Recycling of Ni(II)–citrate complexes using precipitation in alkaline solutions

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Abstract

When the excess of Ni(II) ions as compared to citrate concentration is used both Ni(II) ions and citrate can be precipitated in alkaline solutions. The ratio between Ni(II) and citrate in the precipitate and completeness of citrate precipitation depends on the ratio between the Ni(II) and citrate concentrations in the initial solution and its pH. The data of chemical analysis, potentiometric titration, FT-IR as well as visible spectrophotometric investigations suggest that Ni(II) in the insoluble compound is bound with three –COO⁻ groups and –OH group of the citrate. The insoluble compound also contains SO_4^{2-} and hydroxides. The treatment of this precipitate with H_2SO_4 enables to recover a soluble Ni(II)–citrate complex, which can be reused in practice, and to remove the excess of Ni(II) in the form of insoluble $Ni(OH)_2$.
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1. Introduction

Heavy metals such as Zn, Cu, Ni, Cr, Mo are essential nutrients for plants and animals. However, they become toxic at high concentrations. The toxicity of heavy metals depends mostly on a free ion, i.e. on the concentration of a soluble metal compound rather than on the total metal concentration. The insoluble metal compounds are less bioavailable and toxic. The industrial and agricultural emissions are the reason of enormous pollution of environment with heavy metals. Most of the heavy metals dissolved in wastewater effluents and surface runoff are complexed. Such complexing agents enhance metal solubility as well as their bioavailability [1–3].

Metal complexes are widely used in practice in order to enhance metal solubility or avoid the formation of insoluble metal compounds. The citrate is among those complexing agents, which possess the ability to form strong metal complexes with a number of heavy metals such as Pb(II), Cu(II), Ni(II), Co(II), Pb(II), Fe(III), etc. The citrate as a polydentate ligand forms a number of complexes with Ni(II) both in acidic and alkaline solutions [4–6]. Polynuclear complexes are formed in alkaline solutions.

Soluble nickel citrate complexes are used in nuclear power, metal finishing, dying, painting, printed circuit board industries. The using of citrate as a complexing agent in electroless nickel plating solutions enables to prepare solutions of high quality and high deposition rate [7,8]. Due to accumulation of by-products in plating process the spent solutions become unfit for use and they must be decontaminated.

The chemical precipitation [9,10] is the most cost-effective treatment technology. The possibility to precipitate metals in the form of insoluble compounds, mostly metal hydroxides, in solutions containing complexing agents depends on the complex stability constant (β_n) and the hydroxide solubility product (S) and can be described by the equation

$$ML_n = \frac{\beta_n S L^n}{[OH^-]^m}$$

where ML_n is the metal residual concentration after hydroxide precipitation, L the ligand concentration, n the number of ligand molecules in complex, and m the metal ion valency. The concentration of metal ion in solution decreases with decrease in both the solubility of metal hydroxide and the complex stability constant. Practically the metal removal from solutions containing complexing agents is possible when the $-\log S$ exceeds $\log \beta_n$ 5–6 orders of magnitude. However, in many cases more stable complexes are used.

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The oxidative destruction of ligands is used mainly for metal removal from complexing agents containing solutions. When the ligands are completely destroyed to the harmless substances CO_2 and N_2, the metals are precipitated in the form of insoluble compounds. Hydrogen peroxide, which gives only water as a reaction product, is the most environmentally friendly oxidizing agent. Its disadvantage is the slow reaction rate; therefore, the use in practice is limited. The ozone is the most powerful oxidizing agent, which decomposes all known ligands. Its use in practice is limited by strong hazardous influence onto environment. The use of electrolysis enables both to destroy the ligands onto anode and to recover metals onto cathode. However, the oxidation of organic matter to the harmless substances onto anode is a complicated task in most cases [11].

When excess of metal ions is used, the ability of carboxylic ligands to form soluble metal complexes considerably differs from that of amino ligands. It is possible to remove carboxylic metal complexes by the excess of metal ions in the form of insoluble compounds from both acidic (pH 3–4) and alkaline (pH > 12) solutions; meanwhile, the amino complexes totally remain in the solution. The excess of Ni(II) causes the precipitation of carboxylic ligands in alkaline solutions. X-ray investigations have shown that the complex formed is amorphous [12].

This study examines the regularities of formation of insoluble nickel–citrate compounds and their chemical composition in alkaline solution. These investigations give the opportunity to recover both Ni(II) and citrate by means of precipitation without ligand destroying and to reuse them in industry.

2. Experimental

The precipitation was carried out at ambient temperature by adding of Ni(II) solution to Ni(II)–citrate solutions by vigorous mixing. pH was adjusted with NaOH or H_2SO_4. The precipitates formed were centrifuged and rinsed with cold (∼5 °C) water.

The experiments were carried out with $NiSO_4 \cdot 7H_2O$ and sodium citrate ($Na_3C_6H_5O_7 \cdot 5.5H_2O$) of analytical grade purity ("Reagent", Russia). The chemical composition of precipitates was determined after their dissolution in the diluted 1:4 H_2SO_4. The citrate concentration was determined after oxidation in the alkaline solutions with $KMnO_4$, its excess was retitrated in acidic solutions with oxalic acid. Ni(II) in the solutions was determined using EDTA as a titrant and murexide as an indicator. Low concentrations of Ni(II) (lower than $0.5 \, \text{mmol} \, \text{l}^{-1}$) were determined photometrically at $\lambda = 490 \, \text{nm}$ using dimethylglyoxime as an indicator [13].

The light absorption spectra were recorded with a Perkin-Elmer Lambda 35 UV-VIS spectrometer at 20 °C in 1 cm thick cells. Deionized water was used as reference.

The infrared spectra of the precipitates were recorded in KBr pellets on a FT-IR (Hartman & Braun, Canada).

The spectra were recorded in the region between 4000 and $500 \, \text{cm}^{-1}$.

3. Results and discussion

Polynuclear metal complexes with the crystalline structure have been the subject of numerous structural and spectroscopic studies [14,15]. However, the amorphous complexes are much less investigated. The interaction of Ni(II) with citrate is thoroughly studied in the acidic and neutral solutions. The alkaline solutions of Ni(II)–citrate complexes are investigated much less [16,17].

Fig. 1 shows the effect of added Ni(II) on the concentrations of both Ni(II) and citrate in solutions at pH 11. When the Ni(II) concentration is low compared with that of citrate, the soluble Ni(II)–citrate complexes form. When Ni(II) concentration is three-fold higher than that of citrate the insoluble compounds begin to form. With further increase in Ni(II) concentration the residual Ni(II) and citrate concentrations continuously decreased. Most complete citrate precipitation proceeds at the initial Ni(II) concentrations five- to six-fold higher than the initial citrate concentration.

The proportion of Ni(II) to the citrate precipitated depends on their initial concentrations and the pH (Table 1, Fig. 2). With increase in the initial Ni(II) concentration the residual concentrations of Ni(II) decrease. The residual citrate concentrations are higher in the solutions with their higher initial concentrations. The pH value at which the most complete precipitation takes place depends on the initial concentrations of the substances. As a rule, the residual concentrations decrease with increase in pH. It is worth noting that the extent of citrate removal makes up 70–80% in the most favorable cases. Only the repeated precipitation with excess of Ni(II) makes it possible to remove citrate most efficiently (95–98%). Ni(II) in these cases is completely removed.
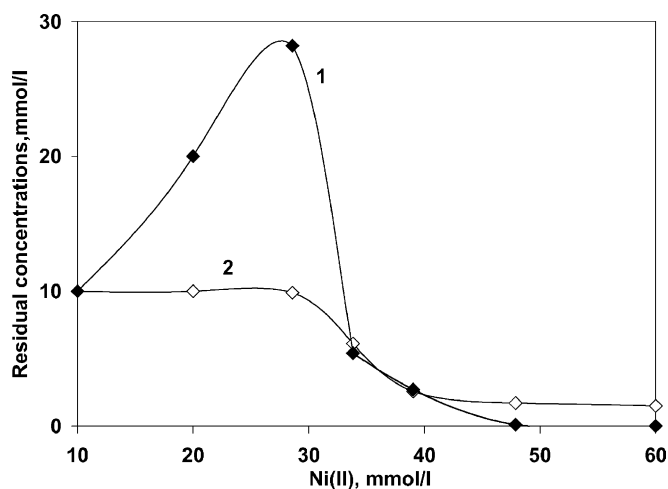

Fig. 1. Effect of Ni(II) concentration on residual Ni(II) (1) and citrate (2) concentrations at pH 11. Initial Ni(II) and citrate concentrations ($10 \, \text{mmol} \, \text{l}^{-1}$).

Table 1
Formation and composition of insoluble Ni(II)–citrate precipitate

pH	Initial concentration (mmol l^{-1})		Residual concentration (mmol l^{-1})		Ni(II):citrate in precipitate (mol:mol)	Extent of citrate removal
	Ni(II)	Citrate	Ni(II)	Citrate		
12	85	50	1.4	42	6.4	0.16
	104	50	0.5	36	6.3	0.28
	209	50	0.2	25	7.2	0.50
	316	50	0.6	18	8.1	0.64
	418	50	0.2	12	12.6	0.76
12.5	24	40	5	31	4.1	0.22
	48	40	1.7	39	4.5	0.03
	94	40	0.6	23	5.8	0.42
	182	40	0.2	13	6.2	0.67
	262	40	0.2	10	8.9	0.75
12.5	5	5	0.1	5	–	0
	10	5	0.2	4.5	20	0.05
	20	5	<0.01	3.6	14	0.28
	30	5	<0.01	3.2	17	0.36
	40	5	<0.01	3	20	0.40
12	104	50	0.5	36	6.3	0.28
	104	100	96	100		0
	104	200	95	195	~1	0.02

The precipitate formed is amorphous [12] and it is filtered with difficulty. It can be separated from solution by centrifugation. In most cases at pH ≈ 11 gel is formed instead of precipitate. The separation of this gel is complicated and needs an additional technique, i.e. ultra-centrifugation or keeping for long time (2–3 days) at elevated (30–50 °C) temperatures. However, in these cases the most complete precipitation of nickel as well as citrate (∼90%) proceeds.

The insoluble compounds are formed when the concentration of Ni(II) is higher than that of the soluble complexes. It means that in alkaline solutions precipitation of Ni(OH)$_2$ is possible. Actually, in these cases the precipitate formed is a mixture of an insoluble Ni(II)–citrate complex and Ni(OH)$_2$. Such a composition of the precipitate was confirmed by further investigations (Table 1). The chemical analysis of pre-

cipitates has shown that the least Ni(II):citrate ratio is about 4. As in alkaline solutions the dissociation of three COO$^-$ groups and –OH group proceeds it may be assumed that 4 mol of Ni(II) and 1 mol of citrate form an insoluble complex. The residual Ni(II) in the precipitate exists, probably, as Ni(OH)$_2$.

In order to reuse the precipitate for the preparation of electroless nickel plating solutions, the precipitate was treated with different amounts of diluted 1:4 H$_2$SO$_4$. The comparison of the experimental data on the treatment of precipitate containing Ni(II), citrate and OH$^-$ (Table 2) with the data of complex formation in alkaline solutions [16,17] suggests that the initial stage in the treatment of precipitate with H$_2$SO$_4$ is the dissolution of Ni(II)–citrate when the pH of solvent–precipitate mixture is higher than 8.5. At these val-
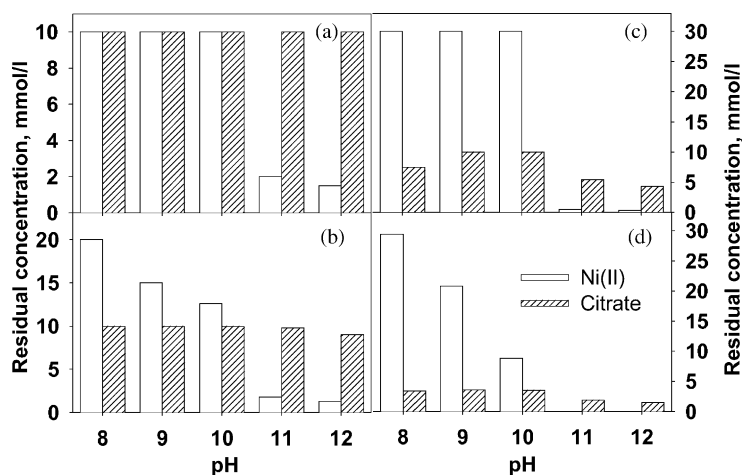

Fig. 2. Influence of pH on residual Ni(II) and citrate concentrations after precipitation. Initial concentrations (mmol l^{-1}): citrate—10; Ni(II)—(a) 10, (b) 20, (c) 40, (d) 60.

Table 2
The ratio between Ni(II) and citrate concentrations in solutions after the treatment with H_2SO_4 of precipitate containing 1 mmol Ni(II)

Treatment conditions		Ni(II):citrate in solution (mol:mol)
pH	Volume of solvent (ml)	
7.5	1	9.6
7.65		8.7
7.9		8.7
8		6.8
8.2		4.9
8.4		4.1
8.6		2.5
8.8		2
8.4	2	5.4
	6	3.8
	8	2
	16	2.3
	24	2.3
	32	2.2

The ratio in precipitate Ni(II):citrate = 6,2:1.

ues of pH the Ni(OH)$_2$ solubility is low. In less alkaline solutions, i.e. at pH 8.5–7.5, dissolution of Ni(OH)$_2$ proceeds.

The leaching of citrate from the precipitate strongly depends on the volume of H_2SO_4 used. The portion of citrate dissolved increases with increase in volume. However, the volumes and concentrations of the solvent used for separation of Ni(II)–citrate complex from Ni(OH)$_2$ are limited by its concentrations in electroless plating solutions where the Ni(II) concentration varies from 0.05 to 0.15 mol l^{-1} and the ratio between Ni(II) and citrate concentrations varies from 0.5 to 2. The conditions when Ni(II) and citrate are dissolved with ratio 2:1 and the Ni(II) concentration is higher than 0.1 mol l^{-1} are shown in Table 2.

The experiments carried out at pH 7 and 8 indicated the essential changes in complex formation (Table 3). The mixing of Ni(II) and citrate solutions of the same pH gives different pH shifts. When pH of the initial solutions is 7, its value in the resulting solution decreases and when pH is 8, its value increases. At pH 2–7 Ni(II) forms complexes with

Table 3
Changes in pH after mixing Ni(II) and citrate solutions

pH value of initial solutions	Initial concentration (mmol l^{-1})		pH value after mixing
	Ni(II)	Citrate	
7	10	10	5.1
	20	10	4.95
	30	10	4.90
	40	10	4.88
	10	20	6.5
	10	30	6.6
	10	40	6.8
8	10	10	9
	20	10	8.7
	30	10	8.6
	40	10	8.3

H_2Citr^-, $HCitr^{2-}$ and $Citr^{3-}$ [4]. The complex formation with decrease in pH indicates the liberation of H$^+$ ions. It is not only the dissociation of three –COOH groups that proceeds in alkaline citrate solutions, but also the dissociation of –OH group is also possible. Therefore, the citrate complexing ability increases. The increased pH value after mixing of Ni(II) and citrate solutions at pH 8 indicates the formation of different complexes. The reason of such a pH change could be the participation of SO_4^{2-} ion in the complex formation. Apparently, the changes in composition of Ni(II)–citrate complex proceed at pH > 8 [16].

Thus, the main stages in Ni(II)–citrate complex recycling are as follows

(1) precipitation of Ni(II)–citrate from spent solutions using excess of a Ni(II) and NaOH;
(2) separation of precipitate;
(3) leaching of Ni(II)–citrate complex from precipitate using H_2SO_4;
(4) separation of Ni(OH)$_2$ precipitate.

Actually, such a regeneration process needs only NaOH and H_2SO_4. The excess of Ni(II) and OH$^-$ may be reused for regeneration of the next portion of spent solution or for the replenishment of working solutions, for instance, in electroless nickel plating.

The pH-metric titration curves of Ni(II)–citrate (Fig. 3) are strongly influenced by the Ni(II) concentration. In the pH range where the –OH dissociates (pH $\sim$ 11) a plateau appears at low Ni(II) concentrations and disappears at high Ni(II) (0.6 mol l^{-1}) concentration. In all cases at pH $\sim$ 13 Ni(II) precipitation takes place. With increase in Ni(II) concentration formation of the precipitates begins and completes at lower pH values, but the demand of NaOH is much higher. Especially high amounts of NaOH are used in the case of high Ni(II) concentrations. Apparently, in this case NaOH is used not only for Ni(II) precipitation, but also for the dissociation of –OH group of citrate and its precipitation. The absence of sharp changes in the titration curves for alkaline solutions at high Ni(II) concentration indicates the gradual change in complex formation [17]. It should be taken into account that the concentrations of citrate decrease with the increase in Ni(II) concentration and such a form of the titration curves is partly due to the formation of the different stability complexes, partly due to the changes in concentrations.

The visible spectra of the residual solutions after precipitation at different Ni(II) and citrate concentrations and pH are similar in appearance and the peak wavelength does not depend on the pH (Fig. 4, curves 1, 2, and 3). When excess of citrate is used and the precipitate does not form the peak wavelength increases with increase in pH (Fig. 4, curves 4 and 5). When the excess of Ni(II) ions is used all the –COO$^-$ groups and, probably, the –OH group of citrate are bound with Ni^{2+} ions and, therefore, the OH$^-$ group of alkali cannot interact with the complex in the solution. It only has influence on precipitate formation.
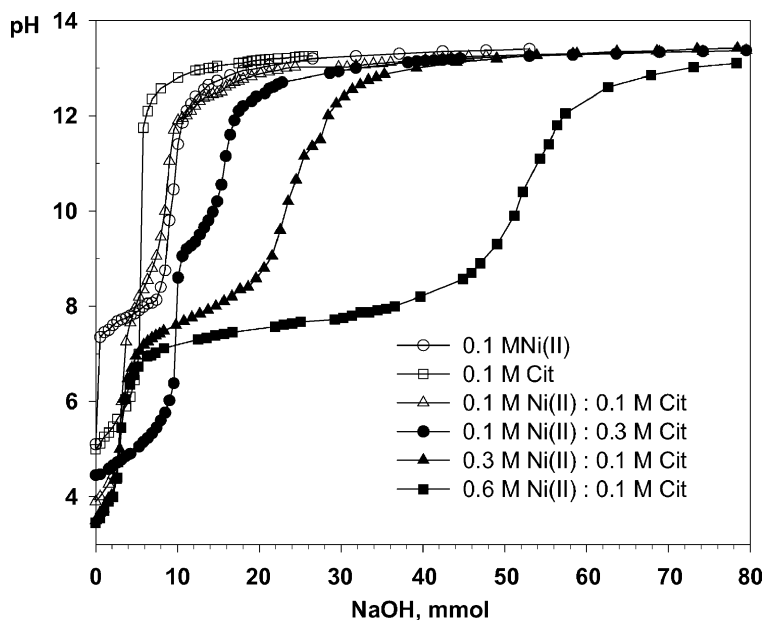
Fig. 3. pH-metric titration of Ni(II)–citrate containing solutions.

The methodology of characterization of amorphous compounds is limited. The results obtained for the solutions are not always applicable for the complexes existing in solid state, but the nature of bindings must be the same in a solid and in a solution, therefore, it would be expected that the insoluble Ni(II)–citrate compound has partly the same bindings as the solution, i.e. the precipitate formed contains the Ni(II) complex coordinated with three –COO⁻ and dissociated –OH of citrate.

FT-IR investigation (Table 4, Fig. 5) has shown the complex composition of the precipitate. In sodium citrate asymmetric (ν_{as}) and symmetric (ν_s) vibrations emerged at 1609 and 1402 cm^{-1}, respectively. The band between 3550 and 3300 cm^{-1} corresponds to characteristic stretching vibration of OH groups (H$_2$O), some contribution of OH from C–OH of citrate vibration is also possible. The bands characteristic of nickel sulfate are at 1110 and 664–612 cm^{-1}. The investigated compound does not show any IR absorption above 1700 cm^{-1} indicating the absence of the free –COOH groups. A very strong band at 1590 cm^{-1} (ν_{as} of COO$^-$) and a feature at 1400 cm^{-1} (ν_s of COO$^-$) are characteristic of complex compounds.

The –OH group gives the deformation vibration bands at 1290, 1210, 1136, 1089 and 1080 cm^{-1}, which are also characteristic of undissociated alcoholic –OH group. In the precipitates investigated the number of bands decreases and their intensity sharply increases in the region 1300–1700 cm^{-1} suggesting the possible substitution of hydrogen in the hydroxyl group by Ni(II). When in complex solution NiSO$_4$ was substituted by NiCl$_2$, the strong feature at $\sim$ 1100 cm^{-1} decreased indicating that this band was also associated with the stretching vibration of C–O–Me [18].

The intensity of the band characteristic of –OH in Ni(OH)$_2$ increases with increase in the solution pH, confirming the data of chemical analysis (Table 1).

Thus, the results obtained show that the precipitate contains Ni(II), citrate, OH$^-$ and SO$_4{}^{2-}$. Precipitation enables to remove both Ni(II) and citrate from the spent solutions using the excess of Ni(II) and OH$^-$. Dissolution of the precipitate formed depends on pH and the volume of the solvent used for treatment. The conditions, under which Ni(II)–citrate dissolves and the excess of Ni(OH)$_2$ remains as a precipitate may be found. Such a peculiarity of Ni(II)–citrate–OH$^-$ precipitate enables to remove the Ni(II)–citrate complex from spent solutions and to reuse them.
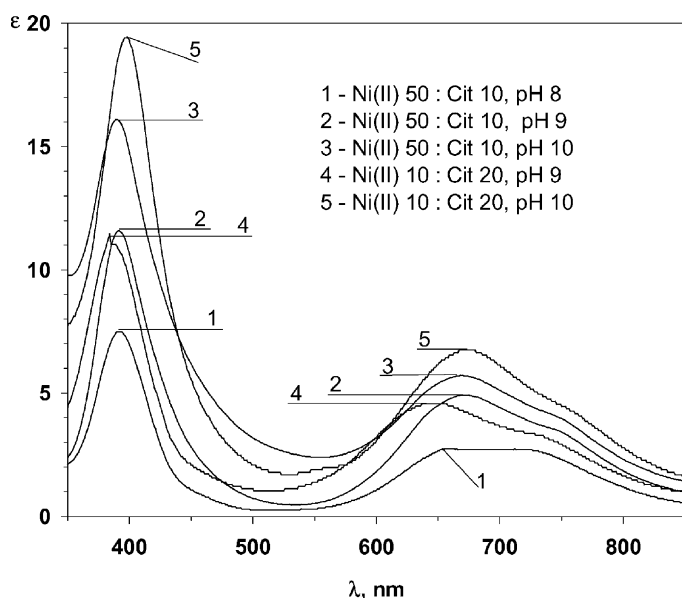

Fig. 4. Visible spectra of Ni(II)–citrate complexes containing solutions.

Table 4
IR bands (cm^{-1}) of Ni(II) and citrate compounds

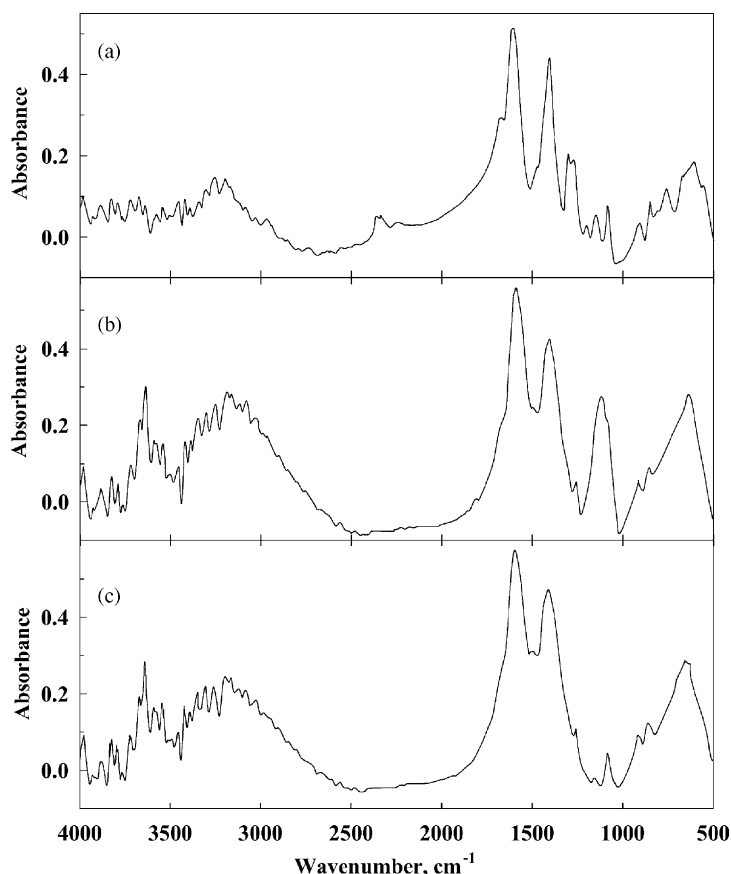| Assignment	Na$_3$ citrate	Ni(II)–citrate complex	NiSO$_4$·7H$_2$O
νOH	3450 s.	3636 s. (Ni–OH)	3450 s. (H$_2$O)
	3233 s.	3420 v.s. (H$_2$O)	3423 s. (H$_2$O)
νCH(CH$_2$)	2970–2919 m.	2970–2910 m.	
ν_{as}COO$^-$	1609 v.s.	1590 v.s.	
ν_sCOO$^-$	1402 s.	1400 s.	
δCH(CH$_2$)	1480 w.	1490 w.	
δCH$_2$(–CH$_2$–COOH)	1260	1256 m.	
δOH(C–OH)	1290, 1210, 1136, 1079 m.	1076 m.	
νC–C(CH$_2$–COO$^-$)	920, 894 m.	910, 879 m.	
ν_{as}SO$_4$		1122 s.–m.	1110 v.s.
δSO$_4$			664–612 s.

v.s.: very strong; s.: strong; m.: medium; w.: weak.

Fig. 5. FT-IR spectra of citrate containing compounds: (a) Na$_3$ citrate, (b) insoluble Ni(II)–citrate using NiSO$_4$ as precipitant and (c) insoluble Ni(II)–citrate using NiCl$_2$ as precipitant.

4. Conclusions

Insoluble Ni(II)–citrate compound forms in excess of Ni(II) in the alkaline solutions. Investigations suggest that the precipitate is composed of the insoluble nickel citrate complex and Ni(OH)$_2$. The content of Ni(OH)$_2$ in the precipitate depends on the initial concentrations of Ni(II) and citrate and the solution pH. Ni(II) is bound by the three –COO$^-$ groups and the –OH group of citrate into an insoluble compound. The insoluble compound also contains SO$_4{}^{2-}$ and OH$^-$ groups.

The treatment of this precipitate with H$_2$SO$_4$ enables to recover Ni(II)–citrate complex and to remove the excess of Ni(OH)$_2$. This excess of Ni(OH)$_2$ can be reused for regeneration of a new portion of Ni(II)–citrate complex.

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