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Sorption of tartrate, citrate, and EDTA onto chitosan and its regeneration applying electrolysis

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Abstract—The equilibrium isotherm data obtained by the sorption of tartrate, citrate, and EDTA onto chitosan were analyzed using Langmuir and Freundlich equations. The process fits best the Langmuir equation. Kinetic investigations showed that the sorption process obeys the pseudo-second-order kinetic equation. Sorption and desorption peculiarities, FTIR investigations, and measurements of molecular weight enable one to hypothesize that sorption proceeds along with the electrostatic interaction between the positively charged $-NH_3^+$ groups of chitosan and the negatively charged $-COO^-$ of carboxylic acids in the formation of amide bonds between the $-NH_2$ groups of chitosan and the –COOH groups of the carboxylic acid. Electrolysis under galvanostatic conditions in a mixture of chitosan with a 0.1 mol L^{-1} Na_2SO_4 solution enables one to destroy the amide bonds in the cathode compartment of the electrochemical cell and to anodize organics in the anodic compartment. The choosing of relevant conditions of electrolysis enables one to obtain chitosan with properties (deacetylation degree, molecular weight, and sorption ability) similar to those of initial chitosan. After electrolysis the regenerated chitosan possesses the same or even higher ability for sorption of the carboxylic acids as the initial chitosan.

Keywords: Chitosan; Sorption; Tartrate; Citrate; EDTA; Regeneration

1. Introduction

The increasing amounts of hazardous substances used in different branches of industry require cost-effective treatment technologies in order to protect the environment. One of such technologies for wastewater treatment is the use of biosorbents.

Different from synthetic ion exchangers, which are used for wastewater treatment, biosorbents are bio-renewable, biodegradable, and rather inexpensive. Chitin-containing sorbents show selective sorption for heavy metal ions. Chitin is the second most abundant natural polymer after cellulose. Chitosan [a 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.[1–4] An amide linkage of chitin is kinetically stable. It can be hydrolyzed to the amine in boiling alkali. However, the production of chitosan from chitin-containing wastes raises the price and limits industrial application of chitosan. Another reason of limited use of chitosan in practice is the decrease in biodegradability after the sorption of hazardous materials. Incineration, which is widely used in such cases, could be complicated due to difficulties in dewatering, as well as due to the high content of nitrogen in chitosan when nitrogen oxides could form.[5,6] The regeneration of chitosan and its reuse could solve the problem of disposal of the spent sorbent.

Over the past century the content of hazardous substances in the environment from anthropogenic activities has been increasing dramatically. The main reason for the enormous pollution of the environment with heavy metals is the use of metal complexes in industry, in agriculture, and in the household. Ligands (complexing agents) enhance metal solubility and mobility in aquatic

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environment systems, where metal complexes are easily assimilated by microphytes and plants. Thus, the ligands enhance the metal access to the food chain. Differently from free metal ions, metal complexes contained in wastes are difficult to decontaminate. Complexing agents have also the potential to perturb the natural speciation of metals, such as Ca, Mg, Fe, and Al and to influence their bioavailability.[7,8]

The most widely used metal ligands in industry are the carboxylic acids such as citrate, tartrate, EDTA (ethylendiaminetetraacetate), glycine, succinate, and malate. These substances are used not only as metal ligands, but also in other fields of industry, that is, in the textile, pharmaceutical, and food industries, as well as in the synthesis of pesticides, dyes, and colorants. The strong complexing agents are also widely used for metal removal from contaminated soils.[9] It is worth noting that usually ligands are used in excess in comparison with heavy metals. Therefore, by decontamination of metal complexes containing wastes, the ligand removal is the most important part. Usually metals from their complex solutions are removed only after oxidative destruction of ligands. In the case of the application of sorption techniques, desorption is the most attractive method for concentrating pollutants.

Desorption of pollutants from chitosan remains poorly investigated. In the case of free metal ions such as Cu(II), Ni(II), Zn(II), Co(II), Hg(II), and some of the metal oxoanions, desorption proceeds in acidic solutions.[10,11] However, in such a medium the dissolution of chitosan precedes unabated, except in sulfuric acid solutions, where chitosan is insoluble. For the desorption of organic compounds, alkaline solutions are used in most cases.[12] Our previous investigations[13] showed that chitosan can be regenerated by applying electrolysis after Cu(II)–EDTA complex sorption and can be reused anew as a sorbent. It is worth noting that the direct application of electrolysis for wastewater treatment containing low concentrations of organics is not effective.[14]

The aim of these investigations was to use chitosan as a sorbent for tartrate, citrate, and EDTA, which are widely used in practice, and to regenerate the chitosan by applying electrolysis.

2. Results and discussion

2.1. Batch sorption experiments

Chitosan is soluble in most of the organic acids.[15] It is usually assumed 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:

$$\text{Chit–NH}_2 + \text{HOOC–R} \rightleftarrows \text{Chit–NH}_3^+ + \text{RCOO}^-.$$

The protonation of $–NH_2$ groups of chitosan proceeds at pH <6.3.

Shamov et al.[4] showed that by the sorption of carboxylic acids onto chitosan two types of interactions proceed, that is, an ionic interaction between the amine and carboxylic groups and a hydrophobic interaction between the internal domains of the chitosan helices and the hydrocarbon chains of the carboxylic acids. The last interaction is responsible for the solubilization of chitosan. The branched structure of the carboxylic acids hinders the hydrophobic interactions.

Our preliminary investigations confirmed this assumption. In acidic solutions glycine (aminoacetic acid), maleic, malonic, lactic acids dissolve the chitosan, whereas it remains undissolved in the solutions of carboxylic acids of branched structure such as tartrate, citrate, and EDTA (Table 1). All these acids are sorbed by chitosan. The maximum sorption is achieved at a particular value of pH for each ligand (Fig. 1). Tartrate and citrate are sorbed in a rather wide range of pH and in rather high quantities. The sorption of EDTA is the lowest one. It precedes best at lower values of pH. However, at pH ~2 and lower, the precipitation of insoluble H_4EDTA takes place. The comparison of sorption data with dissociation constants of carboxylic acids (Table 1 and Fig. 1) indicates that in the sorption process both

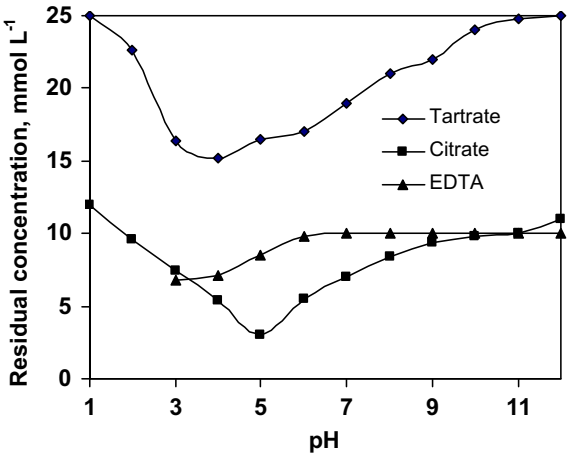

Figure 1. Influence of pH on residual concentration after sorption. Initial concentrations: tartrate, 25 mmol L^{-1}, citrate, 12 mmol L^{-1}, and EDTA, 10 mmol L^{-1}. Load of chitosan: 10 g L^{-1}.

Table 1. Chemical composition and dissociation constants of carboxylic acids

Ligand	Chemical formula	Dissociation constants
Tartrate	HOOC–CHOH–CHOH–COOH	pK_1 2.98; $pK_{1,2}$ 4.62
Citrate	$HOOCCH_2$–CH(OH)COOH–CH_2COOH	pK_1 3.14; $pK_{1,2}$ 4.77; $pK_{1,2,3}$ 6.39
EDTA	$(HOOCCH_2)N–CH_2–CH_2–N(CH_2COOH)_2$	pK_1 1.5; $pK_{1,2}$ 2.68; $pK_{1,2,3}$ 6.11; $pK_{1,2,3,4}$ 10.17

dissociated and undissociated carboxylic groups take part. Remarkable is the fact that the sorption of all ligands proceeds at pH >6.3 where chitosan is not protonated, though the sorption ability of chitosan is considerably lower. The highest sorption ability of chitosan for carboxylic acids is achieved at such pH values where chitosan is protonated and carboxylic acids are partly dissociated.

Further investigations were carried out at pH values corresponding to the maximum sorption for each acid. The isotherms of ligand sorption onto chitosan were obtained in solutions without background electrolyte (Fig. 2) and in solutions containing 0.2 mol L^{-1} Na_2SO_4 (Fig. 3). It is generally known that the increase of ionic strength does not influence the sorption ability of sorbate in cases where chemical interactions between the functional groups of sorbate and sorbent are present. In the case of sorption accruing due to electrostatic interactions, it is influenced by ionic strength. Data depicted in Figures 2 and 3 show that ionic strength has a considerable influence in the case of citrate. The sorption of tartrate is influenced by ionic strength in less degree. In the case of EDTA sorption, ionic strength has no influence. Such an effect of ionic strength on sorption of carboxylic acids can be related to sorption by chitosan according to both mechanisms, that is, electrostatic interaction between negatively charged $–COO^-$ groups of the carboxylic acid and positively charged $–NH_3^+$ group of chitosan and chemical interactions between undissociated acid groups –COOH and the amino groups of chitosan.

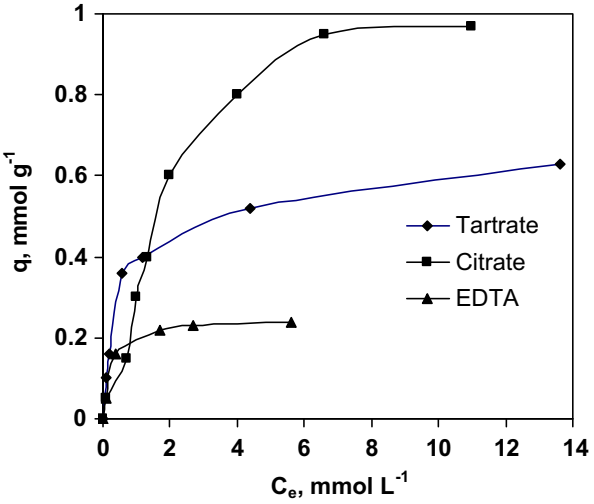

Figure 2. Sorption isotherms for tartrate at pH 4, citrate at pH 5, and EDTA at pH 3.

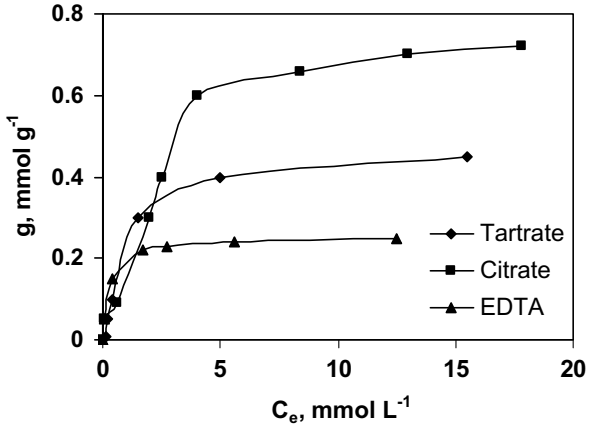

Figure 3. Sorption isotherms for tartrate at pH 4, citrate at pH 5, and EDTA in solutions containing 0.2 mmol L^{-1} Na_2SO_4 at pH 3.

The sorption peculiarities were evaluated by testing the experimental data according to the Langmuir and Freundlich isotherms.[16] The Langmuir isotherm describes the sorption isotherm in the case of monolayer coverage:

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

where K_a is 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 the solution and in the sorbent, respectively. In the linear form this equation could be presented as

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

The plot C_e/q_e versus C_e enables to determine K_a and q_m. These parameters are presented in Table 2. The high values of regression coefficients R^2 indicate the reliability of the sorption of carboxylic acids according to Langmuir process, that is, the sorption proceeds with the formation of a monolayer of sorbate onto the chitosan surface.

To a lesser extent the equilibrium data were also well described with the Freundlich model:

$$q_e = K_F C_e^{\frac{1}{n}},$$

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

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.

In order to evaluate possible chemical interactions, kinetic measurements were carried out as well. The results of investigations are presented in Figure 4. The reaction order was calculated according to the pseudo-first-order equation:[17]

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

and the pseudo-second-order equation:[18]

Table 2. Parameters of Langmuir and Freundlich equations for ligand sorption onto chitosan

Ligand	Na_2SO_4, mmol L^{-1}	Langmuir equation			Freundlich equation		
		K_a, L $mmol^{-1}$	q_m	R^2	K_F, L g^{-1}	$1/n$	R^2
Tartrate	—	1.88	0.64	0.9956	1.35	0.6302	0.9289
Citrate	—	0.45	1.2	0.9928	1.31	0.6171	0.9526
EDTA	—	3.5	0.25	0.9995	1.22	0.7642	0.9653
Tartrate	200	0.68	0.58	0.9439	2.44	0.745	0.8718
Citrate	200	0.33	0.85	0.97	1.58	0.573	0.9311
EDTA	200	1.01	0.25	0.9999	1.77	0.319	0.9157

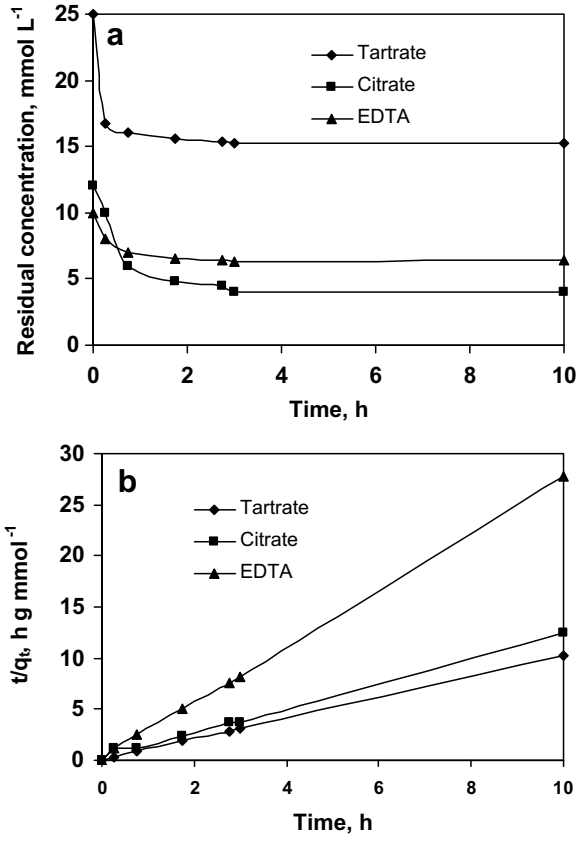

Figure 4. The uptake of tartrate at pH 4, citrate at pH 5, and EDTA at pH 3 by chitosan (a) in dependence on time and test of pseudo-second-order equation for adsorption (b).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e},$$

where q_e is the amount of ligand sorbed onto chitosan under equilibrium conditions, mmol g^{-1}, q_t is the amount of ligand sorbed onto chitosan at time t, mmol g^{-1}, k_1 is the rate constant of pseudo-first-order reaction, h^{-1}, and k_2, the rate constant of pseudo-second-order reaction, g $mmol^{-1}$ h^{-1}.

The calculations according to the first-order kinetic equation showed that the plots are almost linear only for citrate and EDTA for the first 3 h. For tartrate the linear interval of time was not observed. The application of a pseudo-second-order model provides much better correlation of the experimental data in comparison with a pseudo-first-order model (Table 3). The pseudo-second-order rate model fits over the whole time interval. The model is based on the assumption that chemical sorption involving valency forces through sharing or exchange electrons between sorbent and sorbate may be the rate-limiting step. In our case it could be the interaction of the $–NH_2$ groups of chitosan with the dissociated and undissociated –COOH groups of the carboxylic acids. All these acids investigated have more than one, that is, two (tartaric), three (citric), and four (EDTA)–COOH groups, which may interact with two or more $–NH_2$ groups of the same chitosan chain or with $–NH_2$ groups from a different chitosan chain. The latter interactions may lead to cross-linking of chitosan chains.

Table 3. The rate constants and correlation coefficients in kinetic experiments

Ligand	Pseudo-first-order reaction parameters for first 3 h		Pseudo-second-order reaction parameters	
	k_1, h^{-1}	R^2	k_2, g $mmol^{-1}$ h^{-1}	R^2
Tartrate	0.9	0.7463	0.0536	0.9989
Citrate	1.02	0.9327	0.0992	0.9949
EDTA	0.75	0.9013	0.18821	0.9993

Thus, the sorption mechanism of organic acids onto chitosan could be rather complicated. Aside from to electrostatic interactions, which should proceed between COO^- ions of carboxylic acids and the NH_2 groups of chitosan, the chemical interactions between the undissociated –COOH groups of acids and the $–NH_2$ groups of chitosan with the formation of amide groups could take place.[19,20] Such possibility of chitosan amino groups to covalently bind the carboxylic groups is proposed for the cross-linking of chitosan at room temperature using di- and tricarboxylic acids.[20] Hydrophobic interaction is hardly possible due to the branched structure of the ligands investigated.

2.2. Desorption studies

Data depicted in Figure 5 show very low desorption of all substances in acidic and neutral solutions. In alkaline

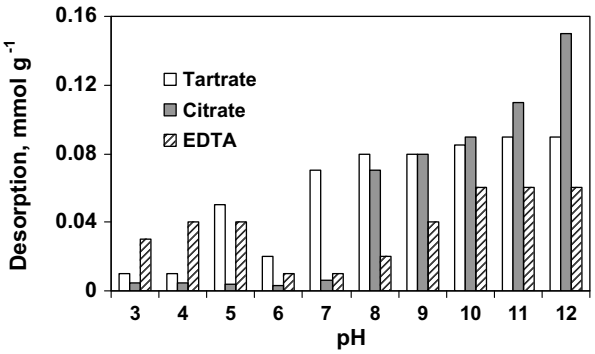

Figure 5. Desorption of tartrate, citrate, and EDTA in 0.1 mmol L^{-1} Na_2SO_4 solution at pH 12. Sorbed quantities: 0.98 mmol g^{-1} tartrate; 0.9 mmol g^{-1} citrate; and 0.32 mmol g^{-1} EDTA.

solutions it is considerably higher. However, desorption in the best case does not exceed 15–20%. Repeated treatment gives only negligible desorbed quantities of organic acids. Sorption ability after such treatment is somewhat higher, though it is considerably lower than that of fresh chitosan (Fig. 6).

Therefore, attempts were made to regenerate chitosan by using electrolysis. It is well known that most of the organic substances can be destroyed electrochemically on the anode.[21,22] In the case of chitosan regeneration, it is important that the current applied should destroy the dissociated substances in solutions or the amide bonds of chitosan. The chitosan chain must survive. The favorable anodic oxidation of carboxylic acids at low current densities enables one to solve this task. Our previous investigations[13,23] showed that chitosan may be successfully regenerated by applying electrolysis after Cu(II)–EDTA and Ni–citrate sorption.

The data of electrochemical experiments under galvanostatic conditions with chitosan after tartrate, citrate, and EDTA sorption are presented in Table 4. It was assumed that during electrolysis, the reconstruction of the $–NH_2$ groups with the formation of free carboxylic acids proceeds in the cathodic part. As during electrolysis, the pH in this part steadily increases, the carboxylate anions are easily transported to the anode where the oxidation of carboxylic acids proceeds. The pH in the anodic part steadily decreases. It is worth noting that during electrolysis the content of organics in both parts—cathodic and anodic—was negligible, probably due to the slow release of acids by chitosan and their rapid oxidation at the anode.

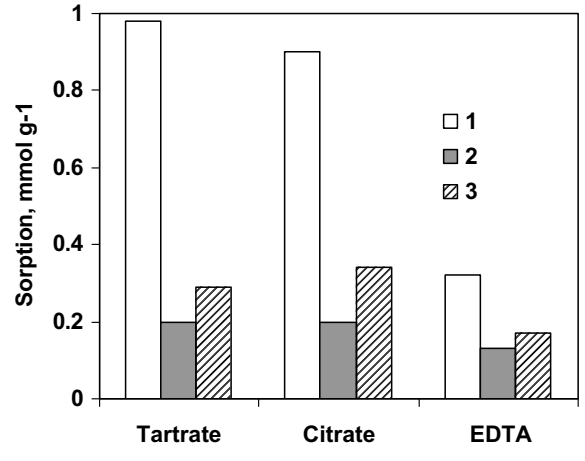

Figure 6. Sorption ability of fresh chitosan (1), second sorption onto sorbed chitosan (2), and sorption onto sorbed chitosan after its treatment with 0.1 mmol L^{-1} Na_2SO_4 solution at pH 12 (3).

During electrolysis some changes in the chemical composition and structure of chitosan could take place. When the applied current quantity (production of current intensity and time) is not sufficient, chitosan is not completely regenerated. In this case the molecular weight is higher than that of the initial chitosan and the deacetylation degree is lower. When the applied current quantity is too high, the molecular weight of the regenerated chitosan is lower, and the deacetylation degree is higher. Apparently, the latter data point to the destruction of chitosan. Despite some possible changes in physicochemical composition of chitosan (for example, a splitting of the chitosan chain) the sorption ability remains high. This is possible in the case when the amine groups are not destroyed. Moreover, if the amide groups are reduced to amine groups, the sorption ability of chitosan increases. Sorption ability of chitosan could increase also owing to different sorption ways of carboxylic acids, that is, the acids investigated can interact with only one amine group or with a maximum of two (tartaric acid), three (citric acid), or four (EDTA) amino groups of chitosan.

The anodic current efficiency was calculated in the most favorable cases when the complete regeneration of chitosan took place. The efficiency is not very high. Apparently, the evolution of oxygen on the anode is the main anodic electrochemical reaction, and the oxidation of carboxylic acids plays a considerably smaller role in the overall anodic process.

The cathodic process is not sufficiently clear. Probably, during electrolysis the evolved hydrogen destroys the amide groups with the formation of $–NH_2$ groups. Further, the low-molecular-weight organic compounds are transported into anodic part and oxidized easily.[23]

2.3. Physicochemical properties

The potentiometric titration curves (Figs. 7–9) of dissolved chitosan show the interactions of its functional groups with OH^- ions. The quantity of OH^- necessary for titration at pH 6–7 corresponds to the number of $–NH_2$ groups in chitosan. After sorption (Figs. 7–9, curves 2) the number of amino groups, that is, the deacetylation degree, decreases. It is worth noting that

Table 4. Physicochemical properties of chitosan and its electrochemical regeneration after the sorption of tartrate, citrate, and EDTA

Sorbed ligand and its quantity, mmol g^{-1}	Conditions of electrolysis		Properties of regenerated chitosan			Current efficiency, %
	Current intensity, mA	Duration of electrolysis, h	Deacetylation degree, %	Molecular weight	Sorption after regeneration, mmol g^{-1}	
Initial chitosan tartrate—0.98			80	150,000		
	0		40	200,000	0.22	
	100	8	70	200,000	0.95	
	400	8	85	120,000	1.02	
	100	16	80	150,000	1.05	10
	400	16	90	80,000	1.2	
	400	24	90	30,000	1.1	
Citrate—0.9	0		45	180,000	0.3	
	100	8	65	150,000	0.35	
	400	8	80	160,000	0.87	8
	100	16	80	160,000	0.83	16
	400	16	85	120,000	1.11	
	400	24	90	40,000	0.97	
EDTA—0.32	0		50	200,000	0.11	
	100	8	65	200,000	0.16	
	400	8	70	150,000	0.25	
	100	16	70	160,000	0.24	
	400	16	80	160,000	0.29	8
	400	24	80	150,000	0.33	3

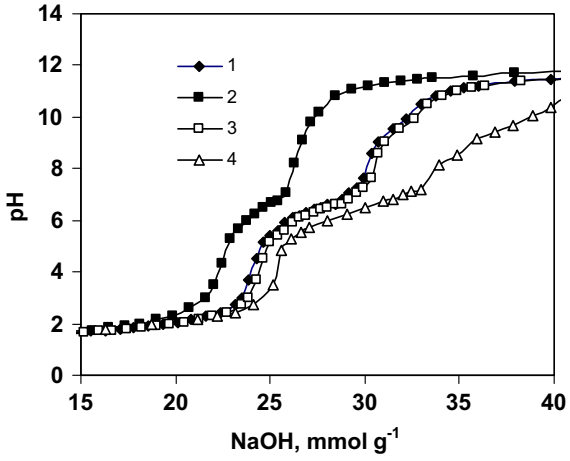

Figure 7. Titration curve: (1) initial chitosan; (2) after sorption at pH 4 in 25 mmol L^{-1} tartrate solution; (3) regenerated for 16 h at 100 mA; (4) regenerated for 24 h and 400 mA.

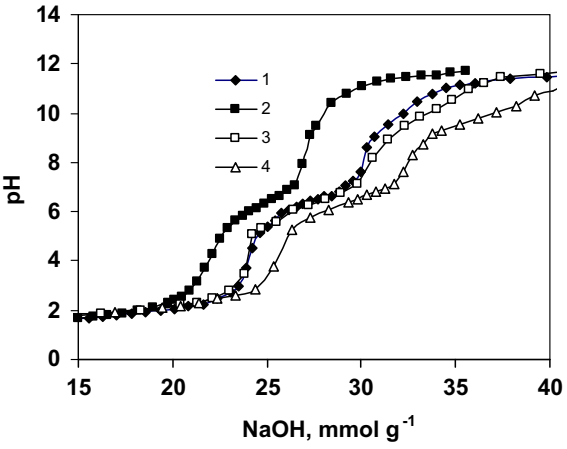

Figure 8. Titration curves of chitosan: (1) initial chitosan; (2) after sorption at pH 5 in 20 mmol L^{-} citrate solution; (3) regenerated for 16 h at 100 mA; (4) regenerated for 24 h and 400 mA.

sorbed quantities (in moles) of tartrate, citrate, and EDTA differ considerably, but the number of free amino groups in chitosan according to titration curves (curves 2 in Figs. 7–9) is comparable in all cases investigated. The reason could be the various numbers of carboxylic groups interacting with the amine groups of chitosan. For example, 1 molecule of citrate can interact with 1, 2, or 3 amine groups of chitosan. During the regeneration, the number of $-NH_2$ groups in chitosan increases (Figs. 7–9, curves 3) when comparing with that after sorption (curves 2). The conditions of electrolysis can be set in such a way that the titration curves of regenerated chitosan (curves 1 and 3) could be coincident with the initial ones. However, the high current densities and long-term electrolysis probably lead to the formation of other functional groups corresponding to the pH range of 8–10 in the titration curve, especially in the case when either tartrate or citrate is sorbed (curves 4). It is possible that in this case the glucosamine ring of chitosan is disrupted with the formation of new functional groups.

FTIR spectra of the compounds of citric, tartaric, and EDTA acids adsorbed onto chitosan were recorded over a frequency region of 3600–400 cm^{-1} and compared with those of free chitosan. After the adsorption of citric, tartaric, and EDTA acids, the intensity of the band corresponding to the characteristic vibration of amide

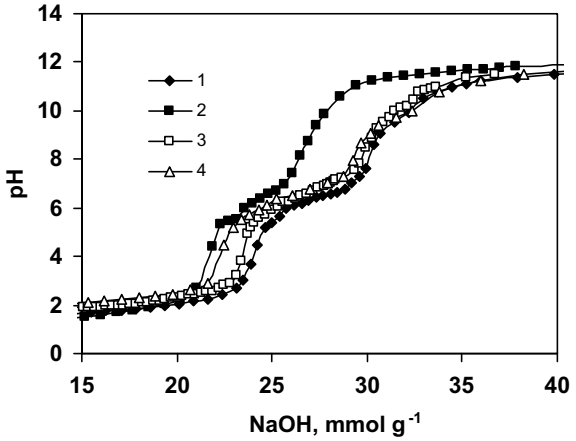

Figure 9. Titration curves of chitosan: (1) initial chitosan; (2) after sorption at pH 3 in 20 mmol L^{-1} EDTA solution; (3) regenerated for 16 h at 400 mA; (4) regenerated for 24 h and 400 mA.

groups at 1650 cm^{-1} and 1550 cm^{-1} in chitosan (Figs. 10–12, spectra b) sharply increased in comparison with that for free chitosan, indicating the participation of the $–NH_2$ group in the reaction with the –COOH of organic acid. In addition, the adsorbed organic acids, particularly in the case of citric acid, give rise to the broad absorption band in the frequency region of 3150–3500 cm^{-1}, due to the strong intermolecular hydrogen-bonding network of free acid groups, as well as several absorption bands in the vicinity of 1700 and 2500–2700 cm^{-1}. FTIR spectra of electrochemically regenerated chitosan in sulfate solutions under optimal conditions (Figs. 10–12, spectra c) were similar to those of free chitosan (Figs. 10–12, spectra a). The absorbance ratio of amide band I at 1655 cm^{-1} and the hydroxyl band at 3450 cm^{-1} ($A_{amide}/A_{hydroxyl}$) after long-term electrolysis (Figs. 10–12, spectra d) increased when compared with that obtained under optimal conditions of electrolysis. There is evidence to suggest that the degree of deacetylation of chitosan increases with an increase in the quantity of current applied for the regeneration of chitosan after the sorption of the carboxylic acids.

The sorption experiments carried out with regenerated chitosan under optimal conditions showed that its sorption ability is similar to that of the initial chitosan. When the current intensity is high, sorption ability of the regenerated chitosan is considerably higher for tartrate and citrate and almost the same of EDTA (Fig. 13). The reason of such sorption peculiarities could also be due to changes in the surface area. The participation of newly formed functional groups in the sorption process during electrolysis is also possible. The modest changes in titration curves after the sorption of EDTA using long-term electrolysis could be explained by its high degree of oxidation and its high resistance to oxidation, which requires considerably higher current quantities than in the case of tartrate or citrate. Actually, the

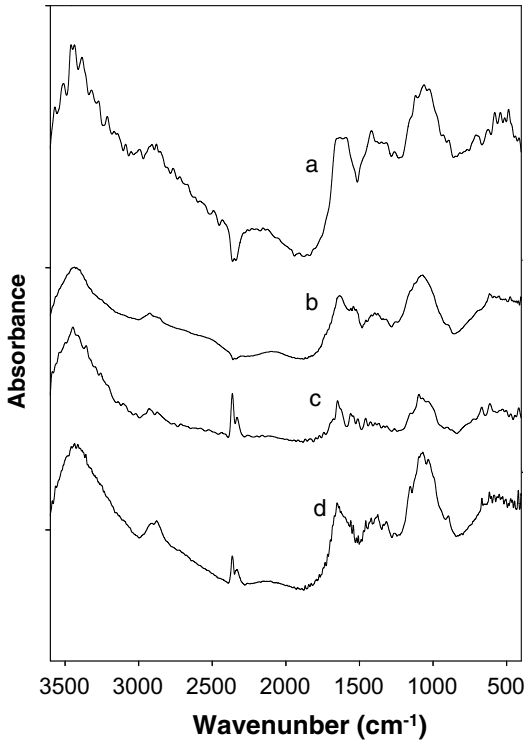

Figure 10. FTIR spectra of free chitosan (a), tartrate sorbed onto chitosan (b), regenerated for 16 h at 100 mA (c), and regenerated for 24 h and 400 mA (d).

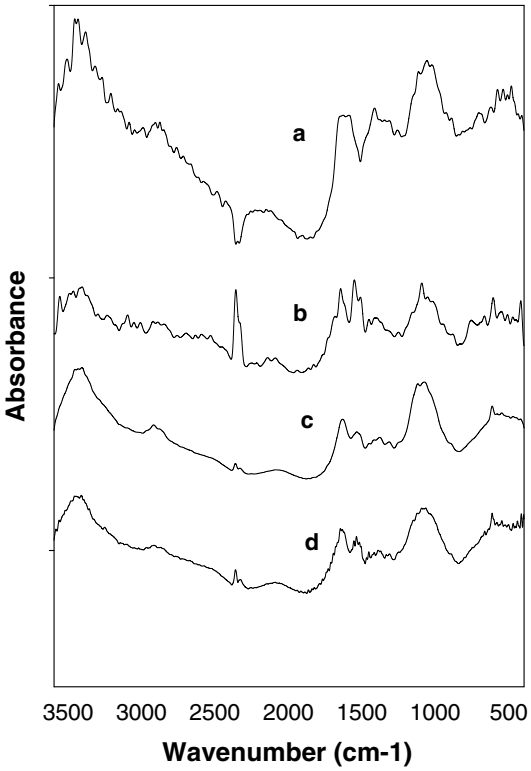

Figure 11. FTIR spectra of free chitosan (a), citrate sorbed onto chitosan (b), regenerated for 16 h at 100 mA (c), and regenerated for 24 h and 400 mA (d).

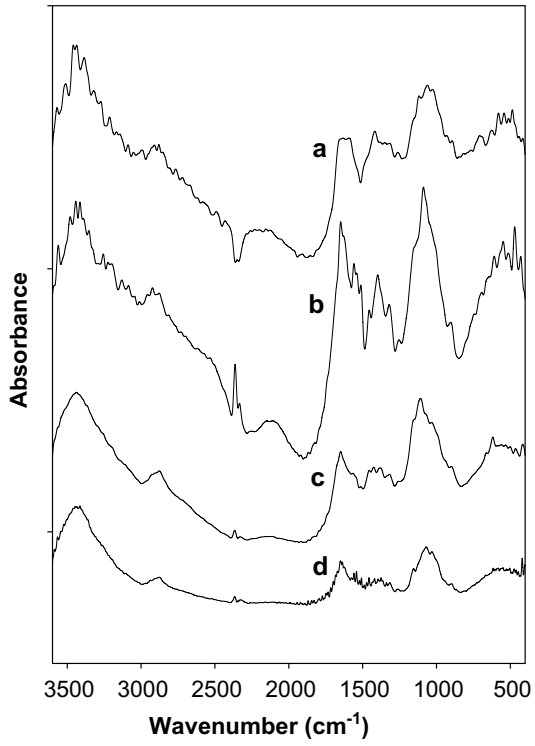

Figure 12. FTIR spectra of free chitosan (a), EDTA sorbed onto chitosan (b), regenerated for 16 h at 400 mA (c), and regenerated for 24 h and 400 mA (d).

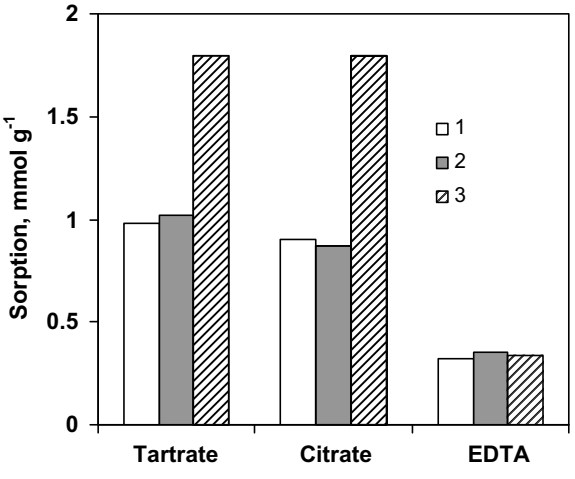

Figure 13. Sorption ability: (1) initial chitosan; (2) regenerated for 16 h at 100 mA for tartrate and citrate and 400 mA for EDTA; (3) regenerated for 24 h and at 400 mA.

differences between the titration curves of chitosan after long-term electrolysis and the initial chitosan are inversely proportional to the oxidation degree of organic acids.

The choosing of relevant conditions for electrolysis enables one to completely regenerate the chitosan for sorption of carboxylic acids and reuse it.

3. Conclusions

The studies under equilibrium conditions showed that the experimental data better fit the Langmuir equation. Kinetic investigations showed that the sorption of carboxylic acids obeys a pseudo-second-order kinetic equation. Chitosan sorbs tartrate, citrate, and EDTA, probably by two mechanisms: (1) electrostatic, that is, the interaction between positively charged $-NH_3^+$ groups of chitosan and negatively charged $-COO^-$ of carboxylic acids, and (2) chemical, that is, the formation of amide bonds between the $-NH_2$ groups of chitosan and the –COOH groups of the carboxylic acid. The oxidative destruction of the released carboxylic acids proceeds at the anode. After the electrolysis the regenerated chitosan possesses the same or even higher ability for sorption of the three carboxylic acids investigated.

4. Experimental

4.1. Sorption and desorption experiments

Chitosan flakes (deacetylation degree about 80) produced by JSC 'Sonat' (Russia) from crab shells were used for experiments.

All sorption experiments were carried out under batch conditions. The load was 10 g of dry sorbent per liter solution in sorption and desorption experiments. Adsorption was investigated at room temperature (19 ± 1 °C) in batch conditions under occasional mixing a few times a day. The pH was checked two times a day and adjusted with NaOH or H_2SO_4 solutions before a constant pH value was reached. After sorption, the chitosan was filtered and rinsed with cold deionized water and dried at 70 °C. The sorbed quantities were determined from the changes of organic substance concentration in the solutions. Desorption was investigated by pouring 0.1 mol L^{-1} Na_2SO_4 solution onto chitosan rinsed and dried after sorption.

The concentration of organics in the solutions was determined after oxidation in alkaline solutions with $KMnO_4$, its excess being retitrated in acidic solutions with oxalic acid.

4.2. Electrochemical regeneration

Regeneration of chitosan was carried out electrochemically under galvanostatic conditions using a IE-51 potentiostat (Russia) and a two-camera cell, cathodic with a volume of 100 mL and anodic with 10 mL, separated by a glass filter. Chitosan (1 g of dry weight before sorption) was loaded in the cathodic compartment. Pt wires were used for both cathode and anode. The electrochemical cell was filled with electrolyte, a 0.1 mol L^{-1} Na_2SO_4 solution. The solution with chitosan was mixed

with a magnetic stirrer during electrolysis. In long-term experiments, when the electrolysis was off, the catholyte and the anolyte were poured out separately from the cells.

The theoretical amount of the removal of sorbed tartrate, citrate, and EDTA onto the anode m, mmol, was determined according to Faraday's law:

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

where I is current intensity, mA; t is time, s; n is the equivalent of substances, for tartrate it is equal to 10, for citrate it is equal to 18 and for EDTA it is equal to 36; and F is Faraday's number equal to 96,500 C. Current efficiency was calculated from the ratio between the amount of carboxylic acids actually removed and that calculated theoretically. The quality of regenerated chitosan was evaluated by the determination of its molecular weight, deacetylation degree, and sorption ability. The FTIR measurements were carried out, as well.

4.3. Determination of physicochemical properties

The molecular weight of chitosan was determined by measuring the viscosity of a 0.05–0.15% solution of chitosan in 0.5 mol L^{-1} HOAc and a 0.5 mol L^{-1} NaOAc solution using an Ostwald viscometer. The molecular weight was calculated by Mark–Houwink equation:

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

where[24] $K_m = 3.5 \times 10^{-4}$ and $\alpha = 0.76$.

The degree of deacetylation was determined by titration with 0.2 mol L^{-1} NaOH after the dissolution of ~0.5 g chitosan in 100 mL of 1 mol L^{-1} HCl solution. The length of plateau at pH ~6, which coincides with the neutralization of the $-NH_3^+$ group of protonated chitosan, corresponds to the degree of deacetylation.

The FTIR spectra of chitosan were recorded in KBr pellets on a Fourier-transform infrared spectrometer (Hartman & Braun, Canada) with 2 cm^{-1} scale resolutions. The spectra were recorded in the region between 4000 and 500 cm^{-1}.

References

1. Gylienė, O.; Šalkauskas, M.; Rekertas, R. *Water Res.* **2002**, *36*, 4128–4136.
2. Lalov, I. G.; Guerginov, I.; Krysteva, M. A.; Farsov, K. *Water Res.* **2000**, *34*, 1503–1506.
3. Wu, F.-Ch.; Tseng, R.-L.; Juang, R.-Sh. *Water Res.* **2001**, *35*, 613–648.
4. Shamov, M. V.; Bratskaya, S. Yu.; Avramenko, V. A. *J. Colloid Interface Sci.* **2002**, *249*, 316–321.
5. Wey, M. Y.; Chen, J. C.; Huang, H. C.; Yeh, C. L. *Combust. Sci. Technol.* **2003**, *175*, 1211–1236.
6. Corell, J.; Toledo, J. M. *J. Hazard. Mater.* **2000**, *80*, 81–105.
7. Nowack, B. *Environ. Sci. Technol.* **2002**, *36*, 4009–4016.
8. Wu, L. H.; Luo, Y. M.; Christie, P.; Wong, M. H. *Chemosphere* **2003**, *50*, 819–822.
9. Wasay, S. A.; Barrington, S. F.; Tokunaga, S. *Environ. Technol.* **1998**, *19*, 369–379.
10. Gao, Y.; Lee, K.-H.; Oshima, M.; Motomizu, Sh. *Anal. Sci.* **2000**, *16*, 1303–1308.
11. Guibal, E. *Sep. Purif. Technol.* **2004**, *38*, 43–74.
12. Christov, L. P.; Driessel, B.; Plessis, C. A. *Process Biochem. (Amsterdam, Neth.)* **1999**, *35*, 91–95.
13. Gylienė, O.; Nivinskienė, O.; Razmutė, I. *J. Hazard. Mater.* **2006**, *137*, 1430–1437.
14. Verhaege, M.; Lissens, G.; Van Hege, K.; Verstracte, M., In: *Recycling and Waste Treatment in Mineral and Metal Processing: Technical and Economic Aspects* (conference proceeding), Lulea, Sweden, 16–20 June; B. Bjorkman, C. Samuelsson, J.-O. Wirkstrom, Eds.; 2002; vol. 1, pp 541–550.
15. Rinaudo, M.; Pavlov, G.; Desbrières, J. *Polymer* **1999**, *40*, 7029–7032.
16. El-Nabarawy, Th.; Kheder, S. A. *Adsorpt. Sci. Technol.* **2000**, *18*, 385–398.
17. Ho, Y. S.; McKay, G. *Water Res.* **1999**, *33*, 578–584.
18. Ho, Y. S.; McKay, G. *Water Res.* **2000**, *34*, 735–742.
19. Ritthidej, G. C.; Phaechamud, Th.; Koizumi, T. *Int. J. Pharm.* **2002**, *232*, 11–22.
20. Bodnar, M.; Hartmann, J. F.; Borbely, J. *Biomacromolecules* **2005**, *6*, 2521–2527.
21. Johnson, D. C.; Feng, J.; Houk, L. L. *Electrochim. Acta* **2000**, *46*, 323–330.
22. Boye, B.; Brillas, E.; Buso, A.; Farnia, G.; Flox, C.; Giomo, M.; Sandonà, G. *Electrochim. Acta* **2006**, *52*, 256–262.
23. Gylienė, O.; Nivinskienė, O. *Chemija (Vilnius)* **2005**, *16*, 7–14.
24. Harish Prashanth, K. V.; Kittur, F. S.; Tharanathan, R. N. *Carbohydr. Polym.* **2002**, *50*, 27–33.