# Use of Metallic Iron for Decontamination of Solution Containing Ni(II)–Citrate

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## Abstract

The use of carbon iron and the mechanical retread of iron surface enables us to remove both Ni(II) and citrate from solutions containing the Ni(II)–citrate complex. The duration of decontamination and the consumption of Fe and acid depend on the complex concentration, pH, load and the presence of background electrolytes. The observed pseudo first order rate constants for citrate removal using carbon steel plates were $k_{obs}$ = 0.42; 0.082 and 0.068 at load 200; 80 and 20 g·l$^{-1}$, respectively.

Chemical analysis, FT-IR and XRD investigations have shown that the precipitate formed contains mainly iron oxides, which exceed the citrate content in the precipitate several times.

**Keywords:** iron, nickel, citrate, decontamination, FT-IR

## Introduction

The main reason for pollution of the environment with heavy metals is the use of metal complexes in industry, agriculture and household. In comparison with free heavy metal ions the metal complexes are more soluble and therefore more harmful 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.

On the other hand the strong complexing agents are widely used for removing metal from contaminated soils. Citrate is used as an environment-friendly extracting agent for heavy metal removal from contaminated soils as an alternative for EDTA. Citrate was found to remove heavy metals from contaminated soils as effectively as EDTA using soil flushing in columns [1-3]. Citric acid is highly effective in removing heavy metals from soils using electrokinetic remediation methods [4, 5].

However, metal-citrate complexes are resistant to biodegradation [6], therefore they should be removed after remediation. Among the other heavy metals (Pb, Cu, Hg, Cd, Co, Zn) nickel distinguishes for the especially stable complexes with citrate (pK~20). As a rule, recovery of metals from complex solutions is performed only after destruction of ligands. Commonly, for ligand destruction chemical and electrochemical oxidations are used. When the ligands are completely destroyed to the harmless substances $CO_2$ and $H_2O$, the metals are precipitated in the form of insoluble compounds. For metal recovery from dilute solutions, mainly sorption is used. However, the increasing volumes of environmental pollution with heavy metals require new and cost-effective remediation technologies.

Over the resent years the use of different industrial wastes for industrial effluent treatment and for the remediation of groundwater and soils has been given intensive study. Iron scrap has been used for a long time for the treatment by cementation or electrocoagulation of effluents containing heavy metal ions [7], or these coagulants are produced separately [8]. Recently, the use of zerovalent iron for decontamination of different organic compounds

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has been investigated very intensively. Very promising results have been obtained in the treatment of chlorinated organic compounds. These compounds are destroyed by zerovalent iron to hydrocarbons and chloride ions [9-11]. This process is proposed for pesticide removal from soils [12]. Zerovalent iron is capable of destroying other organic compounds such as organic dyes [13], nitro aromatic compounds [14], and transforming $NO_3^-$ ions to $NH_4^+$ [15]. In the presence of dissolved oxygen, the zerovalent iron destroys the EDTA to the compounds of lower molecular weight [16].

The mechanism of reactions between zerovalent metals and organic compounds is not yet quite clear. The process is based on iron dissolution from zerovalent iron--containing materials. Supposedly the reductive destruction of contaminants proceeds together with their sorption onto iron corrosion products. Atenas et al. [13] revealed the catalytic effect of iron surface on the destruction of azo compounds.

The main reason for the limited use of zerovalent iron for decontamination of waste effluents is the passivation of iron surface with time. To minimize the loss of iron and to maintain the active surface different means have been proposed, such as iron mixture with sand, aluminum salts [12], contacting with other more electropositive other zerovalent metals [10], the use of zerovalent iron nanoparticles [17]. In Lithuania, rotating systems have been constructed, which enable us to brush up the passive layers formed on the iron surface.

The present work has been carried out with the purpose to investigate the possibilities of using the zerovalent iron for decontamination of solutions containing the Ni(II)–citrate complex, which distinguishes for high stability and wide use in practice, in the case of the mechanical renewal of iron surface.

## Experimental

For experiments carbon steel, containing 90% of Fe and 4% of C, cut into approximately 1.5 cm$^2$ plates for 1g and iron powder, containing ~100% of Fe, were used as a source of zerovalent iron. The solutions containing Ni(II) 10 mmol·l$^{-1}$ and citrate 10 mmol·l$^{-1}$, unless indicated otherwise, were poured onto the iron plates or iron powder and vigorously mixed with a mechanical stirrer. The pH of the solutions was adjusted with a dilute (1:10) $H_2SO_4$ solution. The equilibration time varied from a few hours to several days. Long-term experiments were carried out overnight. After equilibration the undissolved iron was removed from the solutions with a magnet. Filtering through filter paper was used for the separation of the precipitate. Precipitate was analyzed after dying at 105°C.

The quantity of dissolved iron was determined from weight loss after experiment. The chemical composition of the precipitate was determined after dissolution in dilute sulfuric acid. Nickel and iron in the solutions were determined after mineralization of organics with $HNO_3$,

Fe(III) from solutions was removed by adding $NH_4OH$ in excess. The $Fe(OH)_3$ formed was separated by filtering through a glass filter.

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 $\lambda = 490$ nm using dimethylglyoxime. Fe ions in solutions were determined after oxidation to Fe(III) and titrated with EDTA using salycilate as an indicator. 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.

The infrared spectra of the precipitate 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$^{-1}$.

X-ray diffraction (XRD) patterns were recorded on DRON-2 difractometer using Fe K( radiation. A continuous scan mode was used in the range of 5°≤2 θ ≤ 70 min$^{-1}$.

## Results and Discussion

In order to evaluate possibilities of using the zerovalent iron for Ni(II)-citrate containing solution decontamination the experiments were carried out with pure iron powder. They showed that Ni(II) ions as well as citrate are removed from aqueous solutions completely. The rate of reaction depends on the load of iron powder (Fig. 1). The initial green color of the Ni(II)–citrate complex changed rapidly into an intensive redly brown color of the Fe(III)–citrate complex, which disappeared after a complete precipitation of the citrate. The precipitate settled down rapidly after stopping the mixing. Thus, the degree of citrate removal from the solutions was easily followed visually after the changes of the color of solutions. However, the iron powder is very expensive and can find no
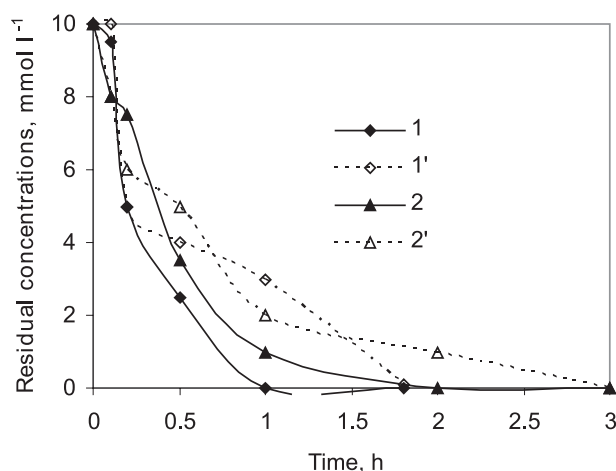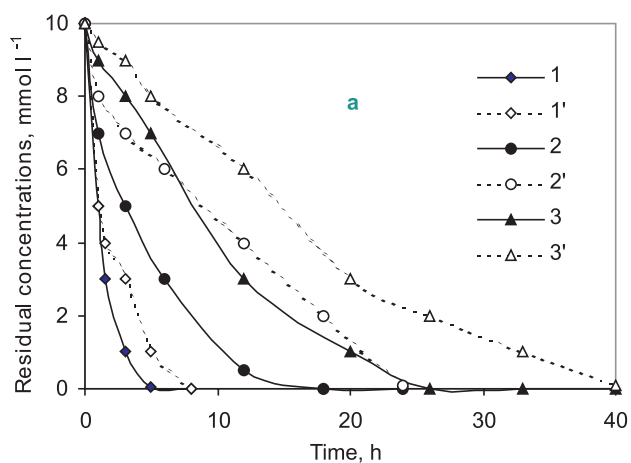


Fig. 1. Influence of treatment time on residual Ni(II) (1, 2) and citrate (1', 2') concentrations in dependence on iron powder load (g·l$^{-1}$): 1 – 20; 2 – 10.

possibilities to use in practice. Therefore, further experiments were carried out with iron scrap.

Experiments carried out using carbon steel for the decontamination of solutions containing the Ni(II)–citrate complex at different initial values of pH (Table 1) showed a crucial influence of pH on the completeness of the removal of the Ni(II)–citrate complex. A complete removal of both Ni(II) and citrate proceeds only in a narrow range of the initial pH values (3–3.5). The precipitation is most complete when the consumption of iron is the highest, though the consumption of sulfuric acid isn't the highest. The demand of iron for decontamination exceeds several times the concentration of Ni(II)–citrate complex. Our previous investigations have shown that the Ni(II)–citrate complex is easily removed from alkaline solutions by Fe(III) [18] and in acidic solutions such precipitation does not proceed [19]. At low pH values (2.5–3) the dissolution of iron prevails, meanwhile at higher values (pH 3.5–4) the process is very slow, and can take several weeks. It is worth noting that the maintenance of the constant values of pH complicates a complete decontamination of the solutions. These results are indicative of a rather compli-

cated mechanism of Ni(II)–citrate complex precipitation with zerovalent iron.

The concentration of the Ni(II)–citrate complex affects the duration of complete precipitation and the demand of Fe for decontamination of solutions (Table 2). With dilution of solutions, the duration of complete precipitation decreases and the demand of Fe for a complete removal of citrate increases. The dilution of solutions increases Fe consumption 10 times for a double removal of 1 mmol citrate.

Besides pH, the load also has a substantial influence on the treatment process (Figs. 2–4). With an increase in Fe load the time of complete removal of both Ni(II) and citrate remarkably decreases, and the decrease in Ni(II) concentration is more rapid than that in citrate concentration (Fig. 2), probably due to the formation of more stable citrate complexes with Fe(III) than with Ni(II). The uncomplexed Ni(II) is more easily removed from solutions than the Fe(III)–citrate complex.

The decrease in residual concentrations is more rapid at the beginning of treatment. Later, with a decrease in concentrations the rate of both Ni(II) and citrate removal decreases as well. The reaction rate best fits the first–order kinetic equation.

Table 1. Influence of the initial pH on the removal of Ni(II)-citrate complex from solutions using zerovalent iron. Load (carbon steel) 5 g in 250 ml.

| Parameters of treatment | pH 2.5 | pH 3 | pH 3.5 | pH 4 |
|---|---|---|---|---|
| Residual Ni(II), mmol·l$^{-1}$ | 0.1 | 0.08 | <0.005 | <0.005 |
| Residual citrate, mmol·l$^{-1}$ | 2.5 | 0.05 | <0.02 | 1.8 |
| Total iron in solutions, mmol·l$^{-1}$ | 2.1 | 0.2 | <0.01 | 0.5 |
| Dissolved Fe, g | 3 | 4 | 4.5 | 3.7 |
| Consumption of H$_2$SO$_4$, mmol | 10 | 7 | 5 | 1 |
| Final pH | 5.5 | 5.7 | 5.8 | 7.2 |

Table 2. Influence of initial concentration on the removal of Ni(II)-citrate complex at initial pH 3.5 and load of carbon steel 2 g in 100 ml solution.

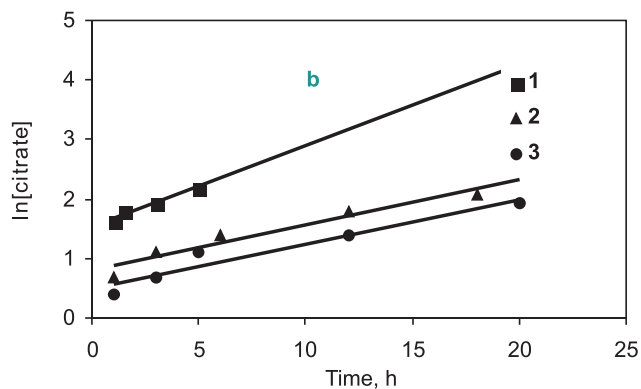| Parameters of treatment | Composition of solutions, mmol·l$^{-1}$ | | |
|---|---|---|---|
| | Ni(II) – 1 Citrate – 1 | Ni(II) – 5 Citrate – 5 | Ni(II) – 10 Citrate – 10 |
| Duration of complete precipitation | <8 | ~24 | ~48 |
| Consumption of Fe, g/mmol citrate | 2.8 | 1.9 | 1.4 |
| Final pH | 6.1 | 6.2 | 6.2 |



Fig. 2. Influence of treatment time on residual Ni(II) (1, 2, 3) and citrate (1', 2', 3') concentrations in dependence on carbon steel load (g·l$^{-1}$): 1 – 200; 2 – 80 and 3 – 40. Initial pH 3.5 (**a**) and test of pseudo-first order equation for the removal of citrate (**b**).

$$\ln c_t = \ln c_0 - kt,$$

where $c_0$ is the initial concentration, $c_t$ is the concentration at time $t$, $k$ is the rate constant of the first-order kinetic, $h^{-1}$. Plotting $\ln c_t$ versus t allows determination of the observed rate constants for citrate removal: $k_{obs}$ = 0.42; 0.082 and 0.068 $h^{-1}$ at load 200; 80 and 20 g·l$^{-1}$, respectively.

Results presented in Table 2 point to a more intensive Ni(II) and citrate removal with a decrease in their concentrations. This allows us to assume that the iron dissolution products have a negative influence on further Ni(II)–citrate precipitation.

The consumption of Fe also depends on its load in solution (Fig. 3). When increasing the load Fe consumption remarkably decreases. Apparently the larger surface enables more effective and more rapid decontamination; meanwhile the higher iron dissolution retards citrate precipitation.

The pH changes (Fig. 4) indicate a rapid process at the initial stage of treatment as well. When the load and surface of iron are high, the value of pH increases from 3.5 to pH 7 and after 3 h decreases. In the case of a higher iron load the decrease in pH is much slower and correlates with residual Ni(II) and citrate concentrations in the solutions.

The rapid changes in the initial stage of decontamination and the slow changes in the further stages suggest the possibility of accelerating the process by periodically removing the precipitate formed before. The results of experiments carried out using the filtration of solutions every 4 h are presented in Fig. 5. Differently from a continuous process (Fig. 2), in this case the concentrations of Ni(II) and citrate decrease more slowly at the initial stage of the process, but at its end the decrease in the concentrations is more rapid. The total time of decontamination, when the precipitate is removed periodically from the solution, is about half as long as in the case when the precipitate is present in the solution during the entire treatment process. Apparently the components of the precipitate are in equilibrium with the solution components. To heave the reaction in the direction of precipitate formation an excess of dissolved Fe is required.

The decontamination time remarkably decreases when the background electrolyte such as Na$_2$SO$_4$ is added (Fig. 6). The consumption of Fe in this case increases only insignificantly. However, from the practical point of view,
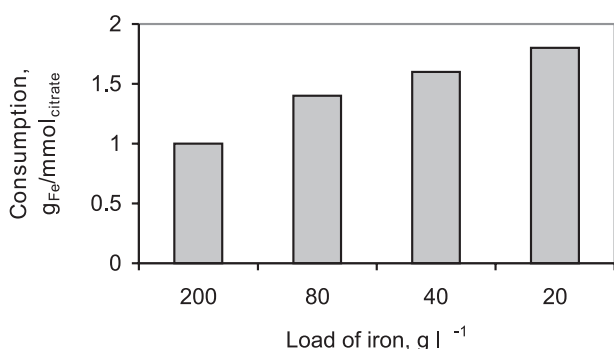


Fig. 3. Influence of Ni(II)-citrate complex solution volume on Fe consumptions for complete citrate removal at pH 3.5 and mass of carbon steel – 2 g.
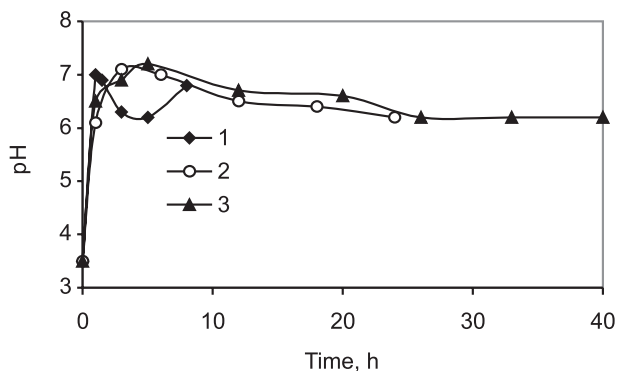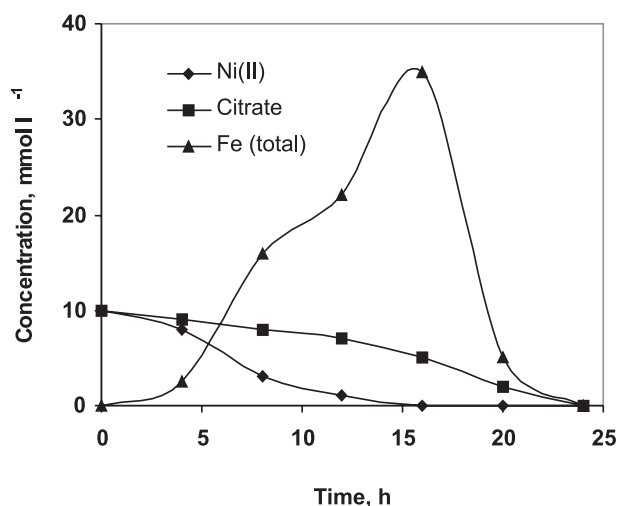


Fig. 5. Influence of the treatment time on residual Ni(II), citrate and total Fe concentrations in case of the separation of precipitate every 4 h. Carbon steel 20 g·l$^{-1}$.
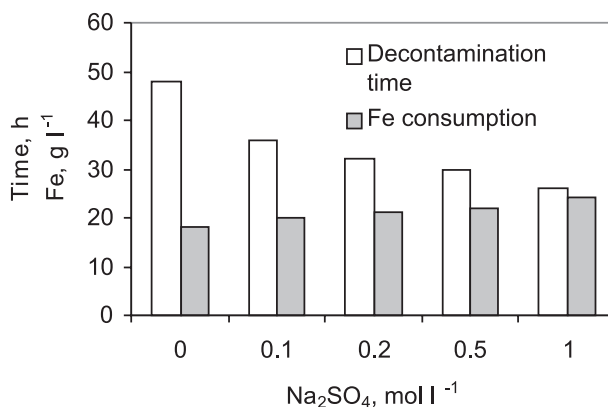


Fig. 4. pH changes with time in Ni(II)-citrate complex solutions in dependence on the load of carbon steel (g·l$^{-1}$): 1 – 200; 2 – 80 and 3 – 40.



Fig. 6. Influence of Na$_2$SO$_4$ concentration on duration of decontamination and Fe consumption. Initial pH 3.5. Carbon steel 20 g·l$^{-1}$.

Table 3. Chemical composition of precipitate formed under condition of Table 1.

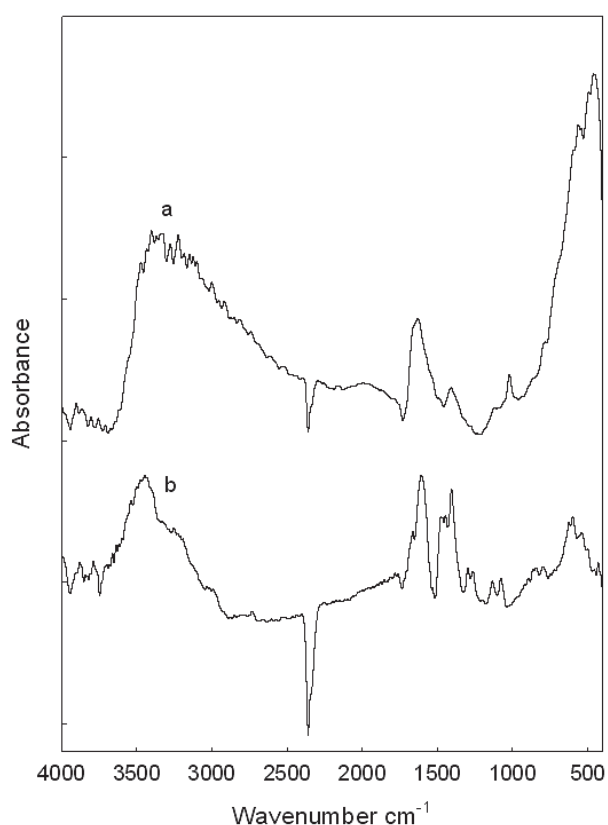| Content in precipitate, % | pH 2.5 | pH 3 | pH 3.5 | pH 4 |
|---|---|---|---|---|
| Ni(II) | 0.7 | 0.8 | 1.05 | 0.7 |
| Fe (total) | 32 | 30 | 25 | 27 |
| Organics (as citrate) | 2.1 | 2.5 | 3.1 | 3.5 |



Fig. 7. FT-IR spectra: a-sodium citrate, b – precipitate formed under conditions of Table 1 at pH 3.5.

the addition of background electrolyte results in additional decontamination problems.

The precipitate formed is compact and easy to filter. Data of the chemical analysis of the precipitate are presented in Table 3. They show that the main constituent of the precipitate is iron, with nickel and citrate making only an insignificant portion. The higher content of organics in the precipitate than the content of Ni is probably related to the dissolution and oxidation of the carbon compounds in carbon steel. It is worth noting that the content of organics released into solutions during the treatment of Ni(II)-citrate with iron is negligible.

FT-IR spectra and XRD patterns confirmed that the chemical composition of the precipitate formed under different conditions of treatment is similar. The presence of citrate ions in the precipitate has been confirmed by IR spectra. In sodium citrate, asymmetric ($v_{as}$) and symmetric ($v_s$) vibrations emerged at 1609 and 1402 cm$^{-1}$, respectively. The band between 3550–3300 cm$^{-1}$ corresponds to a characteristic stretching vibration of OH$^-$ groups ($H_2O$). The study compound does not show any IR absorption above 1700 cm$^{-1}$, indicating the absence of free –COOH groups. A very strong band at 1590 cm$^{-1}$ ($v_{as}$ of COO$^-$) and a feature at 1400 cm$^{-1}$ ($v_s$ of COO$^-$) are characteristic of complex compounds.

The precipitate formed in solutions containing (mmol·l$^{-1}$) Ni(II) 1 and citrate 1 at pH 3.5, is crystalline. The XRD patterns obtained for this precipitate correspond to FeO(OH) (~46%) ir $Fe_2O_3$ (~54%). The rest of the precipitate was found to be amorphous $Fe_2O_3$.

Thus, the present study has shown that as a result of decontamination of Ni(II)–citrate complex containing solutions the precipitate formed contains mainly iron oxides and co-precipitated citrate as well as Ni.

## Conclusions

The use of zerovalent iron for decontamination of solutions containing Ni(II)–citrate complex enables removal of both Ni(II) and citrate from the solutions. The duration of decontamination and the consumption of Fe depend on the complex concentration, pH, the load of iron and the presence of background electrolyte. The removal of the precipitate formed from solution during the treatment process considerably decreases the time of complete decontamination.

The precipitate formed contains mainly iron oxides, which exceed the citrate content several times. The precipitate is compact and easy to filter.

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