



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

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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

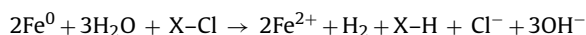
strong complexes with copper ions. Recently, as an alternative to environmentally dangerous EDTA, the biodegradable copper ligands such as tartrate $\text{HOOC-CH(OH)-CH(OH)-COOH}$ and quadrol (N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine) $((\text{OH})(\text{CH}_3)\text{CH-CH}_2)_2\text{-N-CH}_2\text{-CH}_2\text{-N-(CH}_2\text{-CH(CH}_3\text{)(OH))}_2$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

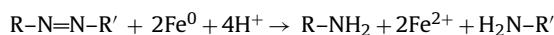
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very attractive. Metallic iron easily removes halogens from such organic compounds as chlorinated solvents, dioxines, pesticides, etc. [7–13]. The reaction proceeds according to the equation:



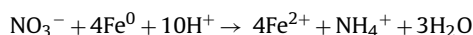
It is worth noting that these compounds are not destroyed by strong reducing agents such as hydrazine, borohydride, and formaldehyde.

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

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