



Decontamination of solutions containing Cu(II) and ligands tartrate, glycine and quadrol using metallic iron

Ona Gylienė*, Tomas Vengris, Ona Nivinskienė, Rima Binkienė

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

ARTICLE INFO

Article history:

Received 29 January 2009

Received in revised form 8 October 2009

Accepted 8 October 2009

Available online 6 November 2009

Keywords:

Cu complexes

Metallic iron

Decontamination

FT-IR spectra

Voltammograms

ABSTRACT

Decontamination of solutions containing Cu(II) complexes with tartrate, glycine and quadrol (N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine) using metallic iron depends on pH and proceeds best in mildly acidic solutions. Cu(II) is completely removed from all solutions containing the ligands investigated. The degree of ligand removal from solutions considerably differs. Tartrate is relatively rapidly and completely removed from solutions. A complete removal of glycine is prolonged. The removal of quadrol from solutions using metallic iron is negligible.

Electrochemical investigations showed that tartrate and glycine have inhibitory influence on anodic dissolution of iron at pH 2 and enhance it at pH 4. Quadrol does not exhibit any significant influence on iron dissolution.

Chemical analysis and FT-IR investigations have shown that the content of organic compounds is the greatest in the precipitate formed in solutions containing tartrate, while it is considerably lower in glycine containing solutions. The precipitate formed in quadrol-containing solutions during the treatment with metallic iron contains only negligible amount of organics.

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1. Introduction

The main reason of enormous pollution of the environment with heavy metals is the use of metal complexes in industry, agriculture and household. Complexation of heavy metals is the most important reaction controlling metal transportation in the environment and their bioavailability. Complexing agents also have the potential to perturb the natural speciation of metals, such as Ca, Mg, Fe, Al and to influence their bioavailability [1,2].

Metal complexes have numerous areas of applications in industry in parallel to their increasing usage in last decades. Complexed metal solutions are widely used in metal finishing, electroplating, painting, dyeing, photography, in the fabrication of semiconductor devices, catalysts, in surface treatment industry, in remediation of soils polluted with heavy metals, etc. The ligands especially in large quantities are used in electroless copper plating solutions in the manufacture of printed circuit boards, which are widely used in the fields of communication, informatics, electronics, etc. EDTA is most widely used for the complexation of copper ions in electroless plating solutions. In order to increase the stability of solutions and improve the quality of coatings the additive of glycine (amino acetic acid $\text{CH}_2\text{NH}_2\text{COOH}$) is used, which also makes

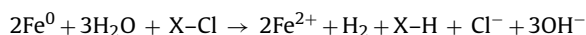
strong complexes with copper ions. Recently, as an alternative to environmentally dangerous EDTA, the biodegradable copper ligands such as tartrate $\text{HOOC-CH(OH)-CH(OH)-COOH}$ and quadrol (N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine) $((\text{OH})(\text{CH}_3)\text{CH-CH}_2)_2\text{-N-CH}_2\text{-CH}_2\text{-N-(CH}_2\text{-CH(CH}_3\text{)(OH))}_2$ have been very intensively investigated [3–6].

The biological treatment widely used for organic wastes is very limited in the case of the treatment of effluents containing the heavy metals, due to their strong bactericidal activity. The presence of strong complexing agents also hinders the metal recovery in the form of insoluble compounds (hydroxide, carbonate, phosphate, oxalate, etc.), which is most widely used in the treatment of effluents containing heavy metals. In practice for decontamination of effluents containing heavy metals and organic compounds, the oxidative destruction of the latter is mainly used. The hydrogen peroxide and ozone are usually used as oxidizing agents. The electrolytic oxidation of organic compounds on the anode is also widely investigated [5]. 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. The sorption is mostly used for metal recovery from dilute solutions. However, the increasing volumes of wastewaters in industry require new and cost-effective decontamination technologies.

In the recent years reductive destruction of organic compounds instead of the oxidative ones has been investigated very intensively. Generally, metallic iron is used as a reducing agent. The abundance of iron scrap in metal industry makes this technology

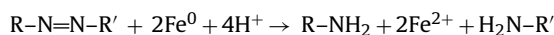
* Corresponding author. Tel.: +370 5 2729127; fax: +370 5 2649774.
E-mail address: gyliene@ktl.mii.lt (O. Gylienė).

very attractive. Metallic iron easily removes halogens from such organic compounds as chlorinated solvents, dioxines, pesticides, etc. [7–13]. The reaction proceeds according to the equation:



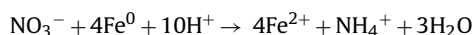
It is worth noting that these compounds are not destroyed by strong reducing agents such as hydrazine, borohydride, and formaldehyde.

Metallic iron is capable to destroy other organic compounds containing unsaturated bonds, for instance the synthetic dyes [14–16]:



The surface acts as a catalyst in this reaction.

Nitrates, nitrites, nitroorganic compounds in the solutions can also be destroyed using metallic iron [17–20]. The ammonium is formed in this case:



When free access of oxygen into solutions is allowed, the oxidative destruction of compounds is possible as well [21]. It is assumed that in this case the active oxygen radical on the iron surface is formed, which leads to the Fenton's reaction. This reaction is enhanced by organic compounds, which form complexes with iron ions and it is resistant to Fenton's reaction. Formate, citrate, maleate, oxalate, and EDTA are used mainly as the ligands for iron ions [22]. Thus, by using the zerovalent iron at the access of oxygen the oxidative, as well as reductive destruction of organic compounds could proceed.

The main reason of the limited use of iron for the decontamination of wastewaters in practice is the passivation of iron surface during the treatment process. To keep the surface active different means have been proposed, i.e., the usage of salts [9] and complexants [23,24]; contact with more electronegative metals [7]; applying electricity in iron columns [25]. In recent years the main scope of works has been devoted to the production of nanoscale iron particles, which enhances the speed and efficiency of the pollutant removal in comparison with metallic iron [26–32]. Usually they are synthesized in non-aqueous solvents using a catalyst and borohydride as a reducing agent. The bimetallic nanoparticles such as Fe–Pd, Fe–Ag are also applied to destroy the organic compounds [33].

Actually, the decontamination of effluents containing organic compounds using iron has not been thoroughly investigated yet and there is possibility that it is more complicated. Along with the reductive effects of metallic iron the hydrogen evolved during iron dissolution can act as a reducing agent as well.

The iron dissolution depending on pH and the presence of an oxidizing agent, for instant oxygen, proceeds with the formation of Fe^{2+} or Fe^{3+} . The latter gives an amorphous precipitate. It is well known that this precipitate acts as a good sorbent for organic and inorganic substances. Fe^{3+} ions also give an insoluble precipitate with some organic compounds [34,35]. Due to the formation of iron hydroxides during decontamination process, the co-precipitation of contaminants also plays an important role. The possible mechanisms of aqueous contaminant removal by metallic iron materials are thoroughly discussed in Refs. [28,36].

The purpose of this work was to investigate the possibilities to use the metallic iron as a decontaminant for solutions containing Cu(II) complexes with ligands tartrate, quadrol and glycine. For investigations the model solutions containing the above mentioned compounds in concentrations comparable with those present in the effluents of manufacture of printed circuit boards, were used. In order to keep the iron surface active its mechanical renewal

was applied. The attempts were also made to evaluate the possible mechanisms of decontamination.

2. Experimental

2.1. Destruction experiments

A pure iron powder and carbon steel pieces as sources of zerovalent iron were used for experiments. The investigations were also carried out with a combined mixture of carbon steel and copper pieces. Decontamination of Cu(II) and ligands tartrate, glycine and quadrol-containing solutions using iron powder was carried out in a polyethylene vessel by vigorous mixing with a magnetic stirrer. For investigations 100 ml of solutions containing a ligand and $\sim 10 \text{ mmol L}^{-1}$ Cu(II) or without Cu(II) were used. Experiments with carbon steel ($\sim 2 \text{ kg}$ weight and 0.5 m^2 area) and copper ($\sim 0.5 \text{ kg}$ weight and 0.1 m^2 areas) pieces were carried out in rotating systems. In this case the pieces were loaded into a rotating barrel and poured with 1 L of solutions containing Cu(II) and ligands. The initial pH was changed from 1 to 7. Solution pH was adjusted with a diluted (1:10) H_2SO_4 solution. Solutions were prepared using chemically pure $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, tartrate, glycine and quadrol by dissolving them in distilled water. The equilibration time varied from a few hours to several days. After experiment the undissolved iron was removed from the solutions with a magnet. It was rinsed with deionized water and acetone. After drying, it was weighted for the estimation of dissolved quantities.

Filtering through a glass filter was used for the separation of the precipitate formed. The experiments were carried out at least twice.

2.2. Analysis of solutions

High ($\sim 10 \text{ mmol L}^{-1}$) Cu(II) concentrations in solutions were determined after its reduction to Cu(I) by means of iodide in acidic solutions. The concentration of iodine formed was determined by titration with a $\text{Na}_2\text{S}_2\text{O}_3$ solution. Low Cu(II) concentrations were determined photometrically at $\lambda = 440 \text{ nm}$ using the indicator diethyldithiocarbamate.

The concentration of ligands was determined by oxidation with the excess of KMnO_4 in alkaline solutions in the presence of Cu(II) as a catalyst and keeping the obtained mixture in a dark place for 15 h. The excess of KMnO_4 was retitrated with oxalic acid in acidic solutions. These concentrations were expressed as O_2 consumption. When Fe ions were present in solutions, in order to oxidize Fe(II) to Fe(III) the aliquot of solution after addition of alkali was kept in an open flask for 1–3 days and mixed occasionally. The formed Fe(III) hydroxides were removed using filtering through glass filters.

Iron in the solutions was determined after mineralization of the dissolved organics with HNO_3 . Fe ions in solutions were determined as Fe(III) by titration with EDTA using sulfosalicylic acid as an indicator.

2.3. Voltammetric investigations

Voltammetric measurements were carried out in a three-camera cell using a potentiostat ПИ-50-1.1 (Russia) at $20 \pm 1^\circ \text{C}$. A carbon steel plate was used as a working electrode; a saturated Ag/AgCl/KCl electrode was used as reference and platinum foil served as a counter electrode. The potential sweep rate was 20 mV s^{-1} .

2.4. Analysis of precipitate

The chemical composition of the precipitate was determined after dissolution in diluted sulfuric acid. The organic compounds

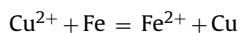
and Cu(II) concentrations were determined as in the case of Section 2.2.

The infrared spectra of the precipitate formed 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} .

3. Results and discussion

3.1. Removal of Cu(II)

Theoretically, the metal replacement by metallic iron can be described electrochemically using standard potentials. For the copper removal reaction:



the potentials are -0.4402 V ($\text{Fe}^{2+} + 2\text{e} = \text{Fe}$) and $+0.337\text{ V}$ ($\text{Cu}^{2+} + 2\text{e} = \text{Cu}$). The reaction rate depends on the difference between the potentials in real solution. Actually, this potential difference is determined by free copper ion concentration. The presence of ligands in solutions diminishes the free copper ion concentration thus decreasing the reaction rate.

Detailed investigations [26,27,37] showed that the free copper ion removal from solutions is more complicated. The reaction proceeds with formation of Cu_2O , which is deposited onto the iron surface or co-precipitated with iron hydroxides. The surface of iron is also covered with hydroxy-compounds of Fe(II) and Fe(III) [15,38]. The presence of ligands forming strong complexes with Cu^{2+} should diminish the Cu^{2+} ion formation. On the other hand, the presence of reducing agents (Fe, H, Fe^{2+}) stimulates the Cu_2O formation onto the surface and in precipitate.

Our investigations were carried out with Cu(II) solutions containing ligands with different functional groups: tartrate—two carboxyl groups ($pK_1 \sim 3.2$; $pK_2 \sim 4.8$), glycine—amino and carboxylic groups ($pK_1 \sim 2.3$; $pK_2 \sim 9.7$) and quadrol—four hydroxyl groups ($pK_1 \sim 6.9$; $pK_2 \sim 8.8$). Cu(II) with all these ligands forms complexes in the ratio 1:2. Thus, in the pH range close to neutral, the Cu(II) complexes with tartrate and glycine are not charged, while the complex with quadrol is positively charged. The point of zero charge for metallic iron is approximately at pH 6.5. The pH of zero charge for iron oxides is higher and for Fe_2O_3 it is 8.8. When the pH is lower than the pH of zero point charge the surface of iron is positively charged [39]. Preliminary investigations showed that Cu(II) removal from solutions containing complexing agents with a noticeable rate proceeds only in mildly acidic solutions, where the iron surface is positively charged. It allows supposing that the electrostatic interactions do not play a crucial role in Cu(II) removal.

Experiments carried out with Cu(II) solutions containing tartrate, glycine or quadrol as a ligand at different values of pH (Fig. 1) have shown that copper in all the investigated cases is easily removed from the solutions. Cu(II) ions are most easily removed from the solutions containing the ligand tartrate (Fig. 1, curves 1 and 1'). The complete removal of Cu(II) from the glycine containing solutions takes more time (Fig. 2, curves 2 and 2'). In both cases the influence of pH on the reaction rate is negligible. The removal of Cu(II) from the quadrol-containing solutions is the slowest (Fig. 1, curves 3 and 3'). In this case the value of pH also has considerable influence.

The decrease in residual concentrations is more rapid at the beginning of treatment. Later, with the decrease in concentrations the rate of Cu(II) removal decreases. Despite the uncomplimentary assessment of the kinetic investigations [40], the kinetic peculiarities of Cu(II) removal were evaluated by testing the experimental data according to the first-order (1) and second-order (2) kinetic

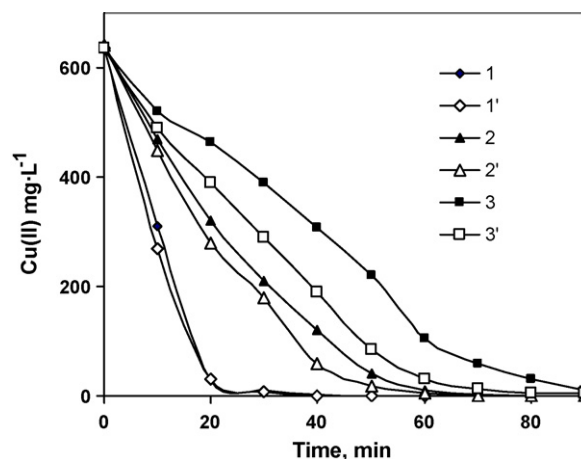


Fig. 1. Changes in Cu(II) concentrations with time in solutions containing 10 mmol L^{-1} Cu(II) and 20 mmol L^{-1} tartrate at initial pH 2 (1) and pH 4 (1'); 10 mmol L^{-1} Cu(II) and 20 mmol L^{-1} glycine at initial pH 2 (2) and pH 4 (2'); 10 mmol L^{-1} Cu(II) and 20 mmol L^{-1} quadrol at initial pH 1 (3) and pH 3 (3'). Load of carbon steel $2.5\text{ m}^2\text{ L}^{-1}$.

equations:

$$c = c_0 \cdot e^{-k_1 t} \quad (1)$$

$$\frac{1}{c} - \frac{1}{c_0} = k_2 t \quad (2)$$

where c is the concentration of Cu(II) at time t , mmol L^{-1} , c_0 is the initial concentration of Cu(II) mmol L^{-1} ; k_1 is the first-order reaction rate constant, min^{-1} or h^{-1} , and k_2 is the second-order reaction rate constant, $\text{L mol}^{-1}\text{ h}^{-1}$.

The plotting in c or $1/c$ versus t enables to determine $-k_1$ or k_2 , respectively. It is worth noting that in some kinetic experiments more or less satisfactory results were obtained applying only the first-order rate equation. While applying the second-order kinetic model gives unreliable results. The parameters are presented in Table 1. The values of the regression coefficients $R^2 > 0.9$ indicate the possible run of process according to the first-order reaction model. The load of iron is huge and available sites of Fe in the reaction exceed the concentration of Cu(II). Actually, it means that the removal of Cu(II) could be the pseudo-first-order reaction.

The presented values of k_1 indicate that the most rapid reaction between Cu(II) and Fe proceeds in tartrate containing solutions and it is the slowest in quadrol-containing solutions. The rate of Cu(II) removal, apparently, is related to the stability of Cu(II) complexes, which could be arranged in the following order: quadrol ($pK_{1,2} \sim 10$) > glycine ($pK_{1,2} \sim 8$) > tartrate ($pK_{1,2} \sim 6$) [3,4]. When the stability of Cu(II) complex is lower, the removal of Cu(II) is more rapid. The effect of ligands could be easily explained in terms of electrode potentials, which depend on the complex stability. The increase in complex stability shifts the Cu/Cu(II) potential to more negative values, accordingly the difference between Fe/Fe(II) and Cu/Cu(II) decreases, thus decreasing the reaction rate. The considerable effect of pH on Cu(II) removal in the case of quadrol also can be due to the fact that with increase in pH the quadrol becomes a stronger chelator. In alkaline solutions quadrol forms very strong ($pK \sim 23$) negatively charged complexes with Cu^{2+} [3,4]. This shifts the Cu/Cu²⁺ potential to more negative values up to $\sim -0.9\text{ V}$. Despite the negative iron surface charge in alkaline solutions and some decrease in Fe/Fe²⁺ potential in the quadrol-containing solutions, which should favour copper removal, the potential difference between the Cu/Cu²⁺ and Fe/Fe²⁺ systems is non-effective for copper reduction.

The obtained results are in good agreement with the results obtained by the authors of work [28], where it is convincingly

Table 1

The pseudo-first-order rate constants and correlation coefficients in kinetic experiments.

Reaction conditions as	First-order reaction parameters	
	k_1	R^2
Fig. 1		
Curve 1	0.16 min ⁻¹	0.9824
Curve 1'	0.18 min ⁻¹	0.9744
Curve 2	0.08 min ⁻¹	0.9386
Curve 2'	0.1 min ⁻¹	0.9216
Curve 3	0.04 min ⁻¹	0.9451
Curve 3'	0.06 min ⁻¹	0.9006
Fig. 2		
Curve 1	0.46 h ⁻¹	0.9383
Curve 2	0.47 h ⁻¹	0.9734
Curve 3	1.11 h ⁻¹	0.9528
Curve 4	0.89 h ⁻¹	0.9877
Fig. 3		
Curve 1	0.12 h ⁻¹	0.8825
Curve 2	0.05 h ⁻¹	0.9081

shown that the reduction plays the basic role in Cu²⁺ removal from the solutions, meanwhile the sorption by ferrous and ferric hydroxides is characteristic of metals with more negative potentials.

3.2. Removal of ligands

The removal of organic compounds using zerovalent iron is a much slower process. Preliminary investigations have shown that remarkable changes in ligand concentrations proceed only after the treatment for several hours in mildly acidic solutions, when the corrosion of iron proceeds.

Experiments carried out with the iron powder (Table 2) indicate that the ligand removal strongly depends on their nature and to a lesser degree on the initial value of pH. The residual concentrations of ligands after treatment decrease with increase in pH. Tartrate is completely removed from the solutions under most favorable conditions. The degree of glycine removal is much lower. Quadrol, actually, is not removed from the solutions using treatment with iron.

Similar results were obtained in rotating systems using carbon steel. In order to increase the iron corrosion rate the copper load was added to the carbon steel load. The formed galvanic pair Fe–Cu increases the iron dissolution rate. The enhancing effect of metallic

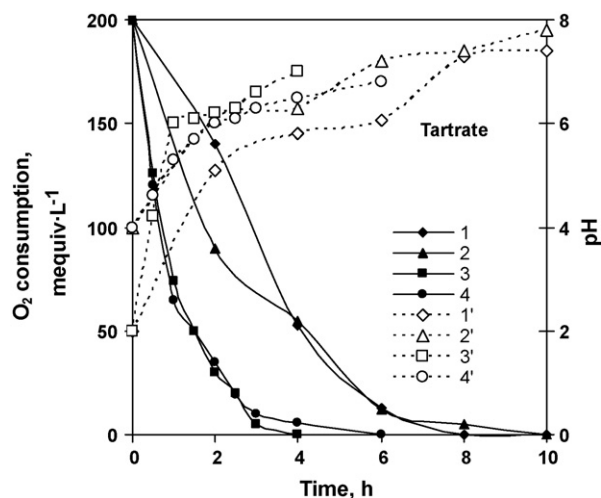
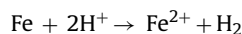


Fig. 2. Changes in organic concentrations (1–4) and pH (1', 2', 3', 4') with time during treatment of solutions containing 10 mmol L⁻¹ Cu(II) and 20 mmol L⁻¹ tartrate with Fe (load 2.5 m² L⁻¹) (1, 1', 2, 2') and mixture of Fe (load 2.5 m² L⁻¹) and Cu (load 0.5 m² L⁻¹) (3, 3', 4, 4') at initial pH 2 (1, 1', 3, 3') and pH 4 (2, 2', 4, 4').

copper on the decontamination is confirmed by the results presented in Figs. 2–5. They also point to the different kinetic behavior of each complexing agent in the decontamination. Tartrate from solutions is removed completely during 8–10 h when the carbon steel is used (Fig. 2, curves 1 and 2). The removal rate considerable increases when the load is composed of carbon steel and copper (Fig. 2, curves 3 and 4). The process obeys the first-order equation (Table 1). Remarkably, the influence of the initial values of pH is inconsiderable. Such a modest influence of pH on the decontamination could be explained by elimination of free H⁺ ions in iron dissolution reaction, when Fe²⁺ or Fe³⁺ are formed:



The consumption of acid in iron dissolution confirms the increased amounts of dissolved iron at lower pH (Table 2) and changes in the pH values during tartrate removal (Fig. 2, curves 1'–4'). Initially the values of pH rapidly increase. Later its increase is very slow. Thus, the main removal of tartrate proceeds at almost unchanging pH values.

Table 2

Treatment of Cu(II) and tartrate, glycine and quadrol-containing solutions with iron powder for 5 h. Load 20 g L⁻¹.

Composition of solutions	Concentrations after treatment, mmol L ⁻¹		Composition of precipitate ^a (mg g ⁻¹)			Dissolved iron (g L ⁻¹)
	Ligand	Fe (total)	Ligand	Cu (total)	Fe (total)	
Cu(II) 10 mmol L ⁻¹ Tartrate 18 mmol L ⁻¹						
pH 2	2.4	~0	18	0.4	171	40.5
pH 4	3.6	~0	27	0.8	178	20
pH 5	~0	~0	32	1.1	160	15
Cu(II) 10 mmol L ⁻¹ Glycine 25 mmol L ⁻¹						
pH 1.5	25	~0	~0	0.5	133	26
pH 2	23	~0	~0	0.3	110	30
pH 4	20	~0	1.2	0.6	150	25
pH 5	15	~0	3	1.1	110	12
Cu(II) 10 mmol L ⁻¹ Quadrol 19 mmol L ⁻¹						
pH 1	19	78	~0	0.6	259	43
pH 2	19	8	~0	0.8	257	30
pH 3	19	2	~0	0.7	198	30
pH 5	18	1.2	0.05	1.4	257	18

^a The rest of precipitate, possibly, consists of iron hydroxy-compounds and basic iron sulfates.

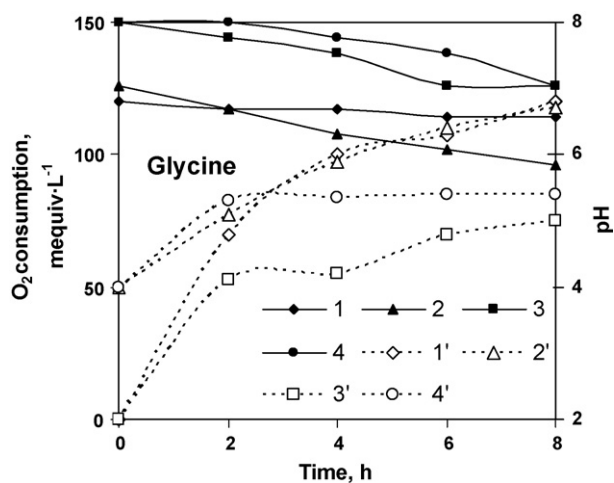


Fig. 3. Changes in organic concentrations (1–4) and pH (1', 2', 3', 4') with time during treatment of solutions containing 10 mmol L^{-1} Cu(II) and 20 mmol L^{-1} glycine with Fe (load $2.5 \text{ m}^2 \text{ L}^{-1}$) (1, 1', 2, 2'); and mixture of Fe (load $2.5 \text{ m}^2 \text{ L}^{-1}$) and Cu (load $0.5 \text{ m}^2 \text{ L}^{-1}$) (3, 3', 4, 4') at initial pH 2 (1, 1', 3, 3') and pH 4 (2, 2', 4, 4').

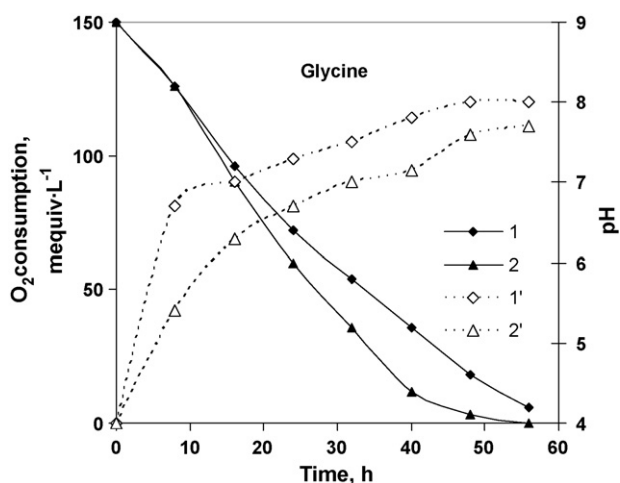


Fig. 4. Changes in organic concentrations (1, 2) and pH (1', 2') with time during treatment of solutions containing 10 mmol L^{-1} Cu(II) and 25 mmol L^{-1} glycine with iron powder at initial pH 2 (1, 1') and pH 4 (2, 2').

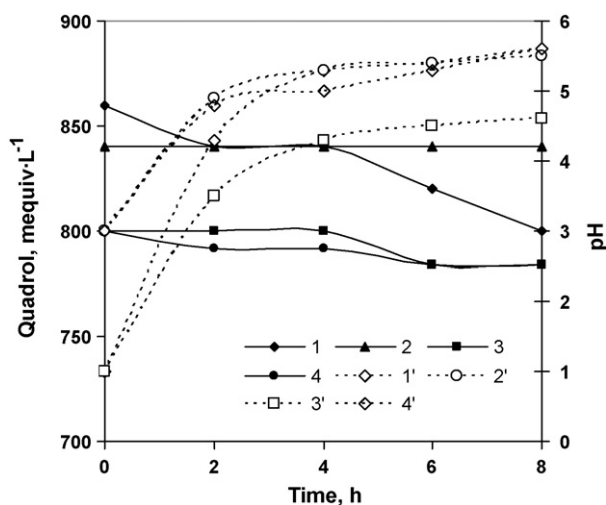


Fig. 5. Changes in organic concentrations (1–4) and pH (1', 2', 3', 4') with time during treatment of solutions containing 10 mmol L^{-1} Cu(II) and 20 mmol L^{-1} quadrol with carbon steel (load $2.5 \text{ m}^2 \text{ L}^{-1}$) (1, 1', 2, 2'); and mixture of Fe (load $2.5 \text{ m}^2 \text{ L}^{-1}$) and Cu (load $0.5 \text{ m}^2 \text{ L}^{-1}$) (3, 3', 4, 4') at initial pH 2 (1, 1', 3, 3') and pH 4 (2, 2', 4, 4').

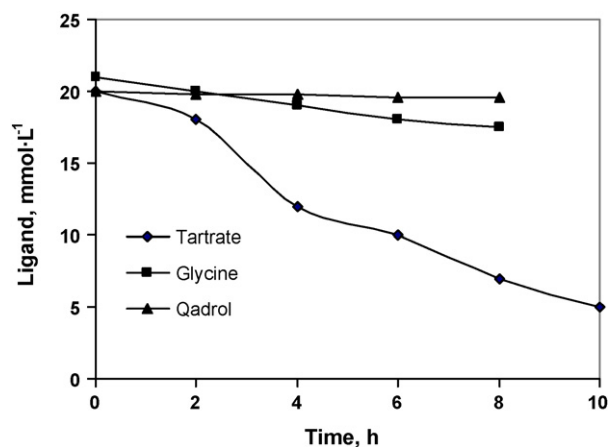


Fig. 6. Changes in ligand concentrations with time during the treatment of solutions containing 20 mmol L^{-1} tartrate at pH 2, 21 mmol L^{-1} glycine at pH 2 and 20 mmol L^{-1} quadrol at pH 1 with carbon steel (load $2.5 \text{ m}^2 \text{ L}^{-1}$).

The fit of tartrate removal to the first-order reaction model presumably points to the simplicity of the process. The formation of insoluble Fe(III)-tartrate compounds in mildly acidic solutions is well known [35]. Thus, it can be assumed that tartrate is removed from solutions as an insoluble Fe(III) compound. The enhancing effect of copper load on the iron dissolution rate and subsequently on the tartrate removal (Fig. 2, curves 3 and 4) partly confirms this assumption.

The removal of glycine from the solutions is slow and more complicated (Figs. 3 and 4). During the first 8 h only ~20% of glycine is removed. It should be noted that in this case the influence of pH and use of copper load have not any considerable effect on the glycine removal. The complete removal of glycine requires a more prolonged treatment (Fig. 4). The reasons of slow removal of glycine from the solutions could be the sorption of glycine by a freshly precipitated $\text{Fe}(\text{OH})_3$, which possesses a high sorption ability, or oxidative destruction of glycine. However, the increase in pH is not favorable for both reactions. Usually Fenton's reaction proceeds best in the pH range 4–6. The dissolution of iron also decreases with increase in pH, meanwhile the removal of the main part of glycine proceeds at higher values of pH, i.e., 6–8 (Fig. 4, curves 1' and 2'). The approximate fulfillment of the process to first-order kinetic reaction (Table 1) is hardly comprehensible in regard to the real mechanism of the reaction. It could be more complicated.

It is worth noting that during the reaction of organic ligands with Fe their reduction could proceed. Thus, the presented consumption of O_2 indicates the maximal possible organic compound concentration in the solution.

In the case of the ligand quadrol any remarkable changes do not proceed (Fig. 5). The process does not depend on the initial pH or presence of copper in the load. The main reactions are the dissolution of iron and reduction of Cu(II).

Our previous investigations with Cu(II)-EDTA complex decontamination [41] have shown that the presence of Cu(II) ions in solutions has a crucial influence on the rate of EDTA destruction. Experiments carried out with solutions containing iron powder and ligands only (Fig. 6) confirmed a remarkable decrease in the rate of ligand removal, when comparing with the solutions containing Cu(II). In order to compare the results it was assumed that the organics present in the solutions correspond to the concentration of the un-destroyed ligand. The presence of metallic copper in the load more strongly influences the increase in ligand removal rate. Such peculiarities of decontamination evidence the electrochemical nature of the enhancing effect of copper. In order to evaluate the

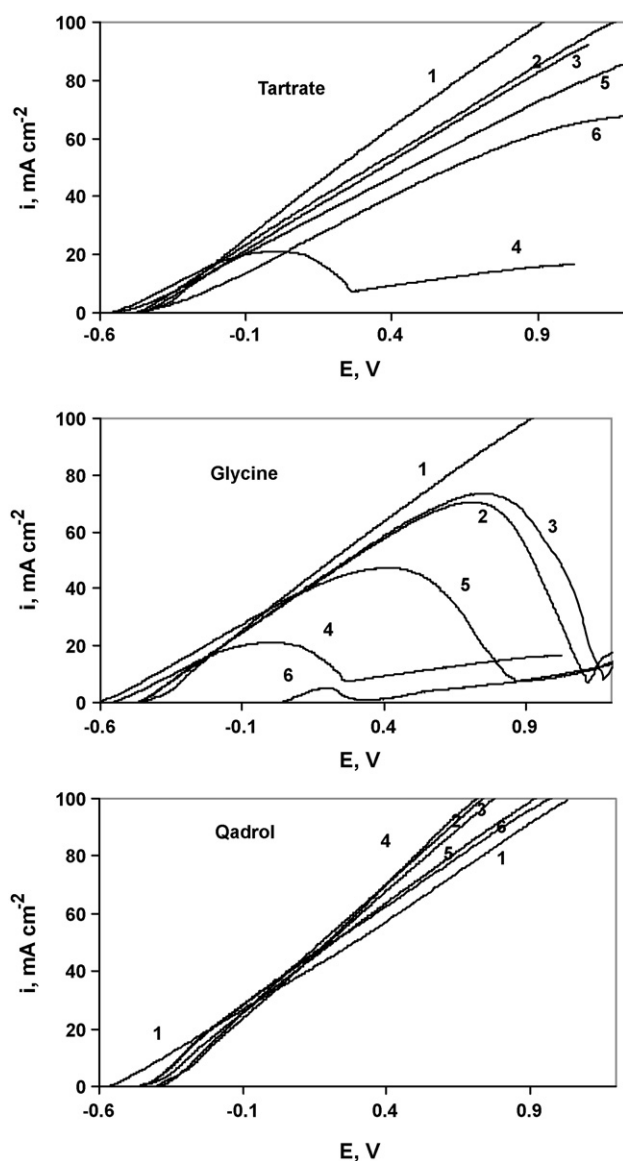


Fig. 7. Anodic voltammetric curves of Fe electrode in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solutions adjusted with H_2SO_4 (1 and 4) containing: 20 mmol L^{-1} tartrate (2 and 5), and $10 \text{ mmol L}^{-1} \text{ Cu(II)}$ and 20 mmol L^{-1} tartrate (3 and 6); 25 mmol L^{-1} glycine (2 and 5), and $10 \text{ mmol L}^{-1} \text{ Cu(II)}$ and 25 mmol L^{-1} glycine (3 and 6) at pH 2 (1–3), pH 4 (4–6); 20 mmol L^{-1} quadrol (2 and 5), and $10 \text{ mmol L}^{-1} \text{ Cu(II)}$ and 25 mmol L^{-1} quadrol (3 and 6) at pH 1 (1–3) and pH 3 (4–6).

role of electrochemical reactions the voltammetric measurements were carried out.

3.3. Anodic voltammetric investigations

Anodic voltammograms recorded in the solutions containing the ligands tartrate, glycine and quadrol (Fig. 7) and in the presence of Cu(II) at various pH demonstrate different behaviour. In the solutions without ligands at pH 2 the dissolution of iron is the main reaction (Fig. 7, curves 1); meanwhile at pH 4 sharp passivation of iron proceeds (Fig. 7, curves 4). The presence of tartrate diminishes the activity of iron anode at pH 2 (Fig. 7, curve 2) and enhances its activity at pH 4 (Fig. 7, curve 5). However, the activity of iron surface in the anodic process remains lower at pH 4. The addition of Cu(II) in solutions somewhat reduces the anodic current at both values of pH (Fig. 7, curves 3 and 6). The presented anodic voltammograms show that the presence of tartrate in the solutions

significantly accelerates the dissolution of iron at pH 4, meanwhile the presence of Cu(II) has some retarding effect.

The passivation effects of glycine are expressed to a more considerable degree. Glycine diminishes the iron surface activity at pH 2 (Fig. 7, curve 2) and enhances its activity at pH 4 (Fig. 7, curve 5). Cu(II) ions have a negligible influence on the anodic process at pH 2 and a very strong passivation effect at pH 4 (Fig. 7, curves 3 and 6). In the presence of glycine in all the cases investigated the passivation of iron electrode occurs at high values of anodic potential. Glycine is known to be a very effective corrosion inhibitor. The inhibition proceeds due to strong adsorption of glycine on the metal surface [42,43].

In the quadrol-containing solutions (Fig. 7) the effects of pH and Cu(II) on the anodic process are expressed to a considerably lower degree. It can be assumed that the presence of quadrol does not have any significant influence on the dissolution of iron. The electrochemical inertness of iron surface to quadrol could be presumably the reason of almost complete remaining quadrol in solution after treatment with metallic iron.

3.4. Composition of precipitate

The chemical analysis of the precipitate (Table 2) is in good agreement with the result of solution analysis. The precipitate formed in the solutions containing tartrate possesses the greatest amounts of organics. The precipitate formed in the solutions containing glycine possesses less organic matter and that formed in the quadrol-containing solutions actually possesses only negligible amounts of organic matter. The composition of the precipitate depends on the initial solution pH. The content of organic matter increases in the precipitate with increase in pH in the case of tartrate and glycine. Herewith, with increase in pH the quantity of dissolved iron decreases. The content of Cu in the precipitate corresponds to the degree of Cu(II) removal from solutions.

FT-IR spectra of tartrate, glycine and quadrol recovered by zerovalent iron were studied over the frequency region of $500\text{--}3600 \text{ cm}^{-1}$ (Fig. 8). The spectra were compared with those of tartrate, glycine and quadrol. The intense absorption bands near 3100 and 3070 cm^{-1} and in the region $700\text{--}500 \text{ cm}^{-1}$ in the FT-IR spectra of the precipitate formed in tartrate, glycine and quadrol-containing solutions indicate the presence of a high concentration of FeO(OH) and iron oxides, respectively. The intense characteristic absorption bands of the investigated compounds ($1\text{--}3'$) decline in the spectra of precipitates. The precipitate formed in the solution containing tartrate (1) contained the greatest amount of organic compounds as was shown by IR absorption at about 1630 cm^{-1} (ν_{as} of COO^-) and 1410 cm^{-1} (ν_{s} of COO^-). The FT-IR spectra of the precipitate formed in the solution containing quadrol (3) did not show any additional IR absorption in the vicinity of 3300 cm^{-1} and $2960\text{--}2870 \text{ cm}^{-1}$ indicating the absence of $\text{CH}_3\text{--CH(OH)--CH}_3$ groups of quadrol (3'). This indicates the absence of quadrol in the precipitate.

The reasons of different behavior of the ligands in decontamination are likely due to their different interactions with iron surface, dissolved Fe(II) and Fe(III) ions and possible different behavior in co-precipitation. It is known that tartrate forms insoluble compounds with Fe(III) ions and, probably, therefore it is completely removed from the solutions. A strong sorption of glycine onto the metallic iron surface, probably, retards its removal from the solutions using metallic iron. The ability of quadrol to form strong complexes with bivalent metal ions and its inertness to the metallic iron surface could be the reasons of persistence of quadrol in the treatment process. The presence of some quantities of organic compounds in the precipitate formed in the solutions containing quadrol could be explained by a high sorption ability of freshly precipitated iron (III) hydroxides.

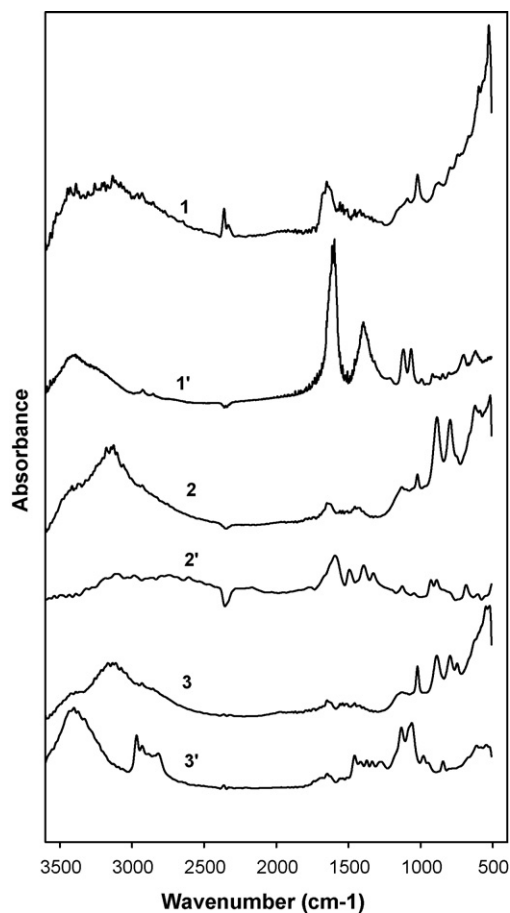


Fig. 8. FT-IR spectra of the precipitate formed in solutions containing ligands treated with metallic iron (1–3) and pure ligands (1', 2, 3'). Ligands: 1, 1'—tartrate; 2, 2'—glycine; 3, 3'—quadrol.

4. Conclusions

Copper ions are easily and rapidly removed from the ligands tartrate, glycine and quadrol-containing solutions using metallic iron. The rate of copper removal depends on the complex stability. Among the ligands, only tartrate is rapidly and completely removed from the solutions. The prolonged treatment enables a more complete removal of glycine, meanwhile quadrol remains completely in solutions.

The reasons of different degree of ligand removal in decontamination process are likely due to their different interactions with iron surface, dissolved and insoluble iron compounds.

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