1.7	4.1
4	0.14	8.4	1.5	2.5
10	0.06	5.2	0.9	2.0
16	<0.005	3.0	0.4	0.7
22	<0.005	0.5	0.008	0.3
28	<0.005	0.2	<0.005	0.15

$I = 400 \text{ mA}$  ( $i_k = 10 \text{ mA cm}^{-2}$ ;  $i_a = 400 \text{ mA cm}^{-2}$ ;  $E = 12-14 \text{ V}$ ), load  $40 \text{ g l}^{-1}$ .

tosan at this stage of regeneration were considerably worse than those of fresh chitosan. Only an additional treatment for another  $12 \text{ h}$  makes it possible to reach the initial sorption ability. The process of electrochemical regeneration is very slow. In order to intensify the process the experiments were carried out at a current intensity of  $400 \text{ mA}$  and without pH adjustment (Table 4). It means that during electrolysis the catholyte went alkaline. Actually, in alkaline solutions copper was easily deposited onto the cathode and EDTA anion was transferred into the anodic part. It is worth noting, that during the first hours of electrolysis the concentration of EDTA was even higher than that without electrolysis. It means that application of electrolysis enhances the desorption process.

Electrolysis was carried out at a higher current density and load of chitosan in order to intensify the regeneration. A higher load of chitosan leads to higher quantities of both the desorbed Cu(II) and EDTA. An increase in the current intensity enables to reduce the time of regeneration (Table 4). The disadvantage of high current densities is an incompact copper layer. Stripped coating flakes or copper powder may be formed and mixed with chitosan. Because of the electrochemical cell and electrodes used in our experiments, the highest current intensity that could be applied was  $400 \text{ mA}$ .

Table 5

Electrochemical regeneration of chitosan after sorption (sorption carried out at pH 12.5) containing  $0.50 \text{ mmol g}^{-1}$  Cu(II) and  $1.5 \text{ mmol g}^{-1}$  EDTA

Duration of electrolysis (h)	Concentrations in solution ( $\text{mmol l}^{-1}$ )			
	Catholyte		Anolyte	
	Cu(II)	EDTA	Cu(II)	EDTA
0	0.2	0.4	0.2	0.4
1	0.5	0.7	0.4	0.7
5	0.3	0.5	0.4	0.3
10	0.2	0.5	0.3	0.2
18	0.1	0.4	0.2	0.07
24	0.005	0.2	0.1	–
30	<0.001	–	0.08	–
36	<0.001	–	0.005	–

$I = 400 \text{ mA}$  ( $i_k = 10 \text{ mA cm}^{-2}$ ;  $i_a = 400 \text{ mA cm}^{-2}$ ;  $E = 4-5 \text{ V}$ ), pH-3 (catholyte), load  $40 \text{ g l}^{-1}$ .

Table 6  
Summing-up of the results of electrochemical regeneration of chitosan

Conditions of electrolysis correspond to	Initial sorbed quantities (mmol)		Residual Cu(II) in chitosan ( $\text{mg g}^{-1}$ )	Molecular weight	Deacetylation degree (%)	Current efficiency (%)	
	Cu(II)	EDTA				Cu	EDTA
Unexploited chitosan	–	–	–	46000	–85	–	–
Table 3	0.3	0.63	5	103000	–85	0.2	14
Table 4	1.8	5.4	3	960000	–85	0.2	9.7
Table 5	2	6	3	52000	–85	0.7	33

When the sorption proceeds in alkaline solutions, the desorption of both Cu(II) and EDTA is very low at all values of pH (Fig. 8b). Moreover, the electrolysis for chitosan regeneration could be applied only in acidic solutions (pH 3) (Table 5). In neutral or basic solutions desorption is negligible and it is not enhanced by electrolysis. As during electrolysis the pH of the catholyte increases and that of the anolyte decreases, a portion of the anolyte was poured into catholyte and a portion of the catholyte was poured into anolyte in order to avoid addition of large quantities of  $\text{H}_2\text{SO}_4$ . After electrolysis, the catholyte and the anolyte were mixed up and used in the next regeneration cycle. Such regeneration ensures the most effective usage of the substances.

In all the cases investigated the main parts of both Cu(II) and EDTA were removed during the first hours of electrolysis. However, the sorption properties of chitosan at this stage of electrolysis were considerably worse than those of the initially used fresh chitosan. The molecular weight is also considerably higher (Table 6). As the amide bonds are easily formed at pH 3 and they are rather stable, it can be assumed that EDTA cures two or more molecules of chitosan, thus increasing the molecular weight. The determination of DD using potentiometric titration is very approximate, therefore, no changes were found in values of DD after regeneration. The reason of decreased sorption ability of chitosan could be the change in the structure of chitosan, as well. In order to achieve the similar sorption ability electrolysis should be performed for a more prolonged time. The current efficiency in solutions containing low concentrations is, as a rule, very low. It is especially low for Cu(II) as the equivalent of Cu(II) is much lower than that of EDTA (32), which limits the efficiency of electrolysis.

Obviously different mechanisms of Cu(II)–EDTA sorption in mildly acidic and strongly alkaline solutions determine different desorption from the chitosan surface and a different effect on Cu(II) and EDTA electrochemical removal from solutions.

In Fig. 9 the results of regeneration after sorption at pH 12.5 using electrolysis at pH 3 for 24 h and at pH 12 for 16 h and  $I=400$  mA are presented. As the determination of molecular weight and DD requires relatively high quantities of chitosan, all the samples of chitosan used in determinations and the residual ones were dissolved in acetic acid, precipitated with NaOH, dried, weighted and reused for the next regeneration cycle. Anyway, after 10 regeneration cycles the loss made up 1 g in 4 g of initial chitosan. The volumes of electrolyte used in electrolysis were adjusted according to the weight of chitosan.

After 10 regeneration cycles the sorption abilities of chitosan for both Cu(II) and EDTA were similar. The molecular weight

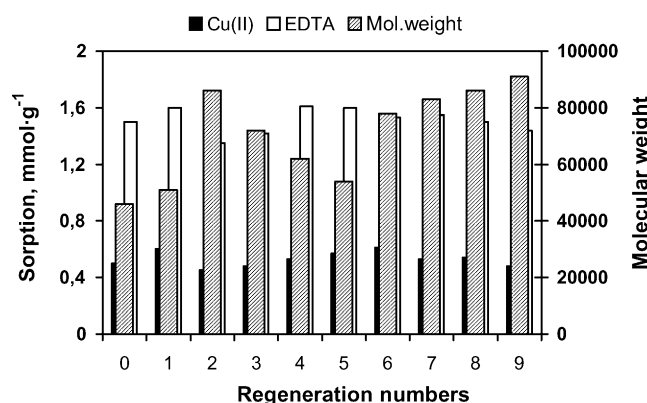


Fig. 9. Effect of regeneration numbers on molecular weight of chitosan and Cu(II) and EDTA sorption from solutions containing  $10 \text{ mmol l}^{-1}$  Cu(II) and  $100 \text{ mmol l}^{-1}$  EDTA at pH 12.5.

of chitosan slightly decreases with regeneration cycles (Fig. 9). Apparently, some destruction of chitosan is possible by prolonged electrolysis. On the other hand, when the electrolysis is only carried out in acidic solutions, the molecular weight is considerably higher than that of initial chitosan. The reason could be the formation of amide bonds in acidic solutions [20]. In alkaline solutions during the sorption the amide bonds seem not to be formed. However, the regeneration of chitosan after sorption in alkaline solutions requires acidifying, as desorption in alkaline solutions is negligible.

FT-IR spectra of free chitosan (Fig. 7a) and those of regenerated chitosan in sulfate solution (Fig. 7f) are similar.

So, chitosan is able to sorb both Cu(II) and EDTA in rather high quantities in weakly acidic or strongly alkaline solutions. Though the sorption mechanisms in acidic and alkaline solutions are different, the application of electrolysis enables to regenerate the chitosan after sorption in acidic, as well as, in alkaline solutions. It is possible that after sorption and regeneration some changes in active groups of chitosan proceed, but these changes do not lead to evident changes neither in sorption properties, nor in FT-IR spectra of chitosan.

#### 4. Conclusions

Chitosan sorbs both Cu(II) and EDTA from their complex solutions in weakly acidic (pH 3–5) and strongly alkaline solutions (pH > 12). The sorption mechanisms in both media are obviously different. In acidic solutions EDTA sorption onto chitosan with formation of amide bonds prevails. In alkaline solutions it is likely that sorption proceeds by coordination of

Cu(II) with the amine group of chitosan, as in alkaline solutions the EDTA alone is not sorbed.

The uptake by chitosan depends on the ratio between Cu(II) and EDTA in solutions. The increase in the concentration of EDTA diminishes Cu(II) sorption.

Application of electrolysis enables to precipitate copper onto the cathode and to oxidize EDTA onto the anode. The efficiency of the process depends on the load of chitosan and current intensity.

## References

- [1] H. Xue, L. Sigg, F.G. Karl, Speciation of EDTA in natural waters: exchange kinetics of Fe–EDTA in river water, *Environ. Sci. Technol.* 29 (1995) 59–68.
- [2] M. Silanpaa, J. Ramo, Adsorption of metal–ethylenediaminetetraacetic acid chelates onto lake sediment, *Chemosphere* 45 (2001) 881–885.
- [3] E. Gilbert, S. Hoffmann-Glewe, Ozonation of EDTA in aqueous solution, influence of pH and metal ions, *Water Res.* 24 (1990) 39–44.
- [4] J. Ramo, M. Sillanpaa, Degradation of EDTA by hydrogen peroxide in alkaline conditions, *J. Cleaner Prod.* 9 (2001) 191–195.
- [5] Verhaege, M., 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, GTC Print AB, Luleå, Sweden, 2002.
- [6] S.N.R. Pakalepati, B.N. Popov, R.E. White, Anodic oxidation of ethylenediaminetetraacetic acid on platinum electrode in alkaline medium, *J. Electrochem. Soc.* 143 (1996) 1636–1643.
- [7] A.J. Chaudhary, J.D. Donaldson, S.M. Grimes, M.-ul Hassan, R.J. Spencer, Simultaneous recovery of heavy metals and degradation of organic species – copper and ethylenediaminetetraacetic acid (EDTA), *J. Chem. Technol. Biotechnol.* 75 (2000) 353–385.
- [8] R. Rhazi, J. Desbrieres, A. Tolaimate, M. Rinaudo, P. Vottero, A. Alagui, Contribution to the study of the complexation of chitosan and oligomers, *Polymer* 43 (2000) 1267–1276.
- [9] E. Guibal, Interaction of metal ions with chitosan based sorbents: a review, *Sep. Purif. Technol.* 38 (2004) 43–74.
- [10] R.-Sh. Juang, F.-Ch. Wu, R.-L. Tseng, Adsorption removal of copper(II) using chitosan from simulated rinse solutions containing chelating agents, *Water Res.* 33 (1999) 2403–2409.
- [11] F.-Ch. Wu, R.-L. Tseng, R.-Sh. Juang, Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan, *Water Res.* 35 (2001) 613–618.
- [12] S. Babel, T.A. Kurniawan, Low cost adsorbents for heavy metals uptake from contaminated water: a review, *J. Hazardous Mater.* 97 (2003) 219–243.
- [13] O. Gylienė, R. Tarozaitė, O. Nivinskienė, Sorption of Ni(II)–citrate complex from electroless nickel plating solutions onto chitosan, *Trans. Inst. Met. Finishing* 82 (1–2) (2004) 38–42.
- [14] 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.
- [15] 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.
- [16] M. Rinaudo, G. Pavlov, J. Desbrieres, Influence of acetic acid concentration on the solubilization of chitosan, *Polymer* 40 (1999) 7029–7032.
- [17] W.S. Wan Ngah, C.S. Endud, R. Mayanar, Removal of copper(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads, *Reactive Funct. Polym.* 50 (2002) 181–190.
- [18] K.H. Chu, Removal of copper from aqueous solutions by chitosan in prawn shell: adsorption equilibrium and kinetics, *J. Hazardous Mater.* 90 (2002) 77–95.
- [19] M. Rinaudo, M. Milas, P.L. Dung, Characterization of chitosan, influence of ionic strength and degree of acetylation of chain expansion, *Int. J. Biol. Macromol.* 15 (1993) 281–285.
- [20] *Standard Methods of Chemical Analysis*, vol. 2: *Industrial and Natural Products and Noninstrumental Methods*, Part B, 6th ed., Frank J. Welcher, 1967.
- [21] Y.Y. Lur'e, A.I. Ribnikova, *Khimicheskii analiz proizvodstvennikh stochnikh vod* (Chemical analysis of industrial effluents), Khimia, Moscow, 1974 (in Russian).
- [22] A. Bernkop-Schnurch, M.E. Krajcicik, Mucoadhesive polymers as platforms for peroral peptide delivery and adsorption: synthesis and evaluation of different chitosan–EDTA conjugates, *J. Control. Rel.* 50 (1998) 215–223.
- [23] E. Norkus, A. Vaškelis, I. Žakaite, Influence of ionic strength and OH<sup>−</sup> ion concentration on the Cu(II) complex formation with EDTA in alkaline solutions, *Talanta* 43 (1996) 465–470.
- [24] E. Norkus, Diffusion coefficients of Cu(II) complexes with ligands used in alkaline electroless copper plating solutions, *J. Appl. Electrochem.* 30 (2000) 1163–1168.