



Decontamination of solutions containing EDTA using metallic iron

Ona Gylienė*, Tomas Vengris, Arvydas Stončius, Ona Nivinskienė

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

ARTICLE INFO

Article history:

Received 3 October 2007

Received in revised form 13 February 2008

Accepted 14 February 2008

Available online 23 February 2008

Keywords:

EDTA

Zerovalent iron

Capillary electrophoresis

Voltammetry

FT-IR spectra

ABSTRACT

EDTA removal from solutions using metallic iron was carried out at different values of pH, iron load and concentrations at free access of air and in closed vessels. The EDTA destruction was investigated using chemical and capillary electrophoresis analysis. Fe corrosion was studied voltammetrically and the composition of the precipitate formed was investigated using FT-IR spectroscopy and chemical analysis. The EDTA decomposition is remarkably enhanced by the addition of Cu(II) to the EDTA solutions and access of air. The precipitation of the derivatives of insoluble Fe with EDTA or its decomposition products proceeds along with the destruction of EDTA. In closed systems the main EDTA removal reaction is precipitation with iron ions.

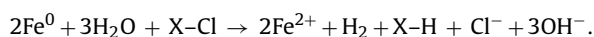
© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Ethylenediaminetetraacetate (EDTA) is widely used in industry, pharmacy, agriculture and household. EDTA is not biodegradable and it is difficult to remove from effluents in wastewater treatment facilities. Therefore, the natural aquatic environment contains rather great amounts of EDTA [1]. As a strong chelating agent it enhances metal solubility and mobility in the environment causing toxic effects for living organisms.

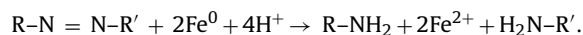
In the practice for decontamination of effluents containing organic compounds the oxidative destruction is used. The hydrogen peroxide and ozone are usually used as the oxidizing agents. The electrolytic oxidation of organic compounds on the anode is also widely investigated [2].

In the recent years reductive destruction of organic compounds instead of oxidative ones is very intensively investigated. As a reducing agent metallic iron is used mainly. The abundance of iron scrap in metal industry makes this technology very attractive. Metallic iron easily removes halogens from such organic compounds as chlorinated solvents, dioxines, pesticides, etc. [3–8]. The reaction proceeds according to the equation:



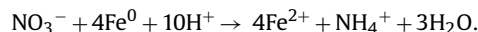
It is worth to note that these compounds are not destroyed by strong reducing agents such as hydrazine, borohydride, formaldehyde.

Metallic iron is capable to destroy other organic compounds containing unsaturated bonds, for instance the synthetic dyes [9–11]. The authors of work [10] established a strong relationship between the composition of the iron oxidized surface layer and kinetic of azodyes decomposition. The proposed mechanism for azodyes decomposition by zerovalent iron involves the formation of free amino groups

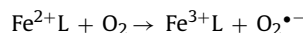
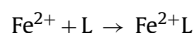


This reaction is catalyzed by an iron surface.

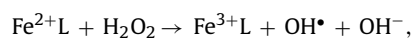
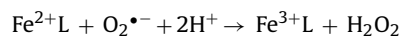
Nitrates, nitrites and nitro-organic compounds in the solutions can also be destroyed using metallic iron [12–15]. The ammonium is formed in this case:



When the free access of oxygen into solutions is allowed, the oxidative destruction of compounds is possible as well [16]. It is assumed that in this case the active oxygen radical on the iron surface is formed, which leads to the Fenton's reaction:



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

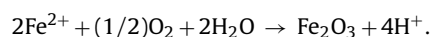
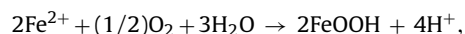


where L is the organic compound, which forms complexes with iron ions and it is resistant against Fenton's reaction. Formate, citrate, maleate, oxalate and EDTA are used as the ligands mainly [17]. However, the authors of the work [16] showed that in the presence of oxygen and at low EDTA concentrations (up to $1 \mu\text{mol l}^{-1}$) the oxidative destruction of EDTA proceeds on the metallic iron surface, as well. Thus, by using zerovalent iron at 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 are proposed, i.e. the usage of salts, which enhance the iron corrosion rate [6], contact with more electronegative metals [4], and applying of electricity in iron columns [18]. In the recent years the main scope of works is devoted to the production of nanoscale iron particles, which destroy the organic compounds very effectively [19–23]. However, the production of nanoscale iron particles is very complicated. Usually they are synthesized in non-aqueous solvents using a catalyst and borohydride as a reducing agent [24]. The bimetallic nanoparticles as Fe–Pd, Fe–Ag are also applied to destroy the organic compounds [22].

Actually, the decontamination process of effluents containing organic compounds using iron has been not 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 reaction depending on pH and the presence of an oxidizing agent, for instant oxygen, proceeds with formation of Fe^{2+} or Fe^{3+} . The latter gives an amorphous precipitate:



It is well known that this precipitate acts as good sorbent for organic and inorganic substances. Fe^{3+} ions also give an insoluble precipitate with some organic compounds [24,25].

Our investigations were carried out with purpose to investigate the possibilities to use the metallic iron as decontaminant for solutions containing EDTA in concentrations comparable with those present in the effluents of manufacture of printed circuit boards, applying mechanical renewal of iron surface. The attempts were also made to evaluate the possible mechanisms of EDTA decontamination process.

2. Experimental

2.1. Decontamination experiments

Removal of EDTA using iron was carried out in open vessel, and in polyethylene vessel tightly covered with plastic lid. As a source of zerovalent iron, pure iron powder ($\sim 3 \text{ mm}$) or carbon steel cut into plates (approximately 5 cm^2 for 1 g of iron) were used. For investigations 100 ml of solutions containing 1 , 10 and 100 mmol l^{-1} of EDTA and 1 and 10 mmol l^{-1} Cu(II) or without Cu(II) were used. The initial pH was changed in region from 3 to 7 . The pH of the solutions was adjusted with a diluted ($1:10$) H_2SO_4 solution. Solutions were prepared using chemically pure $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ by dissolving them in distilled water. These solutions were poured onto the iron and vigorously mixed with a magnetic stirrer. The equilibration time varied from a few hours to several days. After

experiment the undissolved iron was removed from the solutions with a magnet. Filtering through the 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. Fe(III) from solutions was removed by addition of NaOH in excess, meanwhile Cu(II)–EDTA complex remains in solution. In cases, when the concentrations of EDTA were low, the solutions containing 1 mol l^{-1} EDTA and 1 mol l^{-1} NaOH was added to aliquots for copper complexation. The $\text{Fe}(\text{OH})_3$ formed was separated by filtering through a glass filter. Low Cu(II) concentrations were determined photometrically at $\lambda = 440 \text{ nm}$ using diethylditiokarbamate as an indicator [26].

EDTA concentration in solutions was determined complexometrically by titration with Bi(III) in acidic solutions (pH ~ 3 adjusted with HNO_3) [26].

The concentration of EDTA was also established on a P/ACE MDQ Capillary Electrophoresis System apparatus (Beckman Coulter Inc., Fullerton, CA, USA) equipped with a photodiode array (PDA) detector. The detector was operated at 195 and 254 nm and 32 Karat software was used for data acquisition. Fused silica capillaries eCAP (Beckman Coulter Inc., Fullerton, CA, USA) of $75 \mu\text{m}$ i.d., 57 cm total length, and 50 cm effective length were used. All chemical reagents were of analytical grade and purchased from Merck (Darmstadt, Germany).

The background electrolyte was a borate buffer 0.04 mol l^{-1} prepared from a boric acid solution (0.1 mol l^{-1}) by addition of NaOH solution (1 mol l^{-1}) up to pH 8.4 and subsequent dilution. All electrolyte solutions were filtered through a $0.45 \mu\text{m}$ membrane filter and degassed by ultrasonication.

The capillary was rinsed with 0.1 mol l^{-1} sodium hydroxide and water for 5 min and then equilibrated with the background electrolyte for 5 min at the beginning of each day. The capillary was rinsed for 2 min with the background electrolyte between all electrophoretic separations. The solutes were injected in the hydrodynamic mode by overpressure (0.4 psi for 5 s). All the experiments were conducted at 25°C in a liquid thermostated capillary cartridge with an applied voltage of 30 kV .

The samples were prepared by dilution with $5 \times 10^{-4} \text{ NiSO}_4 \text{ mol l}^{-1}$ solution to the initial concentrations of EDTA equal to $2 \times 10^{-4} \text{ mol l}^{-1}$ [27].

The concentration of total organic was determined by oxidation with the excess of KMnO_4 in alkaline solutions in presence of Cu(II) as catalyst and keeping the obtained mixture in dark place for 15 h . The excess of KMnO_4 was retitrated with oxalic acid in acidic solutions [28]. Organic amount was expressed as O_2 consumption calculated by KMnO_4 used. When Fe ions were presented in solutions, in order to oxidize Fe(II) to Fe(III) the aliquot of solution after addition of alkali was kept in open flask for $1\text{--}3$ days and mixed occasionally.

The total organic concentrations were evaluated also by measuring absorbance in UV wave region. UV–visible spectra were recorded with a PerkinElmer lambda 35 UV–vis spectrometer at 20°C in 1-cm length quartz cells.

The quantity of dissolved iron was determined from the weight loss after the experiment.

2.3. Analysis of precipitate

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

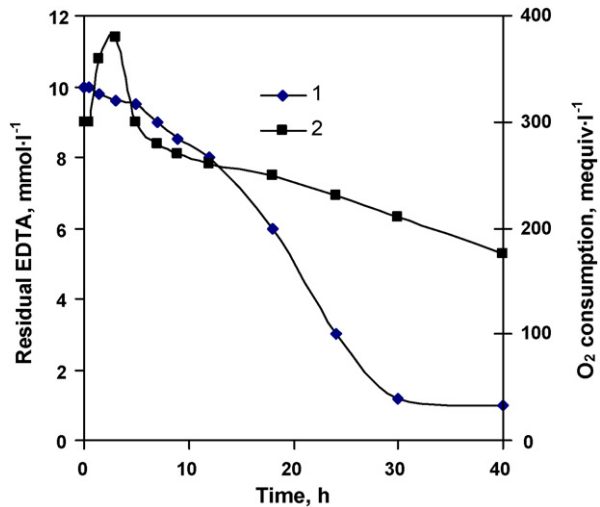


Fig. 1. Changes of the residual concentrations of EDTA (1) and O₂ consumption for the oxidation of the formed organics (2) with time in the solutions containing 10 mmol l⁻¹ EDTA at initial pH 5 using iron powder (load 30 g l⁻¹) in open vessel.

determined as in the case of Section 2.2. Iron in the solutions was determined after mineralization of the dissolved organics with HNO₃. Fe ions in solutions were determined as Fe(III) by titration with EDTA using sulfosalicylic acid as an indicator [26].

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.

2.4. Voltammetric investigations

Voltammetric measurements were carried out in a three camera cell using potentiostat ПИ-50-1.1 (Russia) at 20 ± 1 °C. The 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.

3. Results and discussion

Experiments have shown that the degradation of EDTA is a very slow process. Under conditions of our experiments (Fig. 1) a nearly complete removal of EDTA proceeds only after the treatment with iron powder for ~40 h. The initial increase in the oxygen consumption determined using titration with KMnO₄ indicates the presence of EDTA reduction products in the solutions, which requires higher amounts of KMnO₄ for oxidation. The later decrease in the O₂ consumption and in the residual concentrations of EDTA shows the removal of EDTA or the products of its destruction from the solutions.

The presence of Cu(II) in solutions makes the decontamination process (Figs. 2 and 3) more intensive. The Cu(II) ions are easily removed from the solutions by reduction by zerovalent iron with forming of metallic copper on the iron surface. The EDTA removal rate also increases. The O₂ consumption decrease (indicating EDTA removal, as well) is especially rapid in the case, when the initial concentration of EDTA is low (Fig. 2). The main part of organics is destroyed during first 3 h. The further treatment with iron leads to the slight decrease of the residual organics. About 0.6 mmol l⁻¹ of EDTA are removed during the first hour, meanwhile in the case of high EDTA concentration (Fig. 1) the quantity of removed EDTA from solution during the first hour is ~0.2 mmol l⁻¹. When the initial

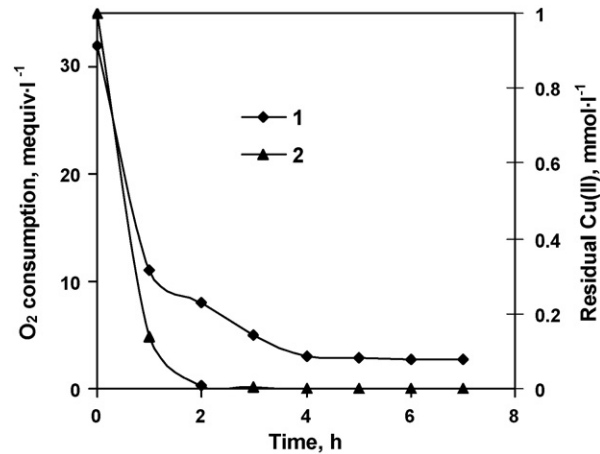


Fig. 2. O₂ consumption for the oxidation of EDTA destruction products (1) and Cu(II) removal kinetics (2) in solutions containing 1 mmol l⁻¹ Cu(II) and 1 mmol l⁻¹ EDTA at initial pH 5 using iron powder (load 30 g l⁻¹) in open vessel.

EDTA concentrations are equal (10 mmol l⁻¹), the presence of Cu(II) (Fig. 3) increased the quantity of removed EDTA from ~0.2 (Fig. 1) to ~0.5 mmol l⁻¹. So, the comparison of the data depicted in Figs. 1–3 show the enhanced influence of Cu(II) on the whole process of decontamination. It is worth noting that the EDTA destruction in solutions containing 10 mmol l⁻¹ EDTA and 1 mmol l⁻¹ Cu(II) initially is rather slow (Fig. 3). The relatively rapid destruction begins after some delay, in this case after 3 h, when the main part of Cu(II) is reduced on the iron surface. During the first 3 h about 1.5 mmol l⁻¹ of EDTA are removed from solution; and during the next 3 h this quantity is equal to 7 mmol l⁻¹. Such a shape of a kinetic curve allows suspecting that the EDTA destruction is a catalytic process. This is known that Cu(II) ions act as homogenous catalyst in oxidative destruction of organics [29]. However, Cu(II) is completely removed from solutions during the first hours of treatment. It is precipitated on the iron surface as metallic copper. Therefore, the action of copper ions as a catalyst is questionable. Presumably, metallic copper deposited on the iron surface changes the catalytic properties of metallic iron. The possibilities to improve the catalytic properties of iron using its bimetallic derivatives with Ni and Pd in case of reductive destruction of organic compounds is widely discussed [30,31].

The same effects for EDTA destruction were obtained when the carbon steel plates were used instead of iron powder (Fig. 4). The reason of inconsiderable differences in EDTA destruction rate using iron powder and carbon steel plates could be the negligible

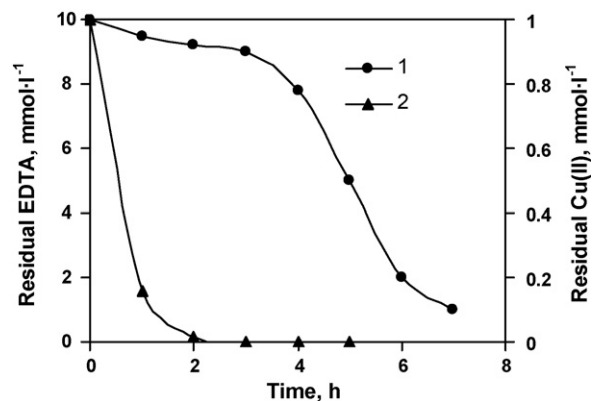


Fig. 3. EDTA destruction (1) and Cu(II) removal kinetics (2) in solutions containing 1 mmol l⁻¹ Cu(II) and 10 mmol l⁻¹ EDTA at initial pH 5 using iron powder (load 30 g l⁻¹) in open vessel.

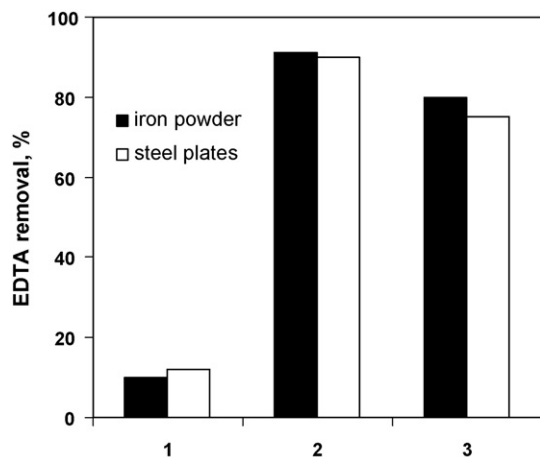


Fig. 4. EDTA removal degree from solutions after 6 h treatment using iron powder and carbon steel plates. Conditions of experiments: 1, as in Fig. 1; 2, as in Fig. 2; 3, as in Fig. 3.

influence of the load above 20 g l^{-1} on the completeness of EDTA removal. The data presented in Fig. 5 show that with the increase in load to 20 g l^{-1} the degree of EDTA removal increases. Further increase in load has no influence on EDTA destruction.

It is worth noting that the use of iron powder instead of carbon steel plates has also inconsiderable influence on the completeness of organic destruction. Thus, such influence of load of metallic iron on the completeness of Cu(II)–EDTA removal allows to assume, that the EDTA removal rate from solutions is connected preferable with reactions in solutions.

The increase in organic removal rate in case of presence of Cu(II) is possible also because of increase in iron dissolution due to occurrence of the galvanic pair Fe–Cu. In order to check up the latter assumption electrochemical investigations were carried out (Fig. 6). Voltammograms obtained immediately after dipping electrodes into solutions indicate somewhat higher anodic currents in the case when the solutions are free from Cu(II) (Fig. 6, curves 1 and 2). However, after long keeping electrodes in Cu(II) free solutions almost complete passivation of steel electrode proceeds, meanwhile in solutions containing Cu(II) ions anodic current remains high even after keeping for 1 day (Fig. 6, curves 3 and 4). Thus, the reason of enhancing effect of Cu(II) ions on decontamination could be also the increased corrosion rate of iron in solutions of Cu(II) ions.

The long term experiments carried out in an open vessel with the purpose to determine the optimal pH value for EDTA and Cu(II) removal from solutions (Table 1) showed that Cu(II) is almost completely removed at all values of pH. The most complete destruction

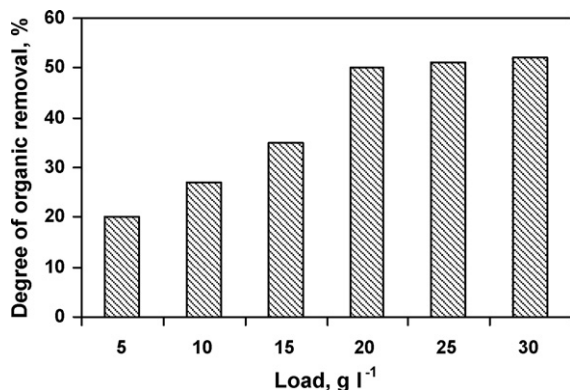


Fig. 5. Influence of carbon steel load on EDTA destruction from solutions containing 1 mmol l^{-1} Cu(II) and 10 mmol l^{-1} EDTA at initial pH 5 in open vessel.

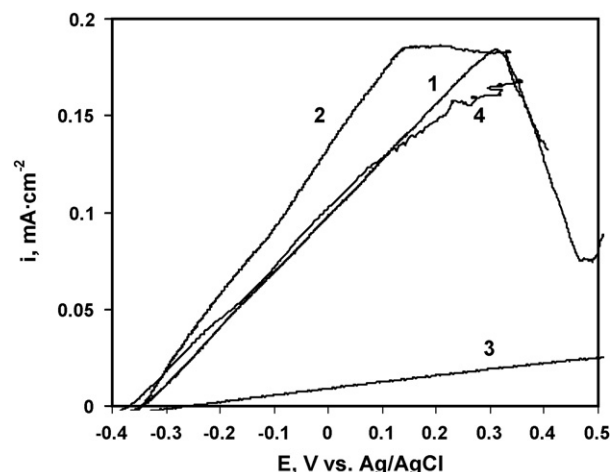
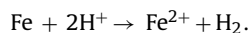


Fig. 6. Carbon steel electrode anodic voltammograms obtained in solutions containing 10 mmol l^{-1} $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ (1 and 3) and 1 mmol l^{-1} CuSO_4 and 10 mmol l^{-1} $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ (2 and 4). Voltammograms recorded immediately after dipping electrode in solutions (1 and 2) and after keeping electrode in appropriate solutions for 24 h (3 and 4).

of EDTA proceeds at pH 5. In this case the residual concentration is about 0.5 mmol l^{-1} . At lower pH values the total residual organic differs inconsiderably from that obtained at pH 5 but the residual EDTA and Fe concentrations are remarkably higher. At pH 7 the degree of EDTA destruction is also rather high; the total content of organics formed during the treatment is also rather high. However, at pH 7 the process is slower. Such a modest influence of pH on the decontamination process could be explained by elimination of free H^+ ions in iron dissolution reaction, when Fe^{2+} or Fe^{3+} are formed.



According to Noradaum and Cheng [16] the presence of oxygen in solutions has the crucial influence on the rate of EDTA degradation. Authors [16] determined that in the pH range 5.5–6.5 and at the EDTA concentration equal to 1 mmol l^{-1} degradation proceeded owing to dissolved oxygen, which forms an active hydroxyl radical on the iron surface. The reaction is sharply retarded at increased EDTA concentrations. To check this assumption the experiments were carried out in open and closed vessels.

The removal of EDTA from its 100 mmol l^{-1} acidic (pH 4) solutions in open vessel is negligible. In closed vessel, as opposed to open vessels, the formation of EDTA containing precipitate proceeds. The concentrations of EDTA and organics with time steadily decreased, though the process was also slow (Fig. 7, curves 1 and 2). In this case the presence of Cu(II) in amount equal to 10 mmol l^{-1} (Fig. 7, curves 3 and 4) had no remarkable influence on EDTA removal from solutions and the decrease of EDTA concentration in solutions remained similar to that in solutions without Cu(II). In this case also there are not remarkable differences between EDTA concentration and oxygen demand for the organics oxidation.

Table 1

Influence of the initial pH on the removal of Cu(II) and EDTA from solutions containing 1 mmol l^{-1} Cu(II) and 10 mmol l^{-1} EDTA using carbon steel

Results of treatment	pH 3.5	pH 4	pH 5	pH 7
Residual Cu(II) (mmol l^{-1})	0.003	0.001	<0.0005	<0.0005
Residual EDTA (mmol l^{-1})	1.6	1.6	0.5	2.2
O_2 consumption (mequiv l^{-1})	160	160	170	320
Total iron in solutions (mmol l^{-1})	2.8	2	~0	2.2
Dissolved Fe (g)	17	10	8	3
Final pH	8.4	8.2	8	8.9

Load 20 g l^{-1} ; treatment time 40 h

Table 2Capillary electrophoresis investigations of solution composition after treatment with carbon steel (load 20 g l⁻¹) for 10 h at initial pH 4

Composition of solution and treatment conditions	FeEDTA (mmol l ⁻¹)	NiEDTA (mmol l ⁻¹)	Other compounds
10 mmol l ⁻¹ EDTA, 1 mmol l ⁻¹ Cu(II); without treatment	–	9–10	–
10 mmol l ⁻¹ EDTA; open vessel	1	0.54	+ 3 other key compounds
10 mmol l ⁻¹ EDTA, 1 mmol l ⁻¹ Cu(II); open vessel	–	–	+ 2 other key compounds
100 mmol l ⁻¹ EDTA, 10 mmol l ⁻¹ Cu(II); closed vessel	84	–	–

Table 3

Chemical composition of precipitate formed during EDTA removal under different conditions at initial pH 4

Composition of solution and treatment conditions	Content in precipitate		
	Fe (total) (mass %)	Organics (as H ₄ EDTA) (mass %)	Ratio Fe(III): EDTA (mol: mol)
Fe + 10 mmol l ⁻¹ EDTA, open vessel; time 40 h	32	8	20
Fe + 10 mmol l ⁻¹ EDTA and 1 mmol l ⁻¹ Cu(II), open vessel; time 40 h	25	12	11
Fe + 100 mmol l ⁻¹ EDTA and 10 mmol l ⁻¹ Cu(II), closed vessel; time 40 h	18	24	4
FeSO ₄ + 100 mmol l ⁻¹ EDTA, closed vessel; time 10 days	11	29	2

Load of iron powder 20 g l⁻¹.

The UV investigation of solutions obtained after treatment under different conditions showed the intense decrease in light absorbance in the UV region, indicating also an intense decrease in concentrations of organics.

Capillary electrophoresis investigations (Table 2) using the determination of EDTA as Ni(II) and Fe(III) complexes, showed that after 10 h treatment in an open vessel EDTA was completely removed from solutions in the case when the Cu(II) ions were present. When the Cu(II) ions were not added to solution, the residual EDTA concentration makes ~1 mmol l⁻¹ after 10 h treatment. In both cases the other possibly compounds forming complexes with Ni(II) and Fe(III) were formed. When the treatment was carried out in closed vessels, the concentration of EDTA remarkably decreased without formation of any intermediate complexing compounds.

The precipitate formed during the treatment was investigated using chemical analysis and FT-IR measurements. The main components of this precipitate are iron hydroxides. The data of chemical analysis (Table 3) show a high content of organics in the precipitate in all the investigated cases. The molar ratio between the iron and organic compounds depends on the treatment conditions. The precipitate formed in a closed vessel, when the access of oxygen from air is hindered, contains the greatest amount of organics. The ratio between Fe ions and EDTA molar contents in precipitate is rather low indicating the important role of precipitation during decontamination.

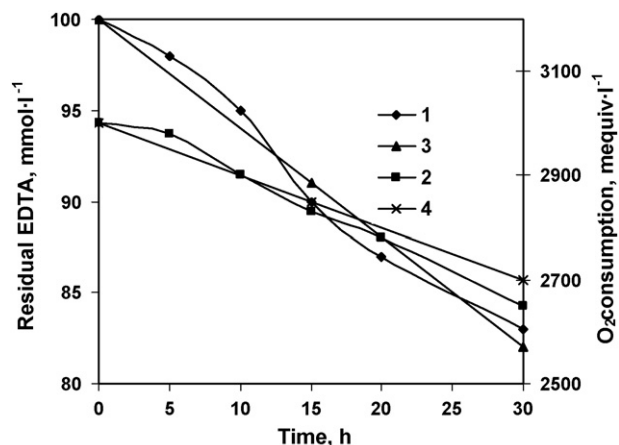


Fig. 7. Changes in the residual concentrations of EDTA (1 and 3) and O₂ consumption for organic oxidation (2 and 4) with time in solutions containing 100 mmol l⁻¹ EDTA (1 and 2); and 10 mmol l⁻¹ EDTA and 100 mmol l⁻¹ Cu(II) (3 and 4) at initial pH 4 using iron powder (load 30 g l⁻¹) in closed vessel.

FT-IR spectra obtained under different treatment conditions are depicted in Fig. 8. In all cases the precipitate formed contains rather great amounts of organic components. The presence of Cu(II) in solutions has also some influence on the composition of precipitate (Fig. 8, spectra a and b). The distinct absorbance peaks at 1670 cm⁻¹ corresponding to –COO⁻ symmetric vibrations and at 1400 cm⁻¹ corresponding to –COOH stretching vibrations indicate the presence of carboxylic compounds in the precipitate.

The reasons of organics precipitation could be various. It is well known that the freshly precipitated iron hydroxides act as sorbent for organic compounds. Fe(III) can form the insoluble organic compounds, as well.

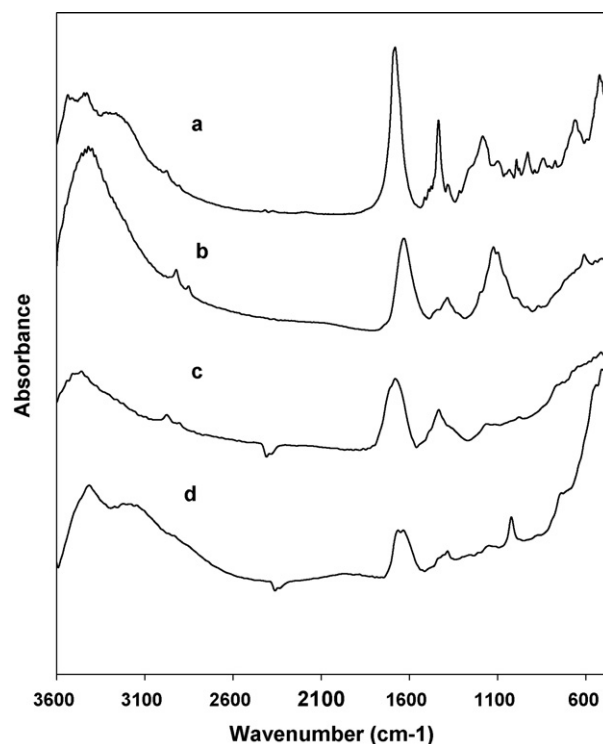


Fig. 8. FT-IR spectra of Na₂EDTA·2H₂O (a) and precipitate formed during treatment with iron powder in open vessel in solutions containing 10 mmol l⁻¹ EDTA and 1 mmol l⁻¹ Cu(II) (b); in closed vessel in solutions containing 100 mmol l⁻¹ EDTA (c) and precipitate formed with FeSO₄ in 100 mmol l⁻¹ EDTA solutions in closed vessel at pH 4 (d).

When the experiments were carried out in closed vessels, according to the capillary electrophoresis analysis no EDTA destruction products were present in the solution, meanwhile the EDTA concentration remarkably decreased. It can be supposed that EDTA is precipitated as insoluble iron compound. It is well known that EDTA form an insoluble compound with an excess of some bivalent metals (Cu(II), Zn(II), Mn(II), Pb(II)), though we failed to find any literature about insoluble Fe(II)–EDTA compounds. To check the possibility whether such a compound exists, the FeSO₄ and EDTA solutions were mixed at pH 4 and kept in a closed vessel for 10 days. The data of chemical analysis presented in Table 3 show that the molar ratio between Fe(II) and EDTA is close to 2 and confirm the assumption that the an insoluble Fe(II) compound similar to Cu₂EDTA·4H₂O really exists [32]. The comparison of the FT-IR spectrum obtained for the EDTA compound precipitated with Fe(II) and the one treated with metallic iron in closed vessels (Fig. 8, spectra c and d) indicates their identity. It makes it possible to draw a conclusion that during the treatment of EDTA with metallic iron in closed systems the formation of insoluble Fe–EDTA compounds proceeds along with dissolution of metallic iron.

Thus, the presented investigation shows that the decontamination of solutions containing EDTA using metallic iron is a very complicated process. At the access of oxygen the destruction of EDTA takes place along with the formation of insoluble organic compounds.

4. Conclusions

Decontamination of EDTA containing solutions using metallic iron is a rather complicated process. The access of air to solutions plays the important role in EDTA destruction. The process is remarkably enhanced by addition of Cu(II) to the EDTA solutions. A catalytic effect of Cu(II) could be explained by an increased Fe corrosion rate. The precipitation of the derivatives of insoluble Fe with EDTA or its decomposition products proceeds along with the destruction of EDTA. In closed systems the main EDTA removal reaction is the precipitation with iron ions.

References

- [1] M. Sillanpää, V. Vičkačkaitė, L. Niinistö, M.-L. Sihvonen, Distribution and transportation of ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid in lake water and sediment, *Chemosphere* 35 (12) (1997) 2797–2805.
- [2] R. Ocossu, A. Polcaro, M. Lavagnolo, M. Mascia, S. Palmas, F. Renoldi, Electrochemical treatment of landfill leachate: oxidation at Ti/PbO₂ and Ti/SnO₂ anodes, *Environ. Sci. Technol.* 32 (22) (1998) 3570–3573.
- [3] J.L. Matheson, P.G. Tratnyek, Reductive dehalogenation of chlorinated methanes by iron metal, *Environ. Sci. Technol.* 28 (12) (1994) 2045–2053.
- [4] F.X.M. Casey, S.K. Ong, R. Horton, Degradation and transformation of trichloroethylene in miscible-displacement experiments through zerovalent metals, *Environ. Sci. Technol.* 34 (2000) 5023–5029.
- [5] C.J. Clark II, P.S.C. Rao, M.D. Annable, Degradation of perchloroethylene in cosolvent solutions by zero-valent iron, *J. Hazard. Mater.* 96 (2003) 65–78.
- [6] H.M. Gaber, S.D. Comfort, P.H. Shea, T.A. Machacek, Metachlor dechlorination by zerovalent iron during unsaturated transport, *J. Environ. Qual.* 31 (2002) 962–969.
- [7] L.I. Xie, Ch.I. Shang, Role of humic acid and quinone model compounds in bromate reduction by zerovalent iron, *Environ. Sci. Technol.* 39 (2005) 1092–1100.
- [8] R.W. Gillham, S.F. O'Hanessin, Enhanced degradation of halogenated aliphatics by zerovalent iron, *Groundwater* 32 (1999) 958–967.
- [9] W.S. Pereira, R.S. Freire, Azo dye degradation by recycled waste zero-valent iron powder, *J. Braz. Chem. Soc.* 17 (5) (2006) 832–838.
- [10] J. Cao, L. Wei, Q. Huang, L. Wang, Sh. Han, Reducing degradation of azo dye by zero-valent iron in aqueous solution, *Chemosphere* 38 (3) (1999) 565–571.
- [11] A.J. Mielczarski, G.M. Atenas, E. Mielczarski, Role of iron surface oxidation layers in decomposition of azo-dye water pollutants in weak acidic solutions, *Appl. Catal. B: Environ.* 56 (4) (2005) 289–303.
- [12] F. Cheng, R. Muftikan, Q. Fernando, N. Korte, Reduction of nitrate to ammonia by zero-valent iron, *Chemosphere* 35 (1997) 2689–2695.
- [13] A. Agrawal, P.G. Tratnyek, Reduction of nitro aromatic compounds by zero-valent iron metal, *Environ. Sci. Technol.* 30 (1) (1996) 153–160.
- [14] D. Mishra, J. Farrell, Understanding nitrate reactions with zerovalent iron using tafel analysis and electrochemical impedance spectroscopy, *Environ. Sci. Technol.* 39 (2005) 645–656.
- [15] Ch. Su, R.W. Puls, Nitrate reduction by zerovalent iron: effects of formate, oxalate, citrate, chlorate, sulfate, borate, and phosphate, *Environ. Sci. Technol.* 38 (2004) 2715–2720.
- [16] Ch.E. Noradaum, I.F. Cheng, EDTA degradation induced by oxygen activation in a zerovalent iron/air/water system, *Environ. Sci. Technol.* 39 (18) (2005) 7158–7163.
- [17] C.Y. Kwan, W. Chu, The role of organic ligands in ferrous-induced photochemical degradation of 2,4-dichlorophenoxyacetic acid, *Chemosphere* 67 (8) (2007) 1601–1611.
- [18] Y. Wu, L. Slater, N. Korte, Effect of precipitation on low frequency electrical properties of zerovalent iron columns, *Environ. Sci. Technol.* 39 (2005) 9197–9204.
- [19] B. Schrick, B.W. Hydutsky, J.L. Blough, T.E. Mallouk, Delivery vehicles for zerovalent metal nanoparticles in soil and groundwater, *Chem. Mater.* 16 (2004) 2187–2193.
- [20] H. Lien, W. Zhang, Transformation of chlorinated methanes by nanoscale iron particle, *J. Environ. Eng.* 125 (1999) 1042–1047.
- [21] W. Zhang, Nanoscale iron particles for environmental remediation, *J. Nanoparticle Res.* 5 (2003) 323–332.
- [22] D.W. Elliott, Field assessment of nanoscale bimetallic particles for groundwater treatment, *Environ. Sci. Technol.* 35 (2001) 4922–4926.
- [23] S. O'Hara, T. Krug, J. Quinn, Ch. Clausen, Ch. Geiger, Field and Laboratory Evaluation of the Treatment of DNAPL Source Zones Using Emulsified Zero-valent Iron 2, Wiley Interscience, 2006, pp. 35–56.
- [24] M. Fan, M. Asce, R.C. Brown, Th.D. Wheelock, F.C. Laabs, Synthesis, characterization, and coagulation of polymeric ferric sulfate, *J. Environ. Eng.* 128 (2002) 483–490.
- [25] O. Gyllienė, M. Šalkauskas, R. Juškėnas, The use of organic acids as precipitants for metal recovery from galvanic solutions, *J. Chem. Technol. Biotechnol.* 70 (1) (1997) 111–115.
- [26] Y.Y. Lur'e, A.I. Ribnikova, Khimicheskii analiz proizvodstvennikh stochnikh vod (Chemical analysis of industrial effluents), *Khimija, Moscow*, 1974, pp. 336 (in Russian).
- [27] S. Pozdniakova, R. Ragauskas, A. Dikčius, A. Padarauskas, Determination of EDTA in used fixing solutions by capillary electrophoresis, *Fresen. J. Anal. Chem.* 363 (1999) 124–125.
- [28] R. Pohloudek-Fabini, T. Beyrich, Organicheskii analiz (Organic Analysis), *Khimia, Leningrad*, 1988, pp. 624 (in Russian).
- [29] D.S. Orlov, L.A. Gristina, Praktikum po khimii gumusa (Handbook of Humus Chemistry), Publisher by Moscow University, 1981, 272 pp. (in Russian).
- [30] T.-T. Lim, J. Feng, B.-W. Zhu, Kinetic and mechanistic examinations of reductive transformation pathways of brominated methanes with nano-scale Fe and Ni/Fe particles, *Water Res.* 41 (2007) 875–883.
- [31] X. Xu, H. Zhou, M. Zhou, Catalytic amination and dechlorination of *para*-nitrochlorobenzene (*p*-NCB) in water over palladium–iron bimetallic catalyst, *Chemosphere* 62 (2006) 847–852.
- [32] O. Gyllienė, J. Aikaitė, O. Nivinskienė, Recovery of EDTA from complex solutions using Cu(II) as precipitant and Cu(II) subsequent removal by electrolysis, *J. Hazard. Mater.* 116 (1–2) (2004) 119–124.