

Heavy metal sorption onto chitosan and chitosan-citrate derivatives

Ona Gyliene^{1*},
Vidmantas Ulevičius¹,
Vadimas Dudoitis¹,
Kristina Plauškaitė¹,
Rita Butkienė¹,
Zenonas Kuodis¹,
Irena Vitėnienė²

¹ State Research Institute Center
for Physical Sciences and Technology,
Savanorių Ave. 231,
LT-02300 Vilnius, Lithuania

² Lithuanian University of
Educational Sciences,
Studentų St. 39, LT-08106 Vilnius

Practical application of chitosan as a sorbent is limited due to its low sorption rates and insufficient mechanical stability to use in filtering systems. In order to improve the sorption properties the chemical modification with citrate has been performed. The sorption rates and capacities were evaluated by determination of the sorbed heavy metal ion amounts. The heavy metal uptake by chitosan increases with decrease in particle size and introduction of citrate. Citrate also enhances sorption capacity. The quantities of citrate introduced into chitosan determine its sorption behavior. The sorption onto chitosan or chitosan containing small amounts of citrate proceeds according to the pseudo-second order kinetic equation and fits the Freundlich equation under equilibrium conditions. The sorption onto chitosan containing high amounts of citrate ($>0.1 \text{ mol g}^{-1}$) is more complicated.

The chitosan-citrate derivative was characterized using potentiometric titrations, Raman and FT-IR investigations.

Key words: chitosan, citrate, modification, FT-IR investigations, Raman spectroscopy

INTRODUCTION

Chitin and its deacylated product chitosan have been intensively investigated due to their biocompatibility, biodegradability and natural renewal of raw material with the purpose to produce new and safe materials. Chitosan and its derivative possess sorption ability for the pollutants of different chemical compositions – dangerous cationic and anionic substances and organic pollutants such as dyes, pesticides, drugs, etc. Chitosan is distinguished for its high sorption capacity for dangerous heavy metal cations, meanwhile natural cations

which are essential for living organisms, such as calcium and magnesium, are not sorbed. The unique action of chitosan as a sorbent is explained by the presence of functional groups such as amine, hydroxyl, acetamido and acetyl in the chain of chitosan. These groups are able to interact electrostatically or to form chemical and coordination bonds with pollutants of different types. This type of sorption is called chemisorption, which remarkably differs from physical sorption. Usually in the case of physical sorption the uptake rates and sorbent capacity increase with increase in temperature, meanwhile in the case of physical sorption these parameters decrease. This peculiarity of chitosan also broadens the field of its possible application.

* Corresponding author. E-mail: gyliene@ktl.mii.lt

The main reasons of limited use of chitosan as a sorbent in practice are its low sorption rate in comparison with synthetic ion exchangers [1–5] and complicated regeneration, which could be done using several techniques, i. e. solvent extraction, electrochemical regeneration, etc. [6–8]. However, their application in practice is not described.

The intrinsic physical structure of chitosan determines a slow diffusion inside chitosan particles and, as a consequence, a slow sorption rate. In order to increase the available sites for sorption different means have been proposed: a decrease in particle size, an increase in porosity, reduction in crystallinity, coating on inert materials (sand, glass particles), etc. Another possibility to increase the sorption capacity is the grafting of supplementary functional groups [9–13]. Usually grafting and crosslinking enable improvement of physical and chemical properties of chitosan (mechanical stability, resistance to acidic environment, etc.). However, as a rule, these means reduce the sorption capacity. The widely used glutaraldehyde crosslinking also diminishes the availability of chelating sites resulting in strong reduction of the sorption capacity for uptake of heavy metals.

It has been shown [9, 13–15] that the granulation of chitosan to microsize also has an insignificant effect on sorption kinetics. The sorption rate and capacity remarkably increase only when the nanosize chitosan material (nanoparticles and nanofibres) is used. Due to a high surface area per unit mass and a porous structure in a swollen state the chitosan nanofiber-based sorption system is distinguished for high sorption kinetic rate and high sorption capacity. The Cu(II) adsorption data obtained on chitosan nanofibres were 6 and 11 times higher than the highest values obtained for chitosan microspheres and chitosan scales, respectively [15]. However, the generation of nanofibres proceeds using the electrospinning technique and is very expensive. Therefore, the production of chitosan nanofibres in quantities sufficient to be used in practice has not been solved yet.

The sorption properties of chitosan and its derivatives have been investigated for the most part in solutions; meanwhile the sorption properties of gaseous compounds are much less investigated [16]. Similar regularities of pollutant sorption from gaseous and liquid states and a simpler investigations technique in the case of solutions predetermine the sorption studies in solutions.

We performed the chemical modification of chitosan using citrate with the aim to achieve sorption parameters allowing its application as a sorbent for purification of solutions containing heavy metal salts.

EXPERIMENTAL

For experiments chitosan from crab shells and an experimental specimen of chitosan nanofibers produced by JSC 'Sonat' (Russia) were used. 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 molecular weight was determined viscometrically. The viscosity measurements in 0.5 mol · l⁻¹ acetic acid and 0.2 mol · l⁻¹ sodium acetate buffer solutions were performed using an Ostwald viscometer and recording the efflux time of the solution at 25 °C. The average molecular weight (M) of chitosan was calculated by the Mark-Houwink equation $\eta = K_m M^\alpha$ ($M = (\eta/K_m)^{1/\alpha}$), where η is the intrinsic viscosity, constants $K_m = 3.5 \times 10^{-4}$ and $\alpha = 0.76$ [19].

The infrared spectra of the sorbents 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.

Raman spectra were recorded using an Echelle type spectrometer RamanFlex 400 (PerkinElmer, Inc.) equipped with a thermoelectrically cooled (-50 °C) CCD camera and a fiber-optic cable for excitation and collection of surface-enhanced Raman scattering. The 785 nm beam of the diode laser was used as the excitation source. The 180° scattering geometry was employed. The laser power at the sample was 30 mW, and the beam was focused to a 200 μm diameter spot. The integration time was 300 s. The Raman frequencies were calibrated using the polystyrene standard (ASTM E 1840) spectrum. Intensities were calibrated by the NIST intensity standard (SRM 2241). Experiments were conducted at 20 °C. Spectral analysis was performed by using GRAMS/A1 8.0 (Thermo Scientific) software.

The chitosan modification was also evaluated by titration with a 0.05 mol l⁻¹ H₂SO₄ solution of 100 mg sorbent placed in 50 ml of a 0.1 mol l⁻¹ NaOH solution and kept there for 24 hours.

The chitosan beads were prepared by dissolution of 20 g of chitosan powder in 1 l of 2% acetic acid; then the formed gel solution was dropped into a 100 g l⁻¹ sodium hydroxide solution. The formed beads were rinsed with deionized water (till it reached pH 7) and dried at room temperature.

The cotton fibers were treated in turn for 1 h in dissolved chitosan and sodium hydroxide solutions. After that they were rinsed and dried at room temperature.

The chemical modification of chitosan with citrate was performed in two ways:

– **Method 1:** 10 g of the chitosan fibers were treated with a 0.5 l 10% sodium citrate solution at 4 °C and pH 5.5 and 6 for 24 h, washed and kept at 70 °C for 24 h.

– **Method 2:** 10 g of chitosan powder was dissolved in 250 ml 50% citric acid and kept at 70 °C for 10 h. After that the modified chitosan was precipitated with NaOH, washed with water and dried at room temperature, then at 70 °C for 5 h and crashed to powder.

The approximate quantities of citrate used for the modification of chitosan were determined from the changes in organic substance concentration in the solutions. The con-

centration 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.

All sorption experiments were carried out under batch conditions. The adsorption was investigated at room temperature by pouring solutions containing metal salts onto chitosan. pH was adjusted with NaOH or H_2SO_4 solutions. The sorbed quantities of heavy metal ions were determined according to concentration changes in solutions.

Cu(II) concentrations in solutions were determined photometrically at $\lambda = 440$ nm using diethyldithiocarbamate as an indicator.

Ni(II) concentrations were determined photometrically at $\lambda = 490$ nm using dimethylglyoxime as an indicator.

Cr(VI) in solutions was determined photometrically at $\lambda = 540$ nm using diphenylcarbazide as an indicator.

RESULTS AND DISCUSSION

The main characteristics of chitosan used for the experiments are presented in Table 1.

The main factor enabling the evaluation of the nature of sorption is influence of temperature. As a rule, in the case of chemisorption with an increase in temperature the sorption rate and capacity increase; meanwhile, in the case of physical sorption these values decrease. The data presented in Fig. 1 and Table 2 show a considerable influence of temperature on the sorption rate. The increase in temperature increases the Cu(II) sorption rate on all kinds of chitosan investigated in-

dicating that the chemical interactions play a significant role in the uptake of metals by chitosan. Chitosan in the form of nanofibres possesses the highest sorption rate. It is understandable as the surface of nanofibres is highest among the investigated chitosans and the access to sorbent functional groups is easiest. However, the practical application of chitosan nanofibres for solution purification is complicated due to their low mechanical stability and the tendency to conglutinate and clog in solutions. The flakes possess the lowest surface and, as a consequence, the lowest sorption rate. It is worth noting that at 70°C the differences in sorption rates onto different kinds of chitosan are far less. The reversible chemical reactions and some changes in structure could be the main reasons of such effects.

In order to enhance the sorption rates, chitosans of different physical form were prepared from chitosan powder. The practical application of sorbents requires a particular shape of sorbent allowing its permeability by purification of gases or solutions in flow mode. The attempts were made to produce the chitosan beads similar to ion exchangers, which are widely used in practice. The kinetic properties of beads were evaluated using Cu(II) sorption. The results presented in Fig. 2 show rather low Cu(II) sorption rates onto chitosan beads both onto freshly precipitated and onto the dried ones (curves 1 and 2). The reason could be a very smooth surface of beads.

The sorption rate remarkably increases (Fig. 2, curve 3) when chitosan is precipitated onto cotton fibres, which capacitate the roughness of surface, thus increasing the sorp-

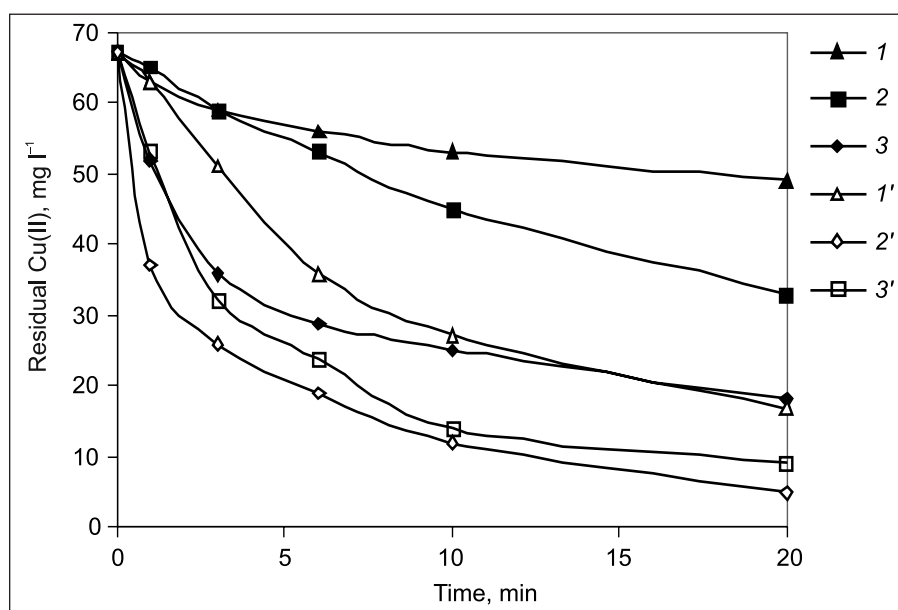


Fig. 1. Cu(II) sorption at 20°C (1, 2, 3) and 70°C (1', 2', 3') onto chitosan flakes (1 and 1'), powder (2 and 2') and fibers (3 and 3'). Load of chitosan 1 g l^{-1}

Table 1. Characteristics of chitosan

Type of chitosan	Molecular weight	Deacetylation degree
Powder	245 000	75
Flakes	250 000	80
Fibres	360 000	90

Table 2. The rate constants and correlation coefficients in kinetic experiments

Curve numbers		Pseudo-first order reaction parameters		Pseudo-second order reaction parameters	
		k_1, min^{-1}	R^2	$k_2, \text{g mg}^{-1} \text{min}^{-1}$	R^2
Fig. 1	Curve 1	0.011	0.8385	30.86	0.9842
	Curve 2	0.006	0.9949	5.3	0.9044
	Curve 3	0.003	0.885	6.09	0.9415
	Curve 1'	0.022	0.9334	96.15	0.99
	Curve 2'	0.018	0.8991	30.3	0.976
	Curve 3'	0.013	0.9598	8.36	0.8856
Fig. 2	Curve 1	0.024	0.5626	14.8	0.9282
	Curve 2	0.015	0.3594	12.6	0.9922
	Curve 3	0.032	0.6007	8.37	0.9142
	Curve 4	0.032	0.4771	18.11	0.9844

The experimental conditions are indicated in the captions to Figures.

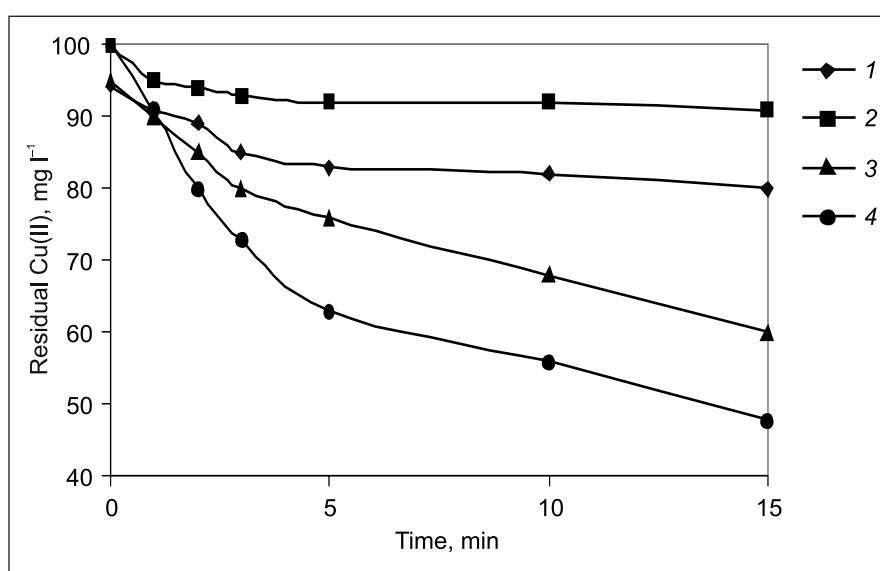


Fig. 2. Cu(II) sorption on modified chitosan: 1 – freshly precipitated chitosan beads, 2 – dried chitosan beads, 3 – chitosan deposited onto cotton fibers, 4 – chitosan nanofibers. Load of chitosan 1 g l^{-1}

tion rate. However, it remains remarkably lower than that onto nanofibers (Fig. 2, curve 4), especially at the beginning of sorption.

For a deeper understanding of the processes taking place during the sorption process the fit of the sorption rates to the first and second order reactions was checked according to the equations [17–20]

$$\log(Q - q_t) = \log Q - k_1 \cdot \frac{t}{2.303}$$

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

where Q is the amount of metal ions sorbed under equilibrium conditions, $\text{mmol} \cdot \text{g}^{-1}$, q_t is the amount of metal ions sorbed by chitosan at time t , $\text{mg} \cdot \text{g}^{-1}$, k_1 is the rate constant of pseudo-first-order sorption, min^{-1} , and k_2 is the pseudo-second order sorption rate constant, $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$. The plotting $\log q_t$ versus t enables calculating the k_1 and plotting t/q_t versus t gives k_2 .

The calculations according to the first order kinetic equation indicates that correlation coefficients in this case are very

low (Table 2). The application of the pseudo-second order model provides a much better correlation of the experimental data in comparison with the first-order model. This model is based on the assumption that chemical sorption may be the rate-limiting step involving valency forces through sharing or exchange of electrons between sorbent and sorbate. In our case it may be the formation of heavy metal ions complex with $-\text{NH}_2$ and $-\text{OH}$ groups of chitosan.

The data presented in Figs. 1, 2 and Table 2 indicate the influence of the surface area on the sorption rate. Chitosan nanofibers demonstrate the best results. However, the resistance of these fibres to the acidic medium and against mechanical actions is poor. In order to improve the properties of chitosan as a sorbent its modification using citrate was performed.

It is assumed that the sorption of citrate proceeds due to electrostatic interactions between the protonated amino group NH_3^+ and carboxylate COOH^- group from citrate. This interaction can proceed only at $\text{pH} < 6.4$, where the amino group is protonated. However, at $\text{pH} < 5.5$ the dissolution of citrate proceeds. Also, the citrate is expected to be sorbed be-

Table 3. Content of citrate (mmol) in 1 g chitosan after modification

Treatment conditions	Nature of chitosan	Content of citrate in 1 g chitosan, mmol
Method 1 pH6	Powder	0.04
	Fibres	0.035
Method 1 pH5.5	Powder	0.1
	Fibres	0.1
Method 2	Powder	0.1

cause of the presence in chitosan of free functional groups $-NH_2$ and $-OH$, which might interact with the $-COOH$ groups of organic acids [14, 21].

Chitosan depending on temperature, concentration and pH is capable of absorbing various quantities of citrate. The peculiarities of citrate sorption onto chitosan at room temperature were thoroughly studied earlier and are described in [22]. In this study the experiments were performed mainly using chitosan treated with citrate at 70 °C. The rough uptake of citrate by chitosan determined according to the citrate changes in solutions as well as the chitosan weight gain are presented in Table 3.

The heavy metal sorption peculiarities (Fig. 3) onto chitosan of different modification under equilibrium conditions were evaluated by testing the experimental data according to the Langmuir and Freundlich isotherms. The Langmuir isotherm describes the sorption in the case of monolayer coverage. Its linear expression is as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L(Q)} + \frac{C_e}{Q},$$

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

The linear form of the Freundlich isotherm is as follows:

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

According to the adsorption theory, the constant K_F indicates the chitosan sorption capacity when the concentration of adsorbate in the solution is equal to 1 mol l⁻¹. The coefficient $1/n$ represents

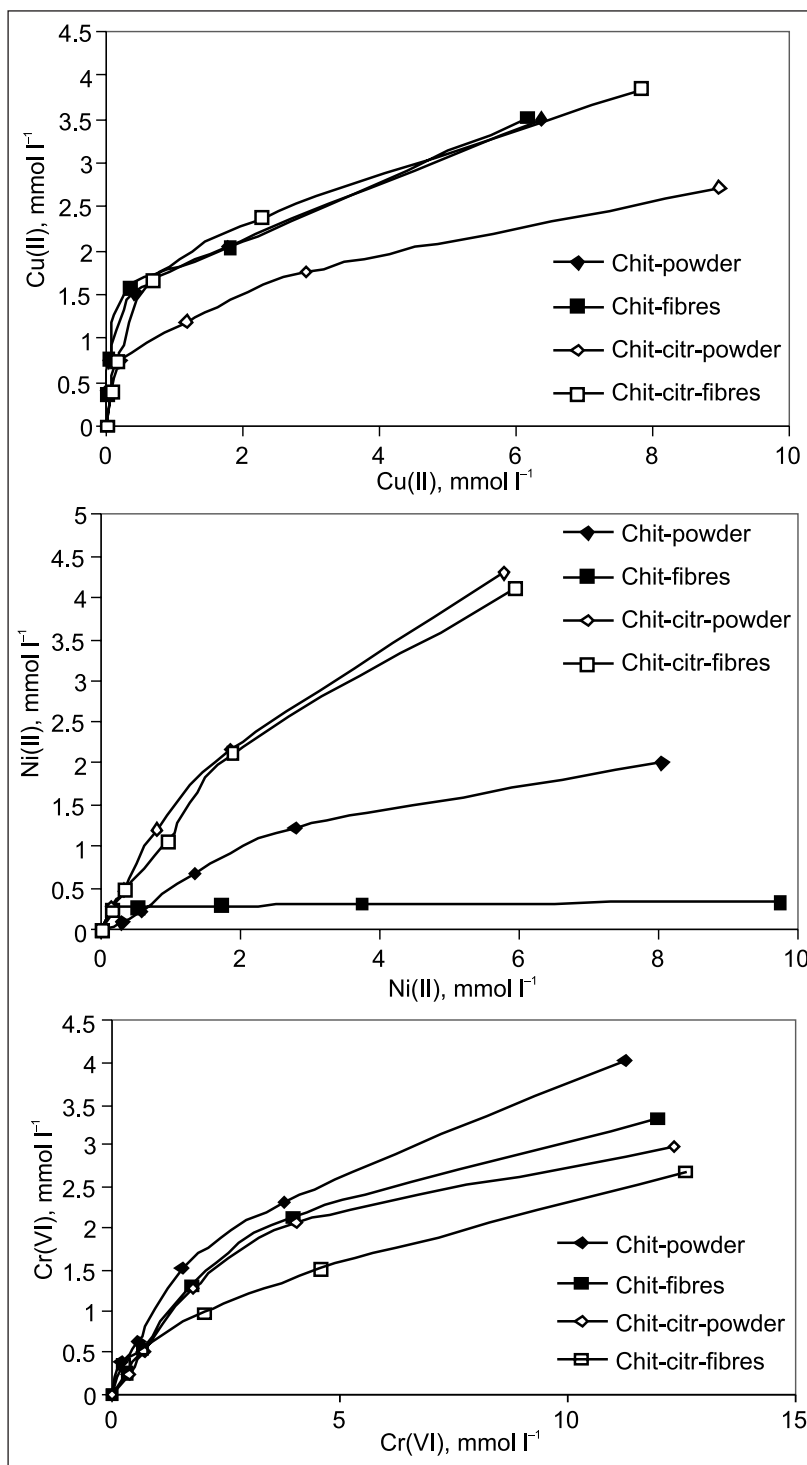


Fig. 3. Cu(II), Ni(II) and Cr(VI) sorption isotherms onto chitosan fibers and powder and chitosan powder treated with citrate according to Method 1 at pH6

Table 4. Langmuir and Freundlich equation parameters for the experimental data of Figure 5

Curve numbers	Langmuir equation parameters			Freundlich equation parameters		
	$Q, \text{mg g}^{-1}$	$K_L, \text{l mg}^{-1}$	R^2	$K_F, \text{l g}^{-1}$	$1/n$	R^2
Cu(II) Curve 1	3.5	10.2	0.9597	1.92	0.28	0.9937
Curve 2	3.4	11.2	0.9557	1.98	0.29	0.9541
Curve 3	2.8	3.6	0.9576	1.16	0.36	0.9784
Curve 4	4.1	5.3	0.969	1.48	0.47	0.922
Ni(II) Curve 1	5.8	2.4	0.7555	1.21	0.75	0.981
Curve 2	6.2	1.9	0.6512	1.07	0.81	0.9888
Curve 3	3.7	0.56	0.363	0.36	0.96	0.9478
Curve 4	1.1	2.3	0.9985	0.28	0.08	0.9894
Cr(VI) Curve 1	4.7	1.5	0.892	0.98	0.61	0.9864
Curve 2	4.3	1.2	0.8645	0.66	0.71	0.9596
Curve 3	3.8	10.6	0.8642	1	0.95	1
Curve 4	3.1	1.2	0.8866	0.71	0.51	0.9975

The experimental conditions are indicated in the Figure captions.

the sorption intensity and adsorbent heterogeneity.

These parameters are presented in Table 4. The results obtained show that the Freundlich equation better describes the sorption process than the Langmuir one. More or less satisfactory fit to the Langmuir sorption is obtained only for Cu(II) ions, meanwhile the sorption of Ni(II) and Cr(VI) does not obey the Langmuir equation at all. All the three investigated heavy metal ions, Cu(II), Ni(II) and Cr(VI), satisfy rather well the Freundlich equation indicating primarily the heterogeneity of sorbent. The reasons could be the sorption of heavy metals by complexation with $-\text{NH}_2$ or $-\text{OH}$ or both groups from the same or different chains of chitosan as well as the differences in chemical and physical microcomposition of sorbent.

It is worth noting that the sorption process obeys the Freundlich isotherm only in the case of pure chitosan or chitosan containing small quantities of citrate (up to 0.04 mmol g^{-1}); meanwhile in the presence of higher amounts of citrate in chitosan the sorption process is more complicated. The sorption capacity remarkably increases in the presence of citrate; however, the shape of the isotherm is not common and does fit neither Langmuir nor Freundlich isotherms. The high sorbed quantities of heavy metals suggest that the number of functional groups during modification increases (Fig. 4).

Kinetic investigations have shown that modification with citrate improves sorption rates of both chitosan powder and chitosan nanofibers (Fig. 5). However, the sorption does not obey neither the first nor the second order

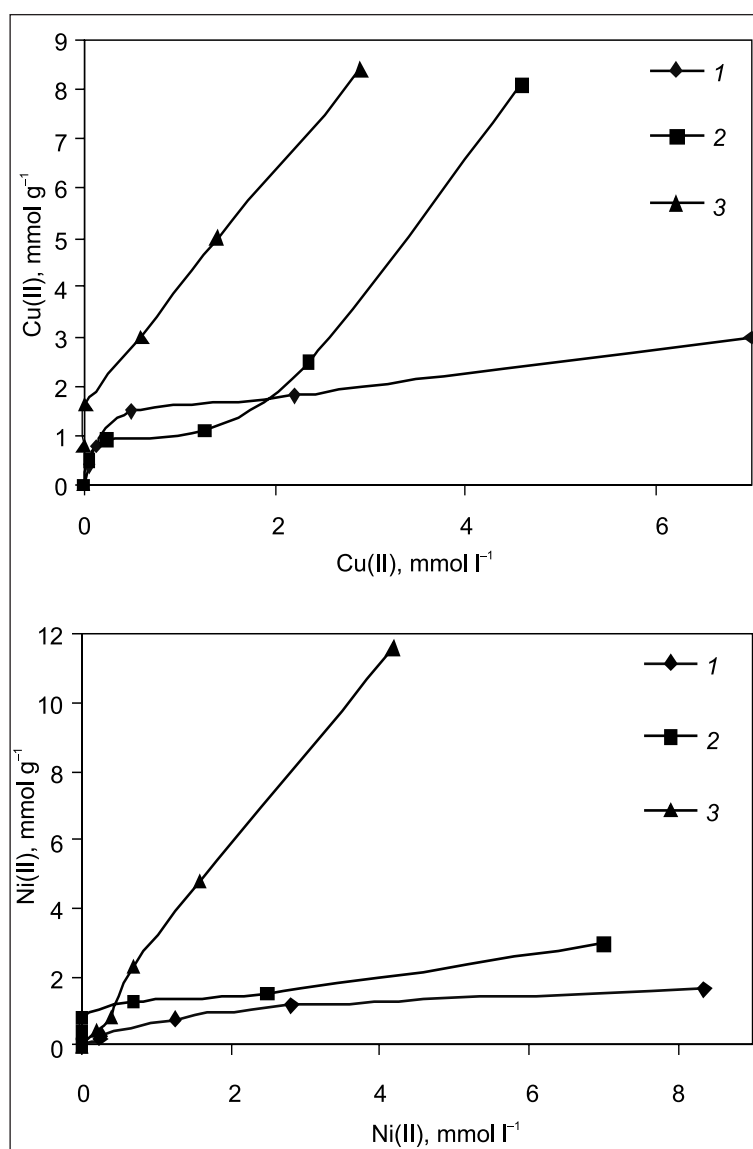


Fig. 4. Cu(II) and Ni(II) sorption isotherms on chitosan fibers (1) and modified chitosan fibers treated at $70 \text{ }^\circ\text{C}$ and containing 0.1 mmol g^{-1} (2), and treated at room temperature containing 0.5 mmol g^{-1} (3)

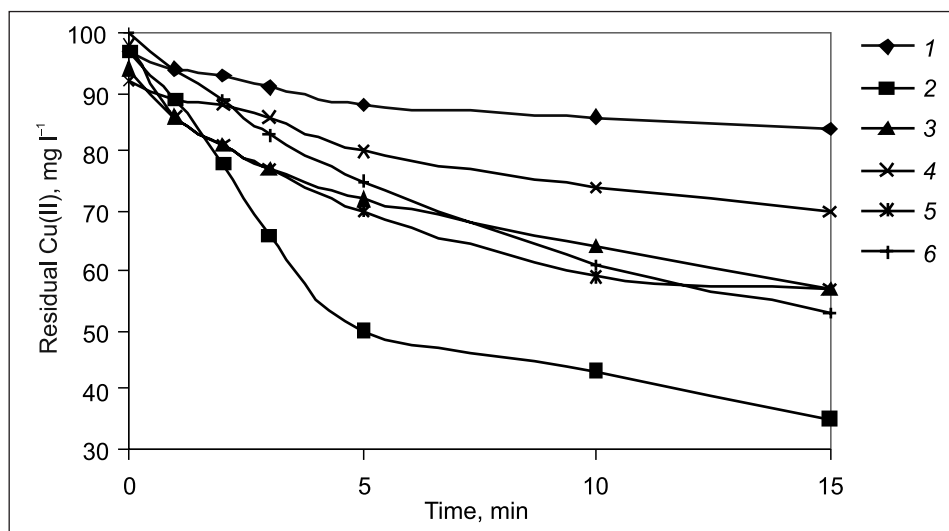


Fig. 5. Cu(II) sorption on modified chitosan: 1 – chitosan powder, 2 – chitosan-citrate powder treated according to Method 2, 3 – chitosan nanofibers, 4 – chitosan nanofibers treated according to Method 1 at pH6, 5 – as in (4) at pH5.5, 6 – chitosan nanofibers containing 0.5 mmol g⁻¹ citrate (treated at room temperature). Load of chitosan 1 g l⁻¹

kinetic equation. Probably, the unpredictable sorption behavior of chitosan in the case of high contents of citrate is caused by a different physical structure of modified chitosan as well as different action of the additional functional citrate groups. Also the sorption action of the chitosan functional groups –NH₂ and –OH could be diminished due to formation of amide or ester groups. Thus, the sorption features of modified chitosan depend on the quantity of citrate introduced.

In order to better understand the sorption process the sorbents were investigated using potentiometric titration, IR and Raman investigations.

It should be noted that pH-metric titrations curves show that the number of active functional groups remarkably increases as compared with the initial chitosan. A distinct plateau at pH~6.5 in pH-metric titration curves (Fig. 6, curve 2) shows the presence of –NH₂ groups. With an increase in the amount of citrate the chitosan titration curves become elongated without distinct shift points (Fig. 6, curves 3 and 4). However, when the chitosan is treated according to Method 2 (Fig. 6, curve 5), the distinct plateau at pH~6.5 remains. The reason could be different chemical bonds formed between citrate and chitosan under different treatment conditions. Moreover, these differences can be evaluated visually. The

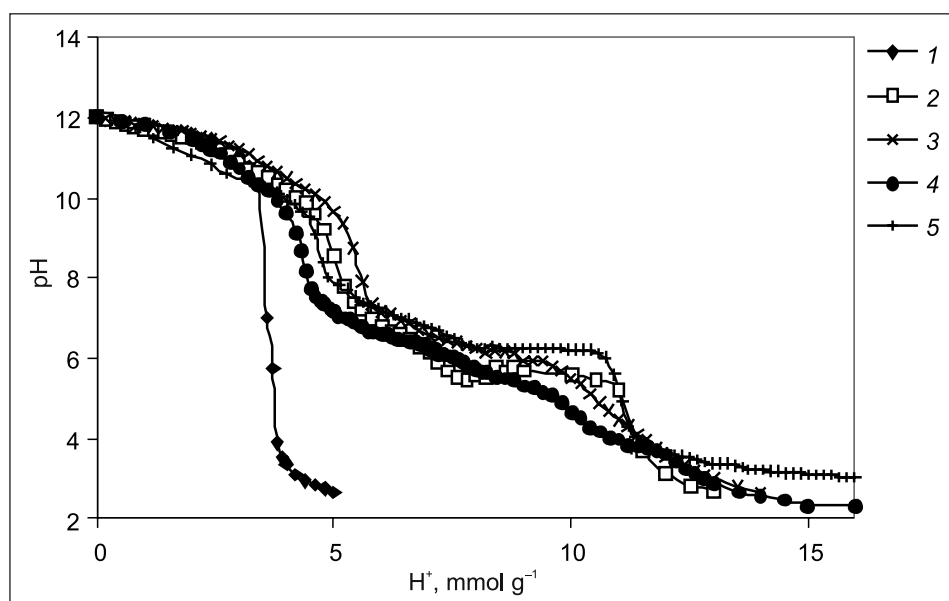


Fig. 6. pH-metric titration curves: 1 – “empty” solution, 2 – chitosan powder, 3 – chitosan powder containing 0.1 mmol g⁻¹ citrate treated according to Method 1; 4 – chitosan powder containing 0.5 mmol g⁻¹ citrate treated at room temperature, 5 – chitosan powder after treatment according to Method 2

color of the sorbent after Cu(II) sorption on pure chitosan and chitosan precipitated from citric acid (Method 2) is blue and that of chitosan containing citrate after treatment at pH6 or room temperatures is green.

There are no considerable differences between the IR spectra of chitosan produced in the form of fibers or powder (Figs. 7 and 8). The changes in the chemical composition of sorbent after the treatment with citrate were clearly shown

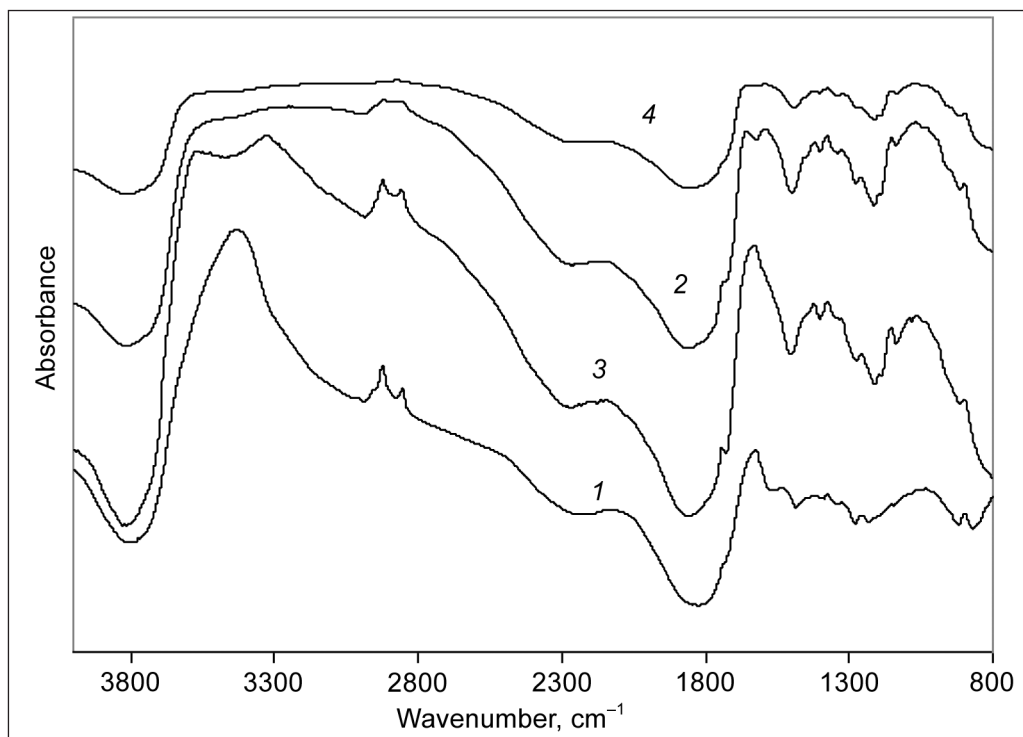


Fig. 7. IR spectra of initial chitosan powder (1), treated at pH6 according to Method 1 (2), then treated with NaOH (3), treated according to Method 2 (4)

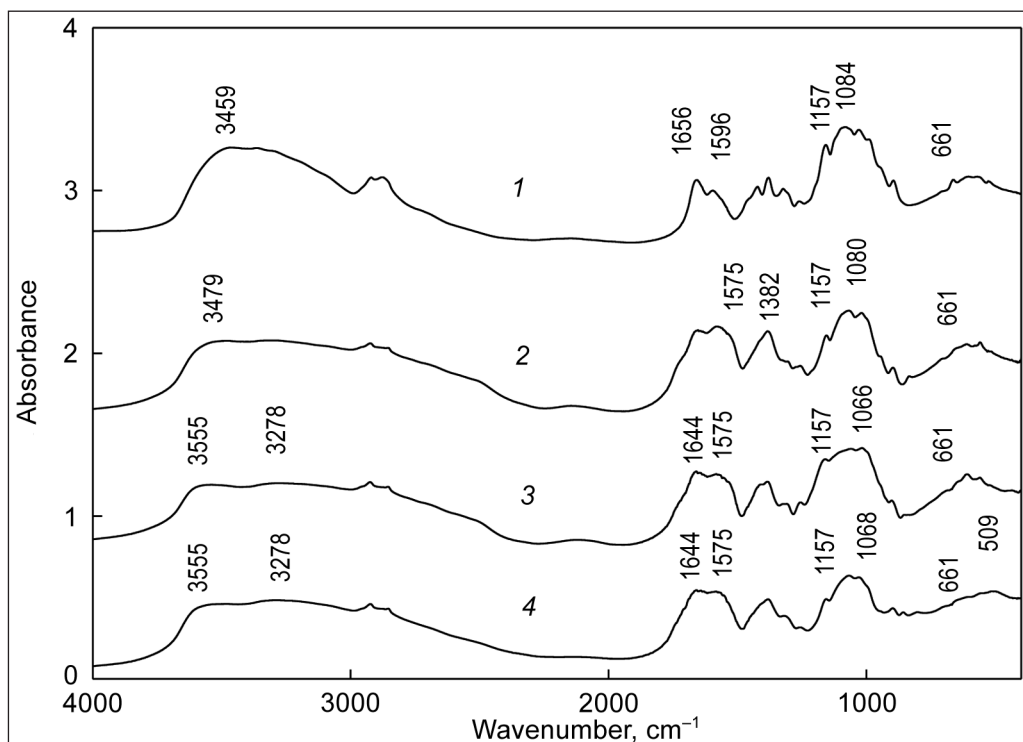


Fig. 8. FTIR spectra: 1 – chitosan fiber, 2 – chitosan fiber treated with citrate according to Method 1 at pH6, 3 – chitosan fiber treated with citrate and copper, 4 – chitosan fiber treated with citrate and chromium

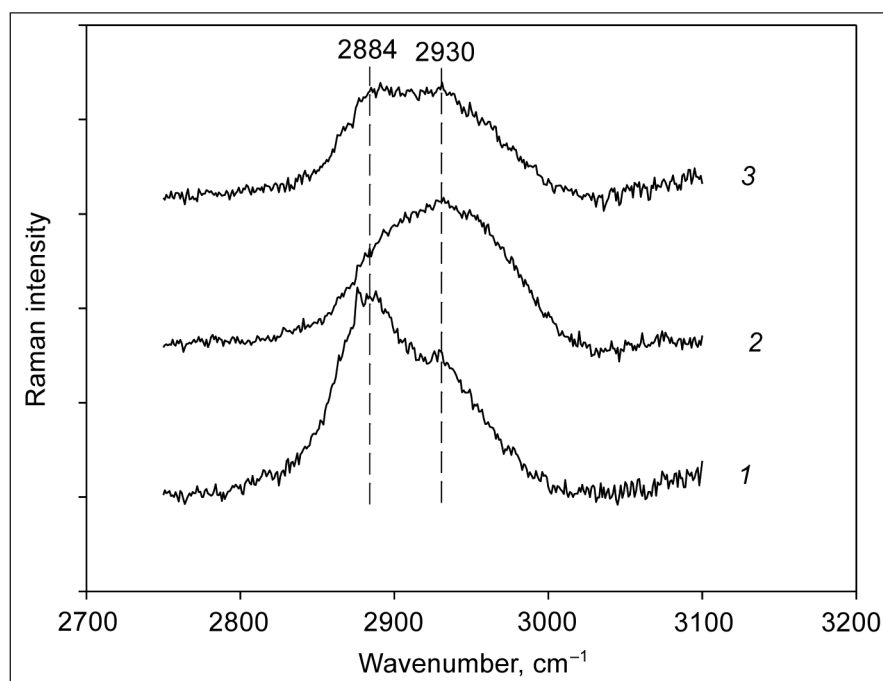


Fig. 9. Raman spectra of chitosan (1), chitosan : citrate : NaOH (mol) = 1 : 1 : 1 (2) and chitosan : citrate : NaOH (mol) = 1 : 0.5 : 1 (3)

by IR investigations. In the region 3000 cm^{-1} to 3700 cm^{-1} of the IR spectrum, chitosan exhibits a band corresponding to stretching vibrations of OH groups. This band ($\sim 3459\text{ cm}^{-1}$) is broad due to the hydrogen bonds within the polysaccharide.

When chitosan interacts with citrate or metal ions, the band becomes unfolded and the stretching of O-H at 3479 cm^{-1} (interaction with citrate ion) and 3555 cm^{-1} (interaction with metal ion), and the stretching of N-H at 3278 cm^{-1} are observed. After treating of chitosan with citrate solution, the absorption band at 1596 cm^{-1} ($-\text{NH}_2$ bending in primary amine [23–25]) disappears. Moreover, new absorption bands at 1575 cm^{-1} and 1382 cm^{-1} emerge. They can be attributed to N-H deformation vibration in NH_3^+ ion and C-O bending vibration in COO^- ion, respectively [23]. However, the stability of bonds in citrate-chitosan derivatives differs depending on the modification method with citrate. Characteristic of chitosan peaks $-\text{NH}_2$ (1596 cm^{-1}), C=O (1650 cm^{-1}) (Fig. 7, spectrum 1) disappear after treatment with citrate giving a broad band in the $1550\text{--}1650\text{ cm}^{-1}$ district. After treatment with a NaOH solution at pH 12 for 24 h, the spectrum of the sorbent modified according to Method 1 becomes similar to the initial one (Fig. 7, spectra 1 and 3); meanwhile that of the sorbent obtained according to Method 2 remains unchanged (spectrum 4). Thus, it could be assumed that by grafting citrate the amidation of amino groups in chitosan proceeds at chitin dissolution in citric acid and keeping the temperature of $70\text{ }^\circ\text{C}$ for a long time.

The absorption bands at 661 cm^{-1} related to bending N-H and at 1157 cm^{-1} related to stretching C-N were weakened. The bands at 1656 cm^{-1} due to the asymmetric vibrations of

N-H and at 1084 cm^{-1} due to the asymmetric vibrations of C-O moved by $12\text{--}18\text{ cm}^{-1}$ and a new broad band at 509 cm^{-1} attributed to metal-oxygen bond emerged after chitosan treatment with metal ions (Fig. 8, curves 1–4). This behavior could be attributed to the fact that NH_2 and OH are coordinated with metal ions.

One might expect that in the case of modification of chitosan according to Method 1 the interaction reactions proceed only on the surface of chitosan. Raman investigations showed that distinct bands at 2884 and 2930 cm^{-1} characteristic of chitosan ν (C-H) symmetric and asymmetric vibrations (Fig. 9, spectrum 1) are overlapped by citrate and form a broad band in this district (spectrum 2). When the quantity of citrate is insufficient to block completely all chitosan groups, the two bands become apparent. These data show that citrate interacts with chitosan not only on the surface, but also in the whole volume. Probably the long treatment terms and comparatively low sizes of chitosan nanofibers and powder enable citrate to penetrate to all the chains of chitosan.

Thus, the modification with citrate enables to increase the sorption rates and sorption capacities. These effects depend on the quantity of citrate introduced into chitosan.

CONCLUSIONS

The sorption of heavy metal ions onto chitosan modified by citrate remarkably differs from that on pure chitosan. The kinetic characteristics and sorption under equilibrium conditions strongly depend on the quantities of citrate introduced in chitosan; meanwhile the characterization of sorbent

using potentiometric titration, IR and Raman investigations points to the importance of the ways of the citrate introduction into chitosan. Despite the fact that citrate penetrates the whole volume of chitosan, its treatment with chitosan at pH 5.5–6 prevents from the formation of amide bands between the $-NH_2$ groups of chitosan and $-COOH$ groups of citrate. When the chitosan is dissolved in citric acid and kept for a long time (~24 h) at 70 °C, presumably the amidation of $-NH_2$ group proceeds.

The interactions of heavy metal ions with modified chitosan proceed both with the $-NH_2$ groups and $-COOH$ groups with the formation of coordinated bonds.

ACKNOWLEDGMENTS

This work was supported by the European Social Fund Agency under EUREKA Project E!5808 BIOSOEX No. VP1-3.1-MM-06-V-01-003.

Received 15 November 2012

Accepted 27 March 2013

References

1. M. Chanda, G. L. Rempel, *Ind. Eng. Chem. Res.*, **36**, 2184 (1997).
2. G. R. Kiani, H. Sheikhoie, N. Arsalani, *Desalination*, **269**, 266 (2011).
3. O. Gylienė, M. Šalkauskas, R. Rekertas, *Water Res.*, **36**, 4128 (2002).
4. D. Kaušpėdienė, J. Snukiškis, A. Gefenienė, *J. Hazard. Mater.*, **99**, 313 (2003).
5. D. Kaušpėdienė, J. Snukiškis, A. Gefenienė, E. Kazlauskienė, *Colloids Surf., A*, **311**, 180 (2007).
6. G. Z. Kyzas, M. Kostoglou, N. K. Lazaridis, *Chem. Eng. J.*, **152**, 440 (2009).
7. M. W. Wan, Ch.-Ch. Kan, B. D. Rogel, M. L. P. Dalida, *Carbohydr. Polym.*, **80**, 891 (2010).
8. O. Gylienė, R. Binkienė, R. Butkienė, *J. Hazard. Mater.*, **171**, 133 (2009).
9. L. Qi, Z. Xu, *Colloids Surf., A*, **251**, 183 (2004).
10. W. S. Wan Ngah, S. Fatinathan, *J. Environ. Manage.*, **91**, 958 (2010).
11. P. Chassary, T. Vincent, E. Guibal, *React. Funct. Polym.*, **60**, 137 (2004).
12. M. S. D. Erosa, T. I. S. Medina, R. N. Mendoza, M. A. Rodriguez, E. Guibal, *Hydrometallurgy*, **61**, 157 (2001).
13. Y. Sag, Y. Aktay, *Biochem. Eng. J.*, **12**, 143 (2002).
14. N. Horzum, E. Boyaci, A. E. Eroglu, T. I. Shahwan, M. M. Demir, *Biomacromolecules*, **11**, 3301 (2010).
15. S. Haider, S.-Y. Park, *J. Membr. Sci.*, **328**, 90 (2009).
16. G. Moussavi, M. Mohseni, *Chemosphere*, **72**, 1649 (2008).
17. K. K. Wong, C. K. Lee, K. S. Low, M. J. Haron, *Chemosphere*, **50**, 23 (2003).
18. Y. S. Ho, G. McKay, *Water Res.*, **33**, 578 (1999).
19. B. Benguella, H. Benaissa, *Water Res.*, **36**, 2763 (2002).
20. Y. S. Ho, G. McKay, *Water Res.*, **34**, 735 (2000).
21. C.-C. Wang, L.-H. Li, H.-T. Lee, Y.-W. Ye, *Colloids Surf., A*, **389**, 246 (2011).
22. O. Gylienė, O. Nivinskienė, T. Vengris, *Carbohydr. Res.*, **343**, 1324 (2008).
23. C. N. R. Rao, *Chemical Application of Infrared Spectroscopy*, Academic Press, New York (1963).
24. A. Pawlak, M. Mucha, *Thermochim. Acta*, **396**, 153 (2003).
25. O. Gylienė, R. Tarozaitė, O. Nivinskienė, *Trans. Inst. Met. Finish.*, **82(1–2)**, 38 (2004).

Ona Gylienė, Vidmantas Ulevičius, Vadimas Dudoitis,
Kristina Plauškaitė, Rita Butkienė, Zenonas Kuodis,
Irena Vitėnienė

SUNKIŲJŲ METALŲ SORBCIJA CHITOZANU IR CHITOZANO-CITRATO DARINIAIS

Santrauka

Dėl nedidelių sorbcijos greičių ir menko mechaninio atsparumo chitozanas nėra plačiai taikomas filtravimo sistemose kaip sorbentas. Siekiant pagerinti chitozано sorbcines savybes jis buvo modifikuojamas citratu. Sorbcijos greitis ir sorbcinis imlumas buvo vertinami pagal sorbuotų sunkiųjų metalų kiekius. Sorbcijos greitis spartėja mažėjant chitozано dalelių dydžiui ir didėjant citrato koncentracijai. Citratas taip pat didina sorbento imlumą sunkiesiems metalams.

Citrato-chitozано darinio sorbcinis elgesys priklauso nuo jame esančio citrato kiekio. Jeigu chitozane yra nedideli citrato kiekiai ($<0,1 \text{ mol g}^{-1}$), tai sorbcijos greitis atitinka pseudo-antrojo laipsnio lygtį, o sorbcija pusiausvyrinėmis sąlygomis vyksta pagal Freundlich'o izotermės lygtį. Kai sorbente yra didesni citrato kiekiai, sorbcijos procesas tampa daug sudėtingesnis.

Chitozано-citrato darinys apibūdintas taikant potenciometrinį titravimą bei IR ir Ramano spektroskopijas.