

Recovery of EDTA from complex solution using Cu(II) as precipitant and Cu(II) subsequent removal by electrolysis

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Abstract

Ethylendiaminetetraacetate (EDTA) is a chelating agent widely used in industry and agriculture. Resistant to chemical and biological degradation EDTA represents a serious ecological problem. In order to avoid the outlet into the environment a new method of EDTA recycling has been proposed. The method involves substituting of the metal ions in EDTA complexes by Cu(II) and formation of an insoluble $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ compound at the excess of Cu(II) ions in weakly acidic solutions. Cu(II) ions substitute such metal ions as Ni(II), Zn(II), Co(II), Cd(II), Ca(II) and Mg(II). After treatment of the precipitate with water only, acidic or alkaline solutions the copper from the suspension formed can be removed by electrolysis. The highest current efficiency under galvanostatic conditions is in alkaline solutions, however, the highest yield of EDTA recovery is in acidic solutions.

FT-IR investigations and chemical analysis of the precipitate formed have shown that in acidic and in alkaline solutions, H_4EDTA and $\text{Na}_2\text{H}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ were formed, respectively. Electrolysis in acidic solutions gives the best results, i.e. the formed H_4EDTA contains the highest amount of EDTA (95%) and the lowest amount of copper (0.01%).

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1. Introduction

Ethylendiaminetetraacetate (EDTA) is one of the most powerful chelating agents widely used in metal finishing, textile, dyeing industries, in printed circuit board manufacture, for remediation of soils polluted with heavy metals, in medicine for treatment of heavy metal poisoning, etc. in order to enhance the metal ion solubility or to avoid the formation of soluble metal compounds. It forms strong complexes with the ratio 1:1 between heavy metal ions and ligand. Such a peculiarity of EDTA hinders the metal recovery in form of insoluble compounds, which is the common practice for treatment of spent solutions containing heavy metal ions. Resistant to chemical and biological degradation EDTA may also be capable to dissolve Fe^{3+} , Al^{3+} , Ca^{2+} , Mg^{2+} and

heavy metals in soils and sediments, facilitating their movement in the hydrological cycle [1]. In a reciprocal manner the behavior of EDTA is itself influenced by the presence of metals.

The oxidative destruction of ligands is mainly used for metal removal from solutions containing complexing agents. After the ligands are completely destroyed to the harmless substances CO_2 and N_2 , the metals are precipitated in form of insoluble compounds. The hydrogen peroxide, which gives only water as a reaction product, is the most environmentally friendly oxidizing agent. Because of the slow reaction rate its use in practice is rare. The ozone is the most powerful oxidizing agent, which decomposes all known ligands. Its use in practice is limited by strong hazardous influence onto environment [2]. The use of electrolysis enables both to destroy the ligands onto anode and to recover metals onto cathode [3]. However, the oxidation of organic matter to the harmless substances onto anode is the complicated task in most cases.

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In order to decrease the treatment costs and the environmental impact the possibilities to recover and reuse ligands have also been studied. The peculiarity of free EDTA to form low soluble H_4EDTA in acidic (pH 0.5–1.5) solutions has been used to recycle spent copper electroless plating solutions. However, bounded with $Cu(II)$ ions EDTA does not form H_4EDTA precipitate. Therefore, the $Cu(II)$ ions are removed by electrolysis [4,5] or by oxalate precipitation in acidic solutions [6].

For recycling of EDTA used for decontamination of lead-polluted soils the substitution of lead by $Fe(III)$ in $Pb(II)$ –EDTA complex at low pH values, followed by precipitation of lead ions with either phosphate or sulfate is proposed. $Fe(III)$ is further precipitated at high pH [7].

The behavior of EDTA at a higher concentration of heavy metal ions as compared with EDTA concentration at its full complexing power is studied much less. The formation of low soluble $Cu_2EDTA \cdot 4H_2O$ compounds from insoluble $Cu(OH)_2$ and H_4EDTA has been known for a long time [8]. The structure and formation regularities of M_2EDTA compounds, where $M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}$ and Pb^{2+} were studied by Leontjeva and co-workers [9,10]. The reaction between $Ag(I)$ and EDTA with formation of insoluble Ag_4EDTA is described in [11]. Conditions of $Cu_2EDTA \cdot 4H_2O$ formation in aqueous solutions with purpose to achieve the most complete precipitation were studied in [12]. The dissociation of this compound in aqueous solutions proceeds according to the equation



The stability constant of $Cu_2EDTA \cdot 4H_2O$ compound is $K = 2.5 \times 10^3$ l/mol and the solubility product $S = 2 \times 10^{-5}$ mol²/l² [13].

Our investigations were carried out with the purpose to precipitate EDTA from solution using the excess of $Cu(II)$ and to remove the copper by means of electrolysis after dissolution of $Cu_2EDTA \cdot 4H_2O$ precipitate in order to obtain a pure product of EDTA.

2. Experimental

All the chemicals used were at least of analytical purity. They were used without further purification.

Precipitation experiments were carried out by addition of $CuSO_4$ solution to Na_2H_2EDTA solutions. pH was adjusted with 1 mol l^{-1} H_2SO_4 or 1 mol l^{-1} $NaOH$ solutions. After formation of precipitate solutions were filtered and thoroughly rinsed with cold ($\sim 5^\circ C$) deionized water. The solid was dried at $80^\circ C$.

The quantities of EDTA and $Cu(II)$ in solutions were determined using standard methods of chemical analysis [14]. EDTA in solutions was determined by two independent methods: complexometrically by titration with $Bi(III)$ and by oxidation in alkaline solutions with $KMnO_4$. $Bi(III)$ with EDTA in acidic solutions (pH ~ 3 adjusted with HNO_3)

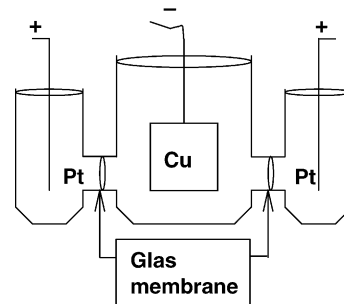


Fig. 1. Electrochemical cell for galvanostatic investigations.

forms strong complexes with EDTA in a ratio 1:1. Pyrocathine violet was used as an indicator. The excess of $KMnO_4$ in alkaline solutions (2 mol l^{-1} $NaOH$) oxidizes EDTA completely to the gaseous state. The EDTA equivalent in this reaction is 36. The excess of $KMnO_4$ was retitrated with oxalic acid in acidic solution. Experiments were carried out 2–3 times, the data obtained were averaged.

$Cu(II)$ was 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 $Na_2S_2O_3$ solution.

Electrochemical investigations were carried out using a potentiostat ПИ-51 (Russia). Voltammograms were recorded in filtrate of suspensions obtained after treatment of 5 g of a dried $Cu_2EDTA \cdot 4H_2O$ compound with 100 ml deionized water, acidic (1 mol l^{-1} H_2SO_4) or alkaline solutions (pH 12 adjusted with $NaOH$) in a standard thermostatically controlled three compartment glass cell ЯСЭ-3 using a Cu sheet of 1 cm^2 area as a working electrode, Pt wire as a counter electrode and $Ag/AgCl/KCl_{sat}$ as reference. Potential values are given versus standard hydrogen electrode.

Experiments under galvanostatic conditions were carried out in a three-compartment glass cell—cathodic with a volume of 80 ml and two anodic of 10 ml each separated by glass membranes (Fig. 1). Five grams $Cu_2EDTA \cdot 4H_2O$ was placed in a cathodic compartment and treated either with deionized water, or alkaline, or acidic solution. The anodic compartment was filled with a filtrate of water suspension, $NaOH$ (pH 12) or 1 mol l^{-1} H_2SO_4 solutions, respectively. The copper sheet (50 cm^2) was used as a cathode and Pt wires as anodes. The suspension was mixed with magnetic stirrer during electrolysis. The long-term experiments were carried out at different constant currents before a complete $Cu(II)$ removal was achieved. The current efficiency for copper was determined from the ratio between mass gain of the cathode and theoretically calculated copper deposition (m) according to Faraday's law

$$m = \frac{M}{2F} It, \quad (2)$$

where M is the copper molar mass equal to 63.54 g, F the Faraday's number equal to 96,500 C, I the current, A and t is the time, s.

The precipitate formed was rinsed with cold ($\sim 5^\circ\text{C}$) deionized water and dried at 70°C . The yield of EDTA regeneration was calculated according to the mass balance considering the mass of precipitate, amounts of solutions taken for analysis and the residual concentrations in cathodic and anodic compartments.

The infrared spectra of precipitates were recorded in KBr pallets with a Fourier transform infrared spectrometer (Hartmann and Braun, Canada). Spectra were recorded in the region between 4000 and 500 cm^{-1} .

3. Results and discussion

The insoluble $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ precipitate in aqueous solutions is formed when the concentration of Cu(II) exceeds that of EDTA. When solutions pH is kept constant, formation of precipitate begins at $\text{pH} \sim 2$ and is most complete at $\text{pH} 5.6$ (Fig. 2). A further increase in pH causes precipitation of insoluble Cu(OH)_2 and dissolution of CuEDTA^{2-} . The completeness of EDTA removal from solution strongly depends on the Cu(II) concentration used for precipitation. With increase in Cu(II) concentration the residual EDTA concentration in solution decreases (Fig. 3). However, a large excess of Cu(II) in many cases is useless.

The formation rate also highly depends on pH. During formation of precipitate pH decreased and its value was kept constant by adding of NaOH solutions. The steady

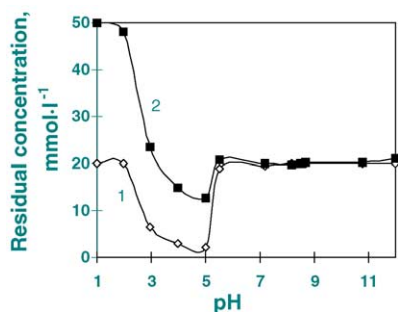


Fig. 2. pH influence on the residual EDTA (1) and Cu(II) (2) concentrations after precipitation in solutions containing 50 mmol l^{-1} Cu(II) and 20 mmol l^{-1} EDTA.

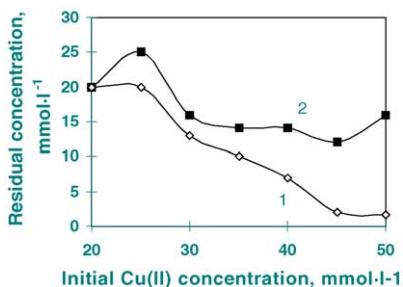


Fig. 3. Influence of Cu(II) concentration on the residual EDTA (1) and Cu(II) (2) concentrations after precipitation. The initial EDTA concentration 20 mmol l^{-1} , pH 5.

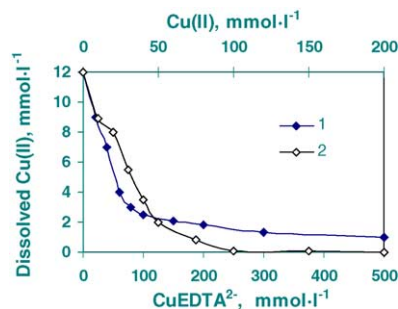


Fig. 4. Dissolution of $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ compound in CuEDTA^{2-} (1) and CuSO_4 (2) solutions at pH 4.

state of precipitation at pH 2.2 is achieved after 10–12 days, meanwhile at pH 5.6 it is achieved after 20–30 min. It has been shown [12] that both the formation rate of insoluble $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ and completeness of precipitation depend on concentrations of Cu(II) , EDTA, temperature and the solution ionic strength. The solubility of the precipitate formed also depends on temperature and the presence of background electrolyte. The increase in temperature from 20 to 100°C increases the solubility of $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ from 5.5 to 10 mmol l^{-1} , meanwhile, the presence of 0.5 mol l^{-1} Na_2SO_4 , K_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$ increases the solubility up to 16 mmol l^{-1} [13].

The presence of electrolytes containing Cu(II) or CuEDTA^{2-} ions considerably decreases the solubility of $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ (Fig. 4). After addition of 100 mmol l^{-1} CuSO_4 , the dissolution of $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ reaches the a limited value. In CuEDTA^{2-} containing solutions the solubility of $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ remains $\sim 0.5\text{ mmol l}^{-1}$.

$\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ precipitate is formed not only in Cu(II) –EDTA solutions but also in other heavy metal–EDTA solutions (Table 1). Cu(II) substitutes Ni(II) , Zn(II) , Co(II) , Cd(II) , Ca(II) Mg(II) in their EDTA solutions. Only Fe(III) forms with EDTA a more stable complex as compared to that of Cu(II) .

In all investigated cases the extent of EDTA removal decreases with decrease in Cu(II) concentration and pH. The precipitate formed is crystalline and easily filtering.

It is unlikely that $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ could be directly used in practice. In order to recover EDTA and reuse them the electrochemical deposition of copper was carried out after

Table 1
 $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ precipitate formation in solutions containing 20 mmol l^{-1} M–EDTA and 50 mmol l^{-1} CuSO_4 , pH 4

Metal ions	Residual concentrations (mmol l^{-1})	
	Cu(II)	EDTA
Ni(II)	15	3.5
Zn(II)	13	2.5
Co(II)	13	2.4
Cd(II)	12	2.0
Ca(II)	18	3.7
Mg(II)	18	3.9
Fe(III)	50	20

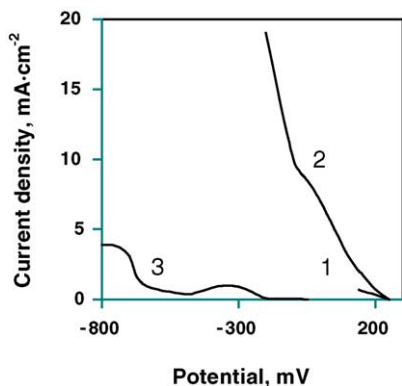
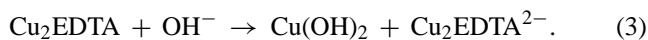


Fig. 5. Voltammograms recorded in filtrate of $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ water suspension (1), in filtrate of $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ alkaline suspension (2) and in acidic $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ solution (3). The potential sweep rate 50 mV s^{-1} .

treatment of precipitate with either water or acidic/alkaline solutions. It is worthy to note that only copper can be completely removed from EDTA solutions by using electrolysis. Electrodeposition of other heavy metals proceeds at more negative potentials.

The electrochemical investigations were carried out in three different suspensions obtained after treatment of $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ with either deionized water or a NaOH solution (pH 12) or a diluted 1 mol l^{-1} H_2SO_4 solution. In all cases the dissolution proceeds in different ways. The solubility of $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ in water is low. Its dissociation proceeds according to Eq. (1) with decrease in pH to 4.6 [13]. In alkaline solutions the insoluble compound is completely destroyed with formation of insoluble precipitate and soluble CuEDTA^{2-} complex:



$\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ compound dissolves in acidic solutions, but its solubility is limited to $\sim 0.1\text{ mol l}^{-1}$.

It is unlikely that copper electrodeposition may proceed from solid phase. Therefore, the voltammograms were recorded in filtrate of these suspensions (Fig. 5). As might be expected, weak dissociation of Cu_2EDTA and absence of support electrolyte in water limits the solution supply with ions. Therefore, the resistance in cell is high and the electrokinetic

reactions are very slow and, as a result, the current cannot exceed 1 mA cm^{-2} (Fig. 5, curve 1). On the other hand, the electrolysis at low current densities in solutions without supplementary substances makes it possible to obtain clean substances.

The reactions proceed most rapidly in alkaline solutions. Copper deposition begins at a rather positive potential and the overvoltage is low (Fig. 5, curve 2). In this case not only copper is deposited, but also a rapid hydrogen evolution proceeds. In acidic solution (Fig. 5, curve 3) copper deposition begins at more negative potentials; the current is low, only at high negative potentials the current increases, due to hydrogen evolution.

When a long-term electrolysis under galvanostatic conditions was applied (Tables 2–4) the electrokinetic parameters considerably differed from those obtained under potentiodynamic conditions. During electrolysis the composition of solution and the copper deposition current efficiency changed, though the pH value during electrolysis did not remarkably change in all investigated cases.

In water suspension (pH 4.6) at the beginning of electrolysis a low current can be applied and the current efficiency is rather high (Table 2). During electrolysis the concentration of EDTA^{2-} free ions increased. The free EDTA^{2-} evolved increased the Cu_2EDTA solubility. As a result, the solution conductivity increased and higher currents were applied. In these weakly acidic solutions the most of the formed EDTA precipitated as H_4EDTA . Due to the absence of supporting electrolyte the anodic compartments were filled with a filtrate suspension, where the oxidation of EDTA may proceed. During the electrolysis a portion of EDTA can be also transferred from the cathodic to the anodic compartments. The analysis of anolite using both complexometric titration with Bi(III) and oxidation of organics with KMnO_4 gave the same results, which proves that EDTA is destroyed completely onto anode.

In alkaline solutions (Table 3), in contrast to water suspension, at the beginning of electrolysis the high current density may be applied and its efficiency was high. The current efficiency decreased only at the end of electrolysis, when the copper ions were removed. With decrease in Cu(II) concentration and the release of EDTA^{2-} anions the $\text{Cu}(\text{OH})_2$ precipitate dissolved and consequently the whole copper was

Table 2
Electrolysis in $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ water suspension

Current I (mA)	Duration of electrolysis t (h)	Current quantity (C)	Cu deposited on the cathode (C)	Current efficiency for Cu(II) (%)	Residual concentrations in solution (mmol l^{-1})			
					Catholite		Anolite	
					Cu(II)	EDTA	Cu(II)	EDTA
0					11.3	5.5	11.3	5.5
5	3.6	64.8	19.1	89	10	2.5		
15	19.4	1050	263.4	76				
25	28	2520	681.9	82	24	19.4	42	14.6
20	13.1	945	55.8	17.9	18	17.7	38	13.1
25	28	2520	5.8	7	~ 0	12.6	1.4	11.1

Table 3
Electrolysis in Cu₂EDTA·4H₂O alkaline suspension (pH 12)

Current <i>I</i> (mA)	Duration of electrolysis <i>t</i> (h)	Current quantity (C)	Cu deposited on the cathode (C)	Current efficiency for Cu(II) (%)	Residual concentrations in solution (mmol l ⁻¹)			
					Catholite		Anolite	
					Cu(II)	EDTA	Cu(II)	EDTA
0					85	85	0	0
100	4	1440	366	77	85	80	0	
50	9.5	1710	508	90	65			
25	4	360	112	94				
10	21.7	782	103	40	18	43	19	
10	23.5	846	34	12	6	38.2	8	
10	26	936	25	8	–	33.6	0.001	27.7

The anodic part filled with NaOH solution (pH 12).

Table 4
Electrolysis of Cu₂EDTA·4H₂O in dilute 1:4 H₂SO₄ solutions

Current <i>I</i> (mA)	Duration of electrolysis <i>t</i> (h)	Current quantity (C)	Cu deposited on the cathode (C)	Current efficiency for Cu(II) (%)	Residual concentrations in solution (mmol l ⁻¹)			
					Catholite		Anolite	
					Cu(II)	EDTA	Cu(II)	EDTA
0					165	85		
100	5.2	1860	521.7	85	73.3	63		
250	6.5	5860	599.4	31				
100	1	360	23.7	20				
50	1	180	8.9	15	5.6	20.4		
20	1	72	2.8	12	0.024	17.4	0.189	
10	10.1	36	4.6	39	0.01	15.6	0.001	
5	10.1	183	10.2	17	~	14.3	~0	
5	6	162	9.6	18	~0	14.6	~0	0.69
25	0.3	27	0.7	8				

The anodic part filled with diluted 1:4 H₂SO₄.

removed from solution. In cathodic part a soluble compound Na₂H₂EDTA was formed. It was precipitated after evaporation of solution. Analysis of EDTA in anolite using titration with Bi(III) and KMnO₄ gave differences up to 50%, which means that a part of organics formed in anodic compartment is not an EDTA complex.

Due to a rather high solubility of Cu₂EDTA·4H₂O in acidic solutions copper deposition was rapid (Table 4). The main portion of EDTA after copper removal precipitated as an insoluble H₄EDTA. The quantity of EDTA in anodic part was also considerably lower.

The composition of precipitate obtained after electrolysis was investigated by FT-IR spectroscopy and chemical analysis. FT-IR spectra of the Cu₂EDTA·4H₂O compound and the precipitate recovered by electrolysis were studied over the frequency region of 500–4000 cm⁻¹. The spectra were compared with those of H₄EDTA, Na₂H₂EDTA·2H₂O and CuSO₄·5H₂O. The FT-IR spectra of the precipitate recovered in water or acidic suspension were identical to those of H₄EDTA. The FT-IR spectra of precipitate did not show any additional IR absorption in the vicinity of 1110 cm⁻¹, indicating the absence of the sulfate group. In the FT-IR spectra of the precipitate recovered in alkaline solutions the absorption bands at 1627 and 1397 cm⁻¹ were related to the asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations,

Table 5
IR bands in Cu(II) and EDTA compounds

Assignment	H ₄ EDTA	Na ₂ H ₂ EDTA·2H ₂ O	CuSO ₄ ·5H ₂ O
ν_{as} COOH	1690v.s.	1673m	
ν_{as} COO ⁻	–	1627vs	
ν_s COOH	1420s.	–	
ν_s COO ⁻		1397s	
ν_{as} SO ₄			1110vs
δ SO ₄			620s

ν_s : symmetric stretching; ν_s : asymmetric stretching; δ : bending; vs: very strong; s: strong; m: medium.

respectively, of the COO⁻ group and corresponded to the spectra of Na₂EDTA·2H₂O (Table 5, Fig. 6).

As expected, the purest precipitate containing 95.9% EDTA and only 0.01% Cu(II) was obtained by electrolysis in

Table 6
Composition of the precipitates recovered after electrolysis

Precipitate formed	EDTA yield (%)	Content (%)	
		Cu(II)	EDTA
H ₄ EDTA (in water suspension)	85	0.02	90.9
Na ₂ H ₂ EDTA·2H ₂ O (in alkaline suspension)	70	0.5	87.1
H ₄ EDTA (in acidic suspension)	95	0.01	95.9

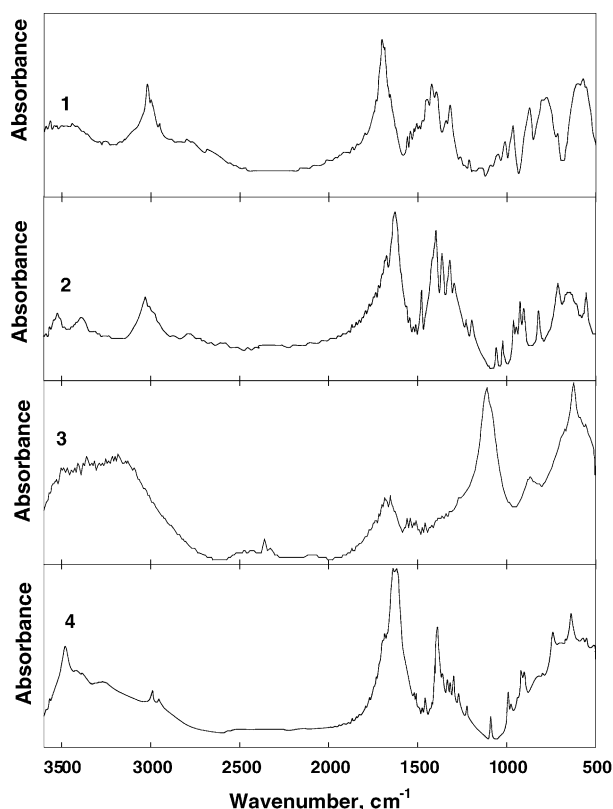


Fig. 6. FT-IR absorbance spectra: (1) H_4EDTA ; (2) $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$; (3) $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ and (4) $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$.

acidic solutions (Table 6). The quantity of Cu(II) is highest in alkaline solutions and simultaneously the yield of EDTA recovery is lowest in these solutions.

Thus, the main portion of EDTA from spent solution can be precipitated in weakly acidic solutions as an insoluble $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ compound. After copper removal by electrolysis the recovered EDTA can be reused. This method can be successfully used in the printed circuit board manufacture, where huge amounts of spent etching solutions are formed. These solutions can be used as a source of Cu(II) ions.

4. Conclusion

A method to recover EDTA from solutions containing Cu(II) , Ni(II) , Zn(II) , Co(II) , Cd(II) , Ca(II) and Mg(II) compounds with EDTA has been proposed. The method involves

substituting the metal ions in EDTA complexes with Cu(II) and formation of insoluble $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$ compound at the excess of Cu(II) ions in weakly acidic solutions. After treatment of the precipitate with either distilled water, or acidic or alkaline solutions the copper from the suspensions formed can be removed by electrolysis. Electrolysis in acidic solutions gives the purest product (H_4EDTA).

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