

Electrochemical regeneration of chitosan after Ni(II)-citrate complex sorption

Ona Gylienė*,

Ona Nivinskienė

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

Chitosan acts as a sorbent of both Ni(II) and citrate in Ni(II)-citrate complex solutions. Citrate is sorbed by chitosan functional groups interacting with citrate-COOH groups. Investigations of desorption in a wide range of pH in solutions containing $0.1 \text{ mol} \cdot \text{l}^{-1}$ NaCH_3COO , NH_4Cl and Na_2SO_4 ensure only insignificant desorption of both Ni(II) and citrate. Electrolysis in mixtures containing sorbed chitosan and the mentioned electrolytes enables to deposit nickel onto the cathode and to oxidize citrate onto the anode. The efficiency of the current and regeneration rate depends on the electrolyte used, the current intensity, and the pH of the solutions. The slow regeneration rate is related to the low current efficiency in solutions containing low concentrations of Ni(II) and citrate. In Na_2SO_4 solutions, regenerated chitosan exhibits sorption ability similar to that of fresh chitosan. Ni(II)-citrate sorption by both regenerated and fresh chitosans obeys the pseudo-second order kinetics equation.

The FT-IR spectra of regenerated chitosan are similar to those of fresh chitosan.

INTRODUCTION

Due to intensive agricultural and industrial activities, pollution of the environment with heavy metals steadily increases. Soluble metal complexes are most dangerous for the environment. Ligands enhance the mobility of heavy metals in the environment and their uptake by plants; thus metals find their way into the human food chain. Differently from free metal ions, metal complexes contained in wastes are difficult to decontaminate.

The increasing amounts of metal complexes used in different branches of industry require cost-effective treatment technologies for wastewaters. One of such technologies is the use of biosorbents. It is mainly agricultural and wood treatment wastes that are used as biosorbents [1-7].

Differently from synthetic ion exchangers, which are used for metal removal from dilute solutions in industry, biosorbents are bio-renewable, biodegradable and rather cheap. However, the sorption capacity of biosorbents in many cases is much lower than that of synthetic ion exchangers. Chitin-containing sorbents show a selective sorption of heavy metal ions. Chitosan, which is obtained from chitin by its deacetylation, is able to sorb both heavy metals and organic compounds [8-11].

The ability of chitosan and its derivatives to sorb heavy metals in many cases is similar to that of synthetic ion exchangers [12, 13]. The presence of organic ligand citrate in solutions with the ligand / metal ratio up to 1 does not remarkably change the uptake of Ni(II) by chitosan [14] or Cu(II) ions [15]. An excess of ligand leads to a decrease in sorption capacity. Both Ni(II) and citrate are sorbed by the same functional groups. During the sorption, a competition between Ni(II) and citrate takes place [14].

Chitosan as compared to other waste materials used for sorption is rather expensive. This is the main reason for its limited usage in practice. Besides, after sorption chitosan becomes toxic and hardly biodegradable. The widely used incineration in such cases could be complicated due to difficulties in dewatering as well as the high content of nitrogen in chitosan when nitrogen oxides can be formed [16, 17]. The regeneration of chitosan and its reuse could solve the problem of disposal of the spent sorbent.

Desorption of both heavy metals and organics from chitosan remains little investigated. In case of free metal ions such as Cu(II), Ni(II), Zn(II), UO_2^{2+} desorption proceeds only in strong acidic solutions. However, in such a medium the dissolution of chitosan proceeds, except sulfuric acid solutions, where chitosan is insoluble. Regeneration is affected by the presence of ammonium chloride [7, 13, 18]. For desorption of organic compounds, alkaline solutions are used in most cases [19].

* Corresponding author. Fax +370-5 2649774. E-mail: gyliene@ktl.mii.lt

This work was carried out with the purpose of regenerating chitosan flakes after sorption of Ni(II)–citrate complex by electrolysis and reusing them for sorption.

EXPERIMENTAL

Chitosan produced from fly larva shells was used as a sorbent for Ni(II)–citrate complex. It was produced by the same procedure as that used for crustacean exoskeletons [20, 21]. The key steps in the extraction of chitin from shells are the removal of proteins and minerals such as calcium carbonate and phosphate by treatment with alkaline and acidic solutions in turn. Chitosan was recovered from chitin by deacetylation using 45% NaOH for 4 h at 100 °C. The recovered chitosan was present as flakes with dimensions of $4.8 \text{ m}^2 \cdot \text{g}^{-1}$, containing 7.8% N and 41.8% C [8].

All sorption and desorption experiments were carried out under batch conditions. The load was 10 g of dry sorbent per litre solution in sorption experiments and 40 g per litre in desorption experiments. The adsorption was investigated at room temperature by pouring Ni(II) and citrate containing solutions onto chitosan. The pH was adjusted with NaOH or H_2SO_4 solutions. Desorption experiments followed the adsorption experiments, which were carried out in solutions containing Ni(II) and citrate $10 \text{ mmol} \cdot \text{l}^{-1}$ each. After sorption, chitosan was filtered and rinsed with cold deionized water and dried at 70 °C. Desorption was carried out in $0.1 \text{ mmol} \cdot \text{l}^{-1}$ NaCH_3COO , NH_4Cl or Na_2SO_4 solutions. The pH was adjusted with NaOH, NH_4OH , CH_3COOH , HCl or H_2SO_4 , respectively, in order to avoid the introduction of foreign ions. The sorbed and desorbed quantities of Ni(II) and citrate were determined from changes of their concentration in the solutions.

Ni(II) in the solutions was determined complexometrically using EDTA as a titrant and murexide as an indicator. Low Ni(II) concentrations were determined photometrically at $\lambda = 490 \text{ nm}$ using dimethylglyoxime. The citrate concentration in the solutions was determined after oxidation in alkaline solutions with KMnO_4 , its excess being retitrated in acidic solutions with oxalic acid.

Regeneration of chitosan was carried out electrochemically under galvanostatic conditions using a Ī Ē-51 potentiostat (Russia) and a three-camera cell – cathodic with a volume of 100 ml and two anodic 25 ml each, separated by a glass membrane. Four grams of chitosan (dry weight before sorption) containing Ni(II)–citrate was loaded in the cathodic compartment. Nickel gauze was used as a cathode and Pt wires as anodes. The electrochemical cell was filled with electrolytes – $0.1 \text{ mol} \cdot \text{l}^{-1}$ NaCH_3COO , NH_4Cl or Na_2SO_4 solutions. The solution with chitosan was mixed with a magnetic stirrer during elec-

trolysis. The pH was adjusted with the corresponding acidic or alkaline solution. In long-term experiments, when the electrolysis was off, the catholyte and the anolyte were poured out separately from the cells.

The content of Ni(II) in chitosan was determined after treatment of 0.02–0.05 g of dried samples with a mixture of H_2SO_4 and H_2O_2 at high temperatures according to [22]. In calculations, citrate concentration in regenerated chitosan was assumed to be equal to Ni(II) concentration.

The current efficiency for Ni(II) and citrate was determined from the ratio of Ni(II) or citrate removed during regeneration and the theoretically calculated mass (m) of nickel deposition or citrate oxidation according to Faraday's law:

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

where M is the molar mass of substances

I – current intensity, A

t – time, s

n – equivalent of substances, for Ni(II) it is equal to 2, and for citrate – 18

F – Faraday's number equal to 96500 C.

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

RESULTS AND DISCUSSION

Sorption experiments carried out using chitosan as a sorbent in a wide range of pH in solution containing electrolytes such as NaCH_3COO , NH_4Cl and Na_2SO_4 (Fig. 1) indicated a similar sorption ability of chito-

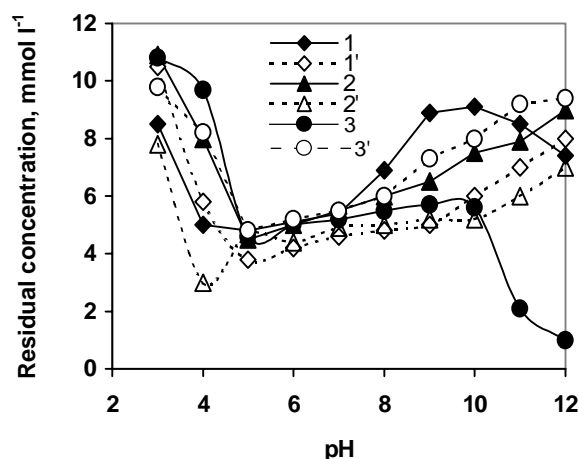


Fig. 1. Influence of pH on residual Ni(II) (1, 2, 3) and citrate (1', 2', 3') concentrations after sorption by chitosan in $0.1 \text{ mmol} \cdot \text{l}^{-1}$ NaCH_3COO (1' 1'), $0.1 \text{ mmol} \cdot \text{l}^{-1}$ NH_4Cl (2, 2') and $0.1 \text{ mmol} \cdot \text{l}^{-1}$ Na_2SO_4 (3, 3') solutions. Initial concentrations: Ni(II) – $10 \text{ mmol} \cdot \text{l}^{-1}$ and citrate – $10 \text{ mmol} \cdot \text{l}^{-1}$. Load $10 \text{ g} \cdot \text{l}^{-1}$

san for Ni(II) and citrate in all electrolytes studied. It was highest in the pH range 5 to 8. The sorption remarkably decreased in more alkaline or acidic solutions.

In solutions containing equal concentrations of Ni(II) and citrate the adsorbed quantities were similar (Fig. 2). With an increase in citrate concentration, the sorbed amount of Ni(II) decreased while that of citrate increased. In solutions containing 30 mmol · l⁻¹ of citrate and 10 mmol · l⁻¹ of Ni(II), citrate sorption reached 1.5 mmol · g⁻¹ and under the same conditions exceeded free Ni(II) sorption up to 6 times. Citrate sorption without Ni(II) strongly depended on pH (Fig. 3) as well. It decreased with an increase in pH. However, in acidic solutions at pH~3 the dissolution of chitosan begins. It is worth noting that citrate sorption by chitosan was remarkably weaker in the absence than in the presence of Ni(II) ions. The successive Ni(II) sorption after citrate sorption depended on the sorbed quantities of citrate and was similar to the sorption from the complex solution. Citrate is probably sorbed by the inte-

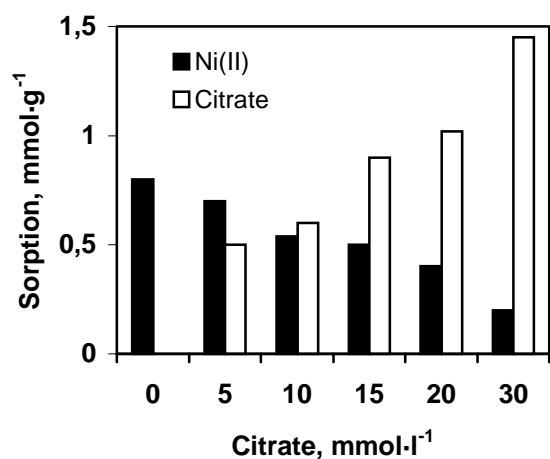


Fig. 2. Influence of citrate concentration on Ni(II) and citrate sorption by chitosan in solutions containing 10 mmol · l⁻¹ Ni(II) at pH 7. Load 10 g · l⁻¹

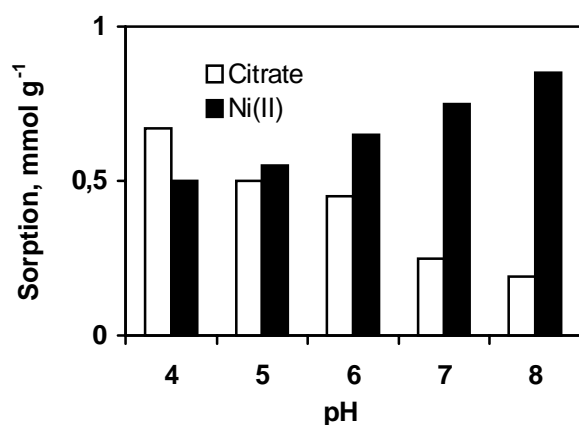


Fig. 3. Influence of pH on citrate sorption by chitosan in solutions containing 10 mmol · l⁻¹ citrate. Ni(II) sorbed after citrate sorption in 10 mmol · l⁻¹ Ni(II) solution at pH 7. Load 10 g · l⁻¹

raction of chitosan functional groups -NH₂ and -OH with -COOH groups of citrate [23]. Ni(II) ions can interact with the same groups forming complexes or chelates [7, 15]. The free groups of citrate not bound with chitosan functional groups can interact with Ni(II) ions forming in this way multi-layer complexes on the chitosan surface.

The sorption of Ni(II)-citrate is an irreversible process. Desorption cannot be performed in alkaline or acidic solutions where the sorption is negligible (Fig. 1). Investigations have shown that Ni(II) and citrate transfer from the chitosan surface to solution proceeds slowly (Fig. 4). The maximum desorption was achieved after 50-60 min and it did not change with time. The desorbed quantity of Ni(II) was only slightly higher at pH 3 as compared to that at pH 5, while the citrate desorption is distinctly higher at higher values of pH. Ni(II) citrate desorption in Na₂SO₄ solutions made up only 3-5% of the total sorbed quantity.

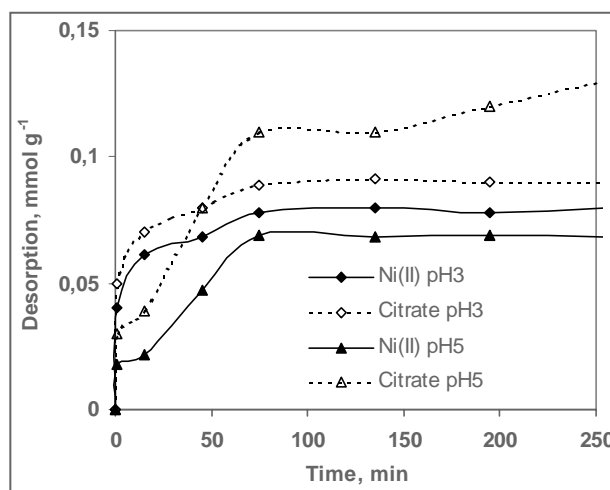


Fig. 4. Ni(II) and citrate desorption kinetics in Na₂SO₄ solution from chitosan containing 0.6 mmol · g⁻¹ Ni(II) and 0.58 mmol · g⁻¹ citrate. Load 40 g · l⁻¹

More detailed investigations of desorption were carried out in the pH range 2 to 12 in solutions containing 0.1 mol · l⁻¹ NaCH₃COO, NH₄Cl or Na₂SO₄ (Fig. 5). In solutions containing NaCH₃COO or NH₄Cl, at pH 2-3, the dissolution of chitosan proceeds. In any case, Ni(II)-citrate desorption proceeds most easily in acidic acetate solutions. At best, Ni(II) desorption makes up ~10% and that of citrate ~15% of the total sorbed quantity (Fig. 5a). In ammonium chloride solutions, both Ni(II) and citrate desorption is considerably lower (Fig. 5b). It proceeds best in alkaline solutions and makes up ~5% for Ni(II) and ~10% for citrate. Desorption is somewhat lower in Na₂SO₄ solutions (Fig. 5c), and is negligible only in neutral solutions. In acidic solutions, the desorption of both Ni(II) and citrate is similar, while in alkaline solutions the desorption of citrate prevails. The rather high desorption in acidic

acetate solutions or alkaline ammonium chloride containing solutions is apparently connected with chemical interactions between sorbate and electrolyte. A higher desorption in acidic Na_2SO_4 solutions versus NH_4Cl solutions as well as in alkaline solutions versus NaCH_3COO is probably related to a higher ionic strength.

The quantities of both Ni(II) and citrate desorbed by a repeated treatment of chitosan with Na_2SO_4 solution are considerably less and make up 1–5%.

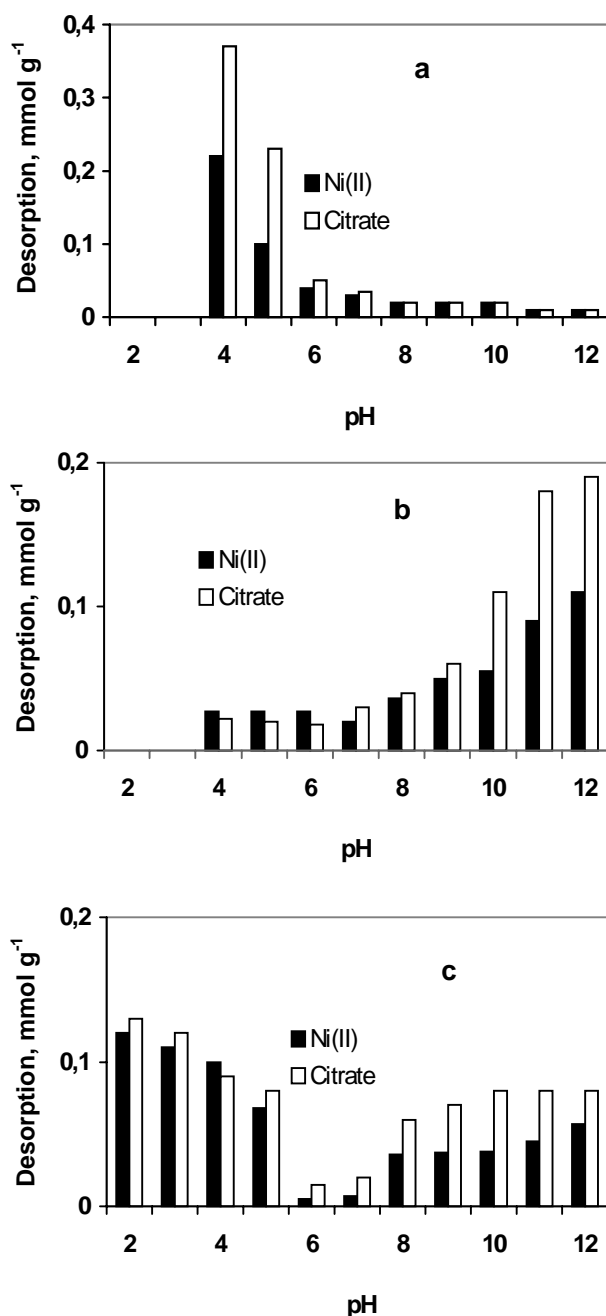


Fig. 5. Influence of pH on Ni(II) and citrate desorption under equilibrium conditions in: *a* – $0.1 \text{ mmol} \cdot \text{l}^{-1} \text{ NaCH}_3\text{COO}$, *b* – $0.1 \text{ mmol} \cdot \text{l}^{-1} \text{ NH}_4\text{Cl}$ and *c* – $0.1 \text{ mmol} \cdot \text{l}^{-1} \text{ Na}_2\text{SO}_4$ electrolytes. Initial content of Ni(II) in chitosan $0.62 \text{ mmol} \cdot \text{g}^{-1}$ and citrate $0.55 \text{ mmol} \cdot \text{g}^{-1}$. Load $40 \text{ g} \cdot \text{l}^{-1}$

Desorption experiments have shown that the regeneration of sorbent cannot be achieved by acidic or alkaline treatment. The usage of the same volumes as in the case of sorption assures at most only a 5–10% desorption. Simply changing the pH does not allow for the regeneration of chitosan. Therefore attempts were made to regenerate chitosan by using electrolysis, which enables to deposit nickel onto the cathode and to oxidize citrate onto the anode. The compact nickel deposition from citrate solutions [24] and the oxidation of citrate to CO_2 and CO onto a Pt electrode [25] proceeds at pH 5. The electrolysis under galvanostatic conditions at these values of pH for 20 hours is tabulated in Table 1. During electrolysis, the main reaction onto the cathode is hydrogen evolution and onto the anode oxygen formation. As a result, the catholyte becomes alkaline and the anolyte acidic. The pH value in the cathodic part was kept constant by adding acids.

Table 1. Electrochemical regeneration of 4 g chitosan containing $0.62 \text{ mmol} \cdot \text{g}^{-1} \text{ Ni(II)}$ and $0.6 \text{ mmol} \cdot \text{g}^{-1} \text{ citrate}$ sorbed. pH 5 and $I = 400 \text{ mA}$

| Duration of electrolysis, h | Residual Ni(II), $\text{mmol} \cdot \text{g}^{-1}$ | | |
|-----------------------------|--|------------------------|--------------------------|
| | Na CH_3COO | NH_4Cl | Na_2SO_4 |
| 5 | 0.32 | 0.42 | 0.5 |
| 10 | 0.15 | 0.25 | 0.23 |
| 15 | 0.025 | 0.05 | 0.025 |
| 20 | < 0.01 | 0.001 | 0.005 |

The bulk of Ni(II) is removed during the first 10 hours. However, the sorption properties of chitosan at this stage of regeneration are considerably worse than those of fresh chitosan. Only an additional treatment for another 10 hours allows reaching the initial sorption ability. The most rapid desorption during electrochemical treatment proceeds in acetate solutions and the slowest one in sulfate solutions. Nevertheless, due to the complicated anodic reactions of acetate and chloride, further electrochemical investigations were carried out with Na_2SO_4 solutions (Tables 2–5). This electrolyte does not take part in electrochemical reactions.

Regeneration of chitosan without pH adjustment (Table 2) at pH 5 and $I = 400 \text{ mA}$ proceeds slowly. After 24 hours of electrolysis the residual content of Ni(II) in chitosan is rather high (Table 6) and the sorption ability is considerably lower. The same regeneration rate can be attained by keeping a constant pH 5 and at a lower current, *i.e.* 200 mA (Table 3). In this case, the concentrations of both Ni(II) and citrate in the catholyte and the anolyte are considerably higher than those at a high current intensity.

An increase in the current intensity and a decrease in pH enable to reduce the regeneration process

Table 2. Electrochemical regeneration of 4 g chitosan containing $0.62 \text{ mmol} \cdot \text{g}^{-1}$ Ni(II) and $0.57 \text{ mmol} \cdot \text{g}^{-1}$ citrate in Na_2SO_4 electrolyte at $I = 400 \text{ mA}$ without pH adjustment

| Duration of electrolysis, h | Concentrations in solution, $\text{mmol} \cdot \text{l}^{-1}$ | | | | | |
|-----------------------------|---|--------|---------|---------|--------|---------|
| | Catholyte | | | Anolyte | | |
| | pH | Ni(II) | Citrate | pH | Ni(II) | Citrate |
| 3 | 12.1 | 0.25 | 2.3 | 1.2 | 0.015 | 1.7 |
| 6 | 12.2 | 0.3 | 1.7 | 1.1 | 0.033 | 2.6 |
| 9 | 12.2 | 0.2 | 1.7 | 1 | 0.3 | 3 |
| 12 | 12.3 | 0.1 | 1.6 | 0.95 | 0.3 | 2.5 |
| 15 | 12.4 | 0.35 | 1.5 | 0.8 | 0.33 | 1.8 |
| 18 | 12.5 | 0.62 | 1.5 | 0.9 | 0.3 | 1.7 |
| 21 | 12.5 | 0.32 | 1.3 | 1 | 0.31 | 1.5 |
| 24 | 12.4 | 0.22 | 1.2 | 1 | 0.32 | 1.4 |

Table 3. Electrochemical regeneration of 4 g chitosan containing $0.56 \text{ mmol} \cdot \text{g}^{-1}$ Ni(II) and $0.62 \text{ mmol} \cdot \text{g}^{-1}$ citrate in Na_2SO_4 electrolyte at pH 5 (catholyte) and $I = 200 \text{ mA}$

| Duration of electrolysis, h | Concentrations in solution, $\text{mmol} \cdot \text{l}^{-1}$ | | | |
|-----------------------------|---|---------|---------|---------|
| | Catholyte | | Anolyte | |
| | Ni(II) | Citrate | Ni(II) | Citrate |
| 4 | 2.5 | 3.5 | 0.06 | 0.6 |
| 8 | 2.4 | 5.4 | 0.08 | 0.8 |
| 12 | 2.1 | 3.8 | 0.13 | 2.1 |
| 16 | 1.4 | 3.6 | 0.14 | 1.6 |
| 20 | 0.8 | 2.7 | 0.1 | 1.2 |
| 24 | 0.6 | 1.4 | 0.08 | 0.7 |

Table 4. Electrochemical regeneration of 4 g chitosan containing $0.65 \text{ mmol} \cdot \text{g}^{-1}$ Ni(II) and $0.55 \text{ mmol} \cdot \text{g}^{-1}$ citrate in Na_2SO_4 electrolyte at pH 3 (catholyte) and $I = 500 \text{ mA}$

| Duration of electrolysis, h | Concentrations in solution, $\text{mmol} \cdot \text{l}^{-1}$ | | | |
|-----------------------------|---|---------|---------|---------|
| | Catholyte | | Anolyte | |
| | Ni(II) | Citrate | Ni(II) | Citrate |
| 3 | 0.1 | 1.8 | < 0.01 | 0.8 |
| 6 | 0.27 | 6.1 | 0.1 | 1.4 |
| 9 | 0.25 | 3.3 | 0.01 | 1.6 |
| 12 | 0.18 | 1.7 | 0.09 | 1.5 |

Table 5. Electrochemical regeneration of 4 g chitosan containing $0.58 \text{ mmol} \cdot \text{g}^{-1}$ Ni(II) and $0.57 \text{ mmol} \cdot \text{g}^{-1}$ citrate in Na_2SO_4 electrolyte at $I = 500 \text{ mA}$ and different values of pH

| Duration of electrolysis, h | pH | Concentration, $\text{mmol} \cdot \text{l}^{-1}$ | | | |
|-----------------------------|------|--|---------|---------|---------|
| | | Catholyte | | Anolyte | |
| | | Ni(II) | Citrate | Ni(II) | Citrate |
| 5 | 4 | 2.5 | 1.32 | 0.05 | 0.6 |
| 5 | 12.3 | 0.2 | 1.32 | 0.09 | 0.8 |

to 12 hours (Table 4). The disadvantage of high current densities is incompact nickel deposition. Stripped coating flakes or nickel powder may be formed and mixed with chitosan. For the electrochemical cell

and electrodes used in our experiments, the highest current intensity that could be applied was 400 mA.

The most rapid regeneration can be achieved when the electrolysis proceeds in acidic and alkaline solutions in turn (Table 5). In this case, the highest current efficiency is obtained for both Ni(II) and citrate (Table 6). The lowest current efficiency and the worst sorption ability of regenerated chitosan are obtained in the case when pH is not adjusted.

Ni(II) and citrate concentrations in the catholyte during electrolysis depend on the duration of electrolysis, current intensity and pH. As a rule, these concentrations reached the maximum with time and then decreased to almost complete removal. An increase in pH leads to a decrease in Ni(II) concentration in the catholyte. Citrate concentrations in the catholyte are slightly higher in stronger acidic solutions. Its concentrations in the anolyte considerably increase with increasing the pH, probably because of a more complete dissociation of citrate in alkaline solutions and its transfer to the anodic part. Ni(II) and citrate concentrations in the electrochemical cell indicate that Ni(II) and citrate desorption rate during electrolysis is much higher than that without electrolysis. The main reason for the slow chitosan regeneration is the ineffective use of the current for nickel deposition from dilute solutions [26].

As during electrolysis the pH of the catholyte increases and that of the anolyte decreases, to avoid addition of large quantities of H_2SO_4 a portion of the anolyte was poured into the catholyte and part

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

| Conditions of electrolysis | Initial sorbed quantities, mmol | | Residual Ni(II) in chitosan, mmol · g ⁻¹ | Ni(II) sorption by regenerated chitosan, mmol · g ⁻¹ | Current quantity, C | Current efficiency, % | |
|----------------------------|---------------------------------|---------|---|---|---------------------|-----------------------|---------|
| | Ni(II) | Citrate | | | | Ni(II) | Citrate |
| Table 2 | 2.44 | 2.3 | 0.22 | 0.45 | 34560 | 1.4 | 11.1 |
| Table 3 | 2.52 | 2.5 | 0.1 | 0.58 | 17280 | 2.7 | 23.9 |
| Table 4 | 2.6 | 2.2 | 0.08 | 0.62 | 21600 | 2.2 | 17.1 |
| Table 5 | 2.32 | 2.3 | 0.12 | 0.60 | 14400 | 2.9 | 26.5 |

Table 7. The rate constants and correlation coefficients in kinetic experiments

| Curve numbers | Pseudo-second order reaction parameters | | |
|-------------------------------------|---|--|----------------|
| | | k_2 , g · mmol ⁻¹ · h ⁻¹ | R ² |
| Fig. 7, curve1 curve2 curve 3 | curve1 | 1.14 | 0.9982 |
| | curve2 | 1.19 | 0.9995 |
| | curve 3 | 0.42 | 0.9999 |

The experimental conditions are indicated in the figure captions.

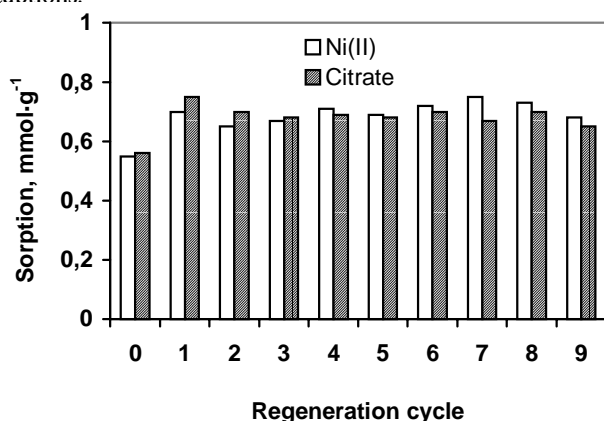


Fig. 6. Influence of regeneration cycles in Na₂SO₄ electrolyte on Ni(II) citrate sorption by chitosan in solutions containing 10 mmol · l⁻¹ Ni(II) and 10 mmol · l⁻¹ citrate at pH 7 and load 10 g · l⁻¹. Regeneration conditions: electrolysis at I = 400 mA, 5 hours at pH 5 and 5 hours at pH 12.2, pH maintained by mixing catholyte and anolyte. Load 40 g · l⁻¹

of the catholyte into the anolyte. 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. After 10 regeneration cycles (Fig. 6) the sorption ability is nearly the same and no visible changes in chitosan structure are observed.

The electrolyte used in the regeneration procedure has the crucial influence on chitosan sorption properties. The sorption rate and sorption ability in sulfate solutions show noticeable changes only after ten cycles of regeneration (Fig. 7), whereas these parameters drastically change in acetate solutions after the first regeneration cycle.

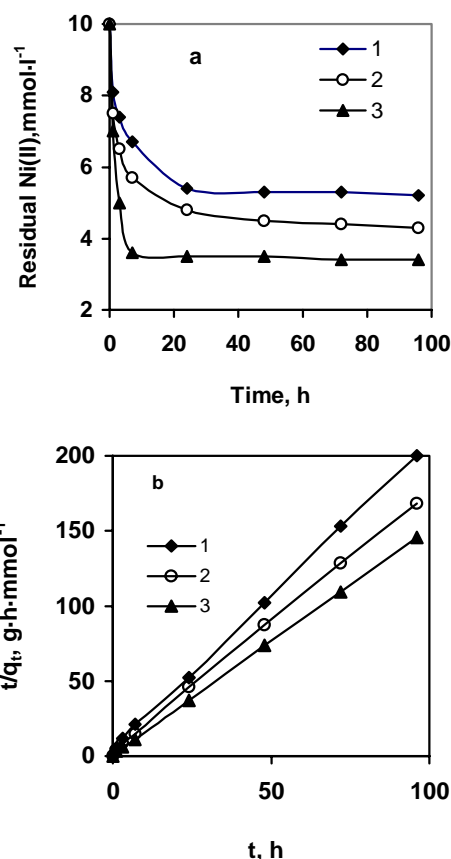


Fig. 7. Uptake of Ni(II) by chitosans (a): 1 – first sorption, 2 – 10th sorption after regeneration in Na₂SO₄ electrolyte and 3 – sorption after regeneration in 2nd NaCH₃COO electrolyte. Initial concentrations 10 mmol · l⁻¹ Ni(II) and 10 mmol · l⁻¹ citrate, pH 7, load 10 g · l⁻¹; (b) – test of pseudo-second order equation for adsorption of Ni(II)

The rate of Ni(II) sorption by regenerated as well as by fresh chitosan can be described by the pseudo-second order kinetics equation [5]

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

where Q is the amount of Ni(II) sorbed under equilibrium conditions, mmol · g⁻¹, q_t is the amount of Ni(II) sorbed by chitosan at time t , mmol · g⁻¹, and k_2 is the pseudo-second order sorption rate constant, g · mol⁻¹ · h⁻¹.

The pseudo-second rate model fits over the whole range of time interval (Fig. 7a, Table 7). This model is based on the assumption that the rate-determining step may be chemical sorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate. In our case it may be the interaction of citrate $-\text{COOH}$ group with $-\text{NH}_2$ and $-\text{OH}$ groups of chitosan [27].

FT-IR spectra of free chitosan, Ni(II)-citrate complex absorbed onto fresh chitosan and chitosan after desorption were recorded over a frequency region of $400\text{--}4000\text{ cm}^{-1}$ (Fig. 8). FT-IR investigations showed that intense bands were observed at about 1620 cm^{-1} (ν_{as} of COO^-) and 1410 cm^{-1} (ν_{s} of COO^-). The difference $\Delta\nu$ between the peaks was higher than 200 cm^{-1} , indicating that some of the COO^- groups were coordinated with Ni(II) ions in monodentate manner. The broadening of the asymmetric stretching vibrational mode of the carboxylate group at 1620 cm^{-1} indicates numerous slightly energetically distinct complexes among chitosan, citrate and Ni(II) ions. In addition, high concentrations of Ni(II)-citrate complex in the solution gave rise to a broad absorption band in the frequency region of $3150\text{--}3500\text{ cm}^{-1}$ due to a strong intermolecular hydrogen-bonding network of free acid groups, as well as several absorption bands near 2700 and 2600 cm^{-1} . IR absorption at 1659 and 1550 cm^{-1} indicated the presence of an amide group, which could be formed by interaction between the carboxylic group of citric acid and $-\text{NH}_2$ of chitosan [28, 29].

The FT-IR spectra of regenerated chitosan in sulfate solution (Fig. 8a) were similar to those of free chitosan (Fig. 8c) and showed IR absorption above 3450 cm^{-1} and at 1596 cm^{-1} , which corresponded to the characteristic stretching (νNH) and bending (δNH) vibrations of $-\text{NH}_2$ group, respectively.

Thus, the irreversible sorption of Ni(II)-citrate complex, its fitting the pseudo-second order kinetics

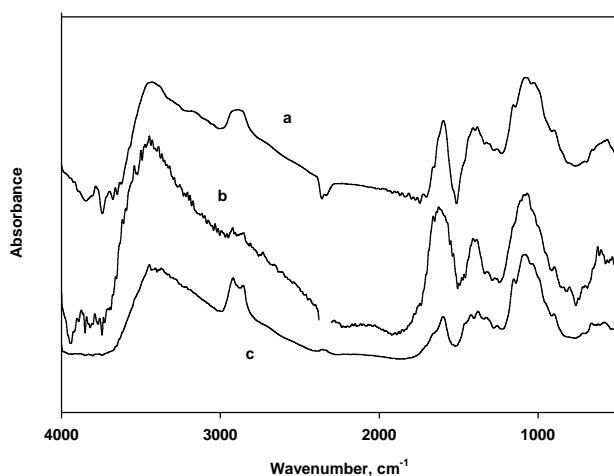


Fig. 8. FT-IR spectra of chitosan: (a) – fresh, (b) – after Ni(II)-citrate sorption from solutions containing $10\text{ mmol} \cdot \text{l}^{-1}$ Ni(II) and $10\text{ mmol} \cdot \text{l}^{-1}$ citrate, pH 7, (c) – regenerated

model, and FT-IR investigations have shown a chemical interaction to proceed during sorption between chitosan and Ni(II)-citrate functional groups. The application of electrolysis enables to destroy the chemical bonds formed between the sorbate and the sorbent and to remove Ni(II)-citrate from chitosan.

CONCLUSIONS

The desorption of Ni(II)-citrate sorbed by chitosan using $0.1\text{ mol} \cdot \text{l}^{-1}$ NaCH_3COO , NH_4Cl and Na_2SO_4 as extractants makes up only 1–5% of the total sorbed quantity. Desorption is enhanced by electrolysis. Electrolysis under galvanostatic conditions in these electrolytes enables to regenerate chitosan by nickel deposition onto the cathode and citrate oxidation onto the anode. The current efficiency depends on the current intensity, pH and the duration of electrolysis. The slow regeneration rate is determined by the ineffective use of the current for nickel deposition in dilute solutions.

Chitosan regenerated in Na_2SO_4 solutions after 10 cycles shows the same sorption properties as in the first sorption. The sorption ability of chitosan regenerated in acetate solutions is higher than that of fresh chitosan.

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Ona Gylienė, Ona Nivinskienė

CHITOZANO, SORBAVUSIO NI(II)-CITRATO KOMPLEKSÅ, ELEKTROCHEMINĖ REGENERACIJA

Santrauka

Ni(II)-citrato kompleksiniuose tirpaluose chitozanas sorbuoja tiek Ni(II) jonus, tiek citrato jonus. Citratas yra sorbuojamas jo –COOH grupėms sąveikaujant su chitozано funkcinėmis grupėmis. Desorbcijos tyrimai, atlikti plaèiame pH verèiø intervale 0.1 mol · l⁻¹ NaCH₃COO, NH₄Cl ir Na₂SO₄ tirpaluose, parodė, kad juose vyksta tik neþymi Ni(II) bei citrato desorbcija. Elektrolizinant sorbuotà chitozanà minètuose tirpaluose ant katodo nusėda nikelis, o citratas yra suoksiduojamas ant anodo. Srovės iðeiga ir regeneracijos greitis priklauso nuo naudojamo elektrolito, srovės tankio ir tirpalø pH. Nedidelis regeneracijos greitis yra sietinas su nedidele srovine iðeiga mažø Ni(II) ir citrato koncentracijø tirpaluose. Na₂SO₄ tirpaluose regeneruoto chitozано sorbcinis pajėgumas yra toks pat kaip ir pirminio chitozано. Ni(II)-citrato sorbcijà tiek ant pirminio chitozано, tiek ant regeneruoto chitozано galima aprašyti pseudo antro laipsnio kinetine lygtimi.

Regeneruoto chitozано FT-IR spektrai yra identiški pirminio chitozано FT-IR spektrams.