

# *Simultaneous electrochemical removal of copper and chemical oxygen demand using a packed-bed electrode cell*

KATSUKI KUSAKABE, HIROSHI NISHIDA, SHIGEHARU MOROOKA, YASUO KATO

*Department of Applied Chemistry, Kyushu University, Higashi-ku, Fukuoka, 812 Japan*

Received 5 December 1984; revised 3 March 1985

Copper ions and chelating agents in water were treated simultaneously by using a packed-bed electrode cell. The cathode packings were graphite particles or graphite felt; the anode packings were platinum-plated titanium pellets,  $\beta$ -PbO<sub>2</sub> particles or oxidized lead spheres. The catholyte contained ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), iminodiacetic acid (IDA) or glycine chelate of copper, while the anolyte contained the corresponding chelating agents. The initial concentration of chelating agents was 0.01 M in each experiment. The electrowinning of copper and the removal of chemical oxygen demand (COD) were achieved in the cathodic and the anodic chamber, respectively, under galvanostatic conditions. The COD was determined by the standard KMnO<sub>4</sub> method.

Of the cathodic packings, the graphite felt gave better results than the graphite particles because of the large surface area of the felt. Of the anodic packings, the platinum-plated titanium pellets and the  $\beta$ -PbO<sub>2</sub> particles showed equal suitability for COD removal. In the case of the platinum-plated titanium pellets, the current efficiency for COD removal of EDTA, NTA and IDA was 1.4, 0.7 and 0.32, respectively, in the range 0–12 kC. The removal of COD for EDTA, NTA and IDA under the same conditions was 41, 36 and 25%, respectively. In the lower pH range the electro-oxidation of EDTA proceeded more efficiently.

## 1. Introduction

Some organic substances dissolved in waste water form stable complexes with heavy metal ions. In this case, the removal of heavy metal ions by displacement with calcium or iron requires large quantities of chemicals and consequently produces a large amount of sludge. The chemical destruction of the complexing agents is not effective for all metal complexes. Thus, electrochemical treatment attracts special interest [1]. Both the recovery of heavy metal ions and the oxidation of organic compounds in waste water can be achieved electrochemically with little consumption of chemicals. Some papers on the electrochemical treatment of waste water containing heavy metal ions have been published [2–5], but studies on the electrochemical

removal of metal chelate compounds are quite few to date [6].

In this investigation, the electrowinning of copper and the electro-oxidation of copper chelate compounds in simulated waste water are performed in a rectangular packed-bed electrode cell. The effects of electrode materials, current and pH on the electrolysis efficiency are discussed.

## 2. Experimental apparatus and procedure

The packed-bed electrode cell, schematically shown in Fig. 1, was rectangular in cross-section. The cation exchange resin membrane (Nafion #427), which was supported by a porous polypropylene plate, divided the bed into an anodic and a cathodic chamber. The feeder elec-

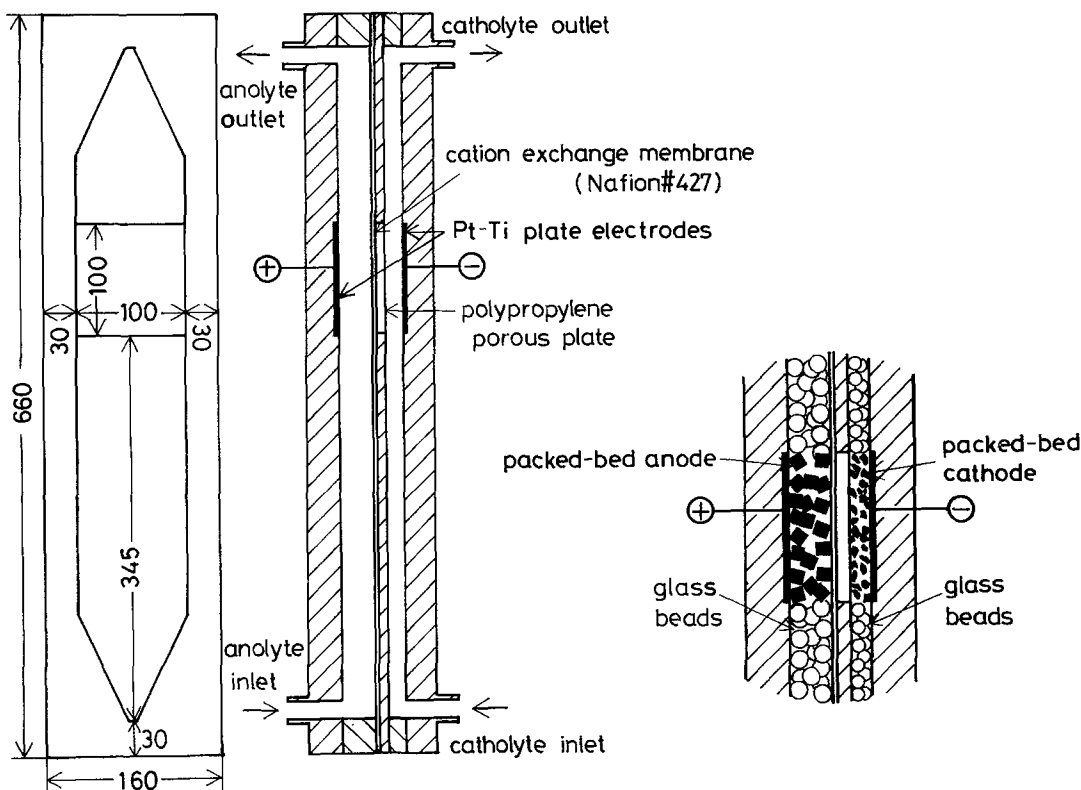


Fig. 1. Schematic view of packed-bed electrode cell. Dimensions in mm.

trodes were platinum-plated titanium (Pt-Ti) plates of  $10 \times 10$  cm and were fixed on the opposing wall of each chamber. The distance between the feed electrode and the membrane in the anodic and cathodic chamber was 5 and 10 mm, respectively. The cathode packings were a graphite felt with surface area  $260 \text{ cm}^2 \text{ cm}^{-3}$  (Nippon Carbon Co., Ltd), or pulverized graphite particles about 2.3 mm in diameter (Tokai Carbon Co., Ltd). The anode packings were Pt-Ti pellets 3 mm in diameter and 3 mm long (Permelec Electrode Ltd), pulverized  $\beta$ -PbO<sub>2</sub> particles about 3 mm in diameter and lead spheres 3 mm in diameter (Sanwa Chemical Co., Ltd). These materials were packed in the space between the membrane and the feeder electrode in each chamber. The remaining space was filled with glass spheres 4 mm in diameter for the anodic chamber and 2 mm in diameter for the cathodic chamber, respectively, to obtain a uniform upward flow of the electrolyte. The lead spheres were pre-oxidized for 12 h in the experimental cell at a fixed current of 2 A using a 1 M

H<sub>2</sub>SO<sub>4</sub> solution. The pre-oxidation was necessary to activate the electrodes and maintain their stability.

The electrolyte was a 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution containing EDTA, NTA, IDA, glycine or copper chelates of these agents. The pH of the anolyte was controlled using NaOH and H<sub>2</sub>SO<sub>4</sub> solutions. The concentrations of EDTA and NTA were determined by titration with an aqueous copper sulphate solution, the indicator being 1-(2-pyridylazo)-2-naphthol. The concentrations of IDA and glycine were measured by gel permeation chromatography. The current efficiency for the electroreduction of copper ions was calculated from the decrease in the copper concentration which was determined by atomic absorption spectroscopy. The COD was measured by the standard KMnO<sub>4</sub> method (JIS K0101). The total organic carbon (TOC) was analysed with a TOC meter (GCT125, Sumitomo Chemical Co.).

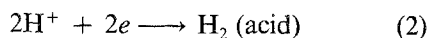
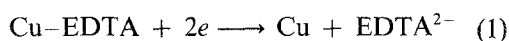
The anolyte and the catholyte were kept at 303 K in each storage tank and were circulated

through each chamber. The anolyte and catholyte volumes were 1.5 and 2 dm<sup>3</sup>, respectively. The superficial liquid velocity was about 10 cm s<sup>-1</sup> for both chambers. The electrolysis was carried out at 303 K galvanostatically using a d.c. power supply.

### 3. Results and discussion

#### 3.1. Cell performance

Possible electrode reactions are as follows.  
Cathode:



Anode:

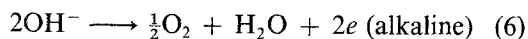
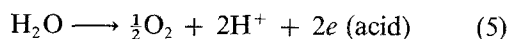
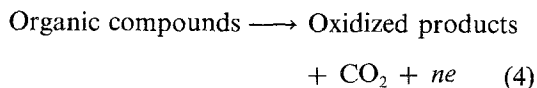


Fig. 2 shows the current–voltage relationship with the cell packed with glass spheres alone. The electrolysis began at above 1.5 V.

Fig. 3 shows the copper concentration and the pH in the catholyte, the EDTA concentration in the anolyte, and the cell voltage as a function of electrolysis time at a fixed current of 1 A. The

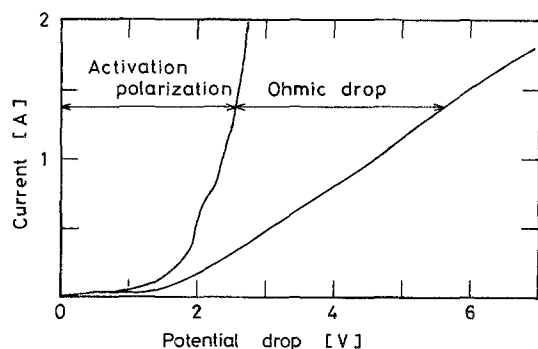


Fig. 2. Current–voltage relationship. Cathode and anode packings: glass beads alone. Catholyte: 0.005 M Cu-EDTA + 0.5 M Na<sub>2</sub>SO<sub>4</sub>, pH 3. Anolyte: 0.005 M Cu-EDTA + 0.5 M Na<sub>2</sub>SO<sub>4</sub>, pH 3. Scan speed 10 mV s<sup>-1</sup>.

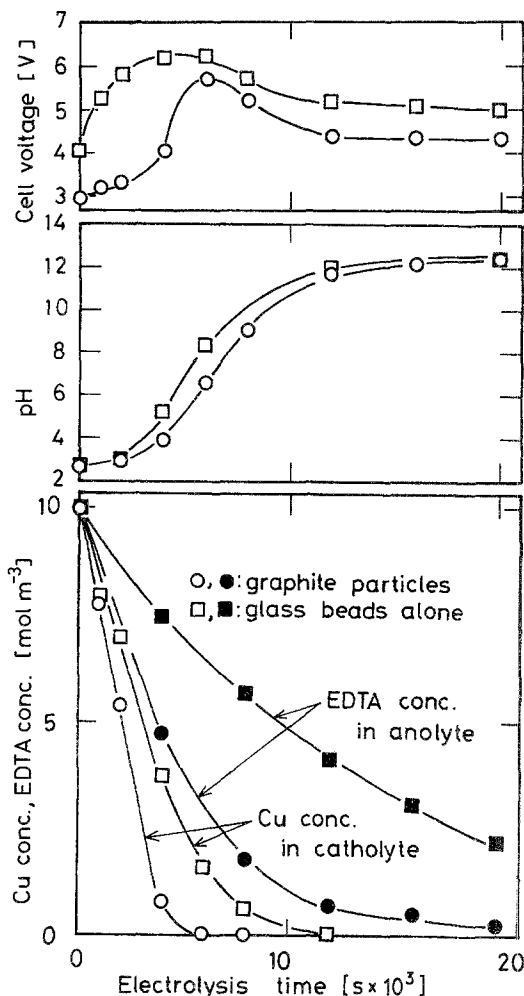


Fig. 3. Changes of cell voltage, pH and concentration of copper and EDTA with time. Cathode packings: glass beads alone or graphite particles. Catholyte: 0.01 M Cu-EDTA + 0.5 M Na<sub>2</sub>SO<sub>4</sub>, pH uncontrolled (pH 2.5–12.5). Anode packings: glass beads alone or Pt-Ti pellets. Anolyte: 0.01 M EDTA + 0.5 M Na<sub>2</sub>SO<sub>4</sub>, pH 3. Current, 1 A.

current efficiency for the recovery of copper and the elimination of COD increased with use of the packed-bed electrodes. Under galvanostatic conditions, use of the packings decreased the electrode potential and suppressed the side reactions 2 or 3 on the cathode and reactions 5 or 6 on the anode. The cell voltage with the packed-bed electrode cell was about 0.7–2.0 V lower than that with the feeder electrodes alone.

The increase in cell voltage in the initial stages of the electrolysis corresponds to the decrease in the copper concentration in the catholyte. The cathodic reaction changes from copper deposi-

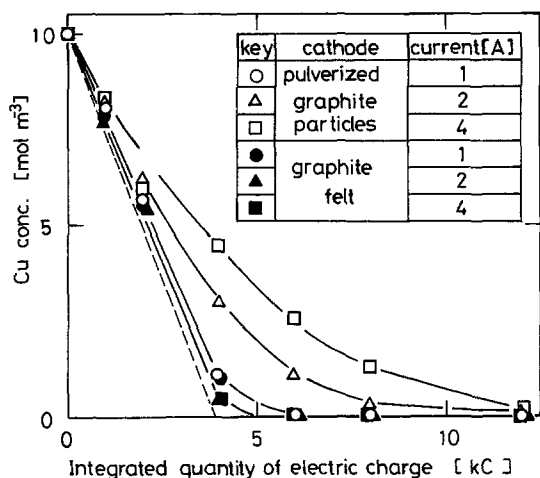


Fig. 4. Change of copper concentration with integrated quantity of electric charge. Cathode packings: graphite particles or graphite felt. Catholyte: 0.01 M Cu-EDTA + 0.5 M Na<sub>2</sub>SO<sub>4</sub>, pH uncontrolled. Anode packings: Pt-Ti pellets or oxidized lead spheres (in order). Anolyte: 0.01 M EDTA + 0.5 M Na<sub>2</sub>SO<sub>4</sub>, pH 3. The broken line indicates current efficiency of 100%.

tion to hydrogen evolution which occurs at a more negative potential. With hydrogen evolution, the conductivity of the catholyte increases rapidly due to the production of OH<sup>-</sup> ions, and the cell voltage decreases.

No permanent degradation of the membrane was observed in the experimental period. The ohmic resistance of the membrane was unchanged.

### 3.2. Recovery of copper

Fig. 4 shows the relationship between the copper concentration and the integrated quantity of electric charge. With the graphite felt cathode, the average current efficiency over 0–4 kC was about 90% at each electrolysis current of 1–4 A. With the graphite particle cathode, however, the current efficiency decreased with increasing cell current. The final attainable concentration of copper was 3 p.p.m. for both cathode materials. No change of EDTA concentration in the catholyte was observed during the electrolysis, thus indicating no electroreduction of EDTA.

### 3.3. Electro-oxidation of chelates

Fig. 5 shows the decreases of COD in the anolyte at pH 3. The initial value of COD in a

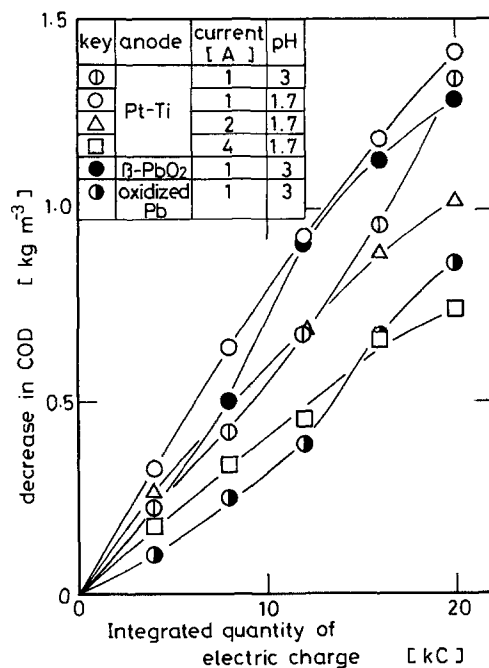


Fig. 5. Effects of anode materials and operating conditions on decrease in COD. Cathode packings: graphite particles for Pt-Ti pellets anode, graphite felt for β-PbO<sub>2</sub> particles or oxidized lead spheres anode. Catholyte: 0.01 M Cu-EDTA + 0.5 M Na<sub>2</sub>SO<sub>4</sub>. COD (initial) = 2.2 kg m<sup>-3</sup>.

0.01 M EDTA solution was 2.2 kg m<sup>-3</sup>. After the passage of 20 kC at a current of 1 A, the COD was lowered by about 60% with both the Pt-Ti pellets and the β-PbO<sub>2</sub> particles, and about 40% with the oxidized lead spheres. The electro-oxidation of EDTA proceeded more efficiently at lower current density.

Fig. 6 shows the effects of pH and complex formation on the removal efficiency of COD with the Pt-Ti pellets. The initial value of COD was 2.2 kg m<sup>-3</sup> for 0.01 M EDTA or Cu-EDTA solution. The removal efficiency of COD was not affected by the complex formation. The electro-oxidation of EDTA and Cu-EDTA took place more efficiently in the lower pH range. This can be explained on the basis of the voltage of oxygen evolution, which occurs at a higher anodic potential in acidic solution than in alkaline solution. When EDTA was electro-oxidized at pH 6, 36% of TOC were removed after the passage of 20 kC. IDA and glycine were found to be the main reaction products in the solution. The concentrations of NTA and oxalic acid were negligible.

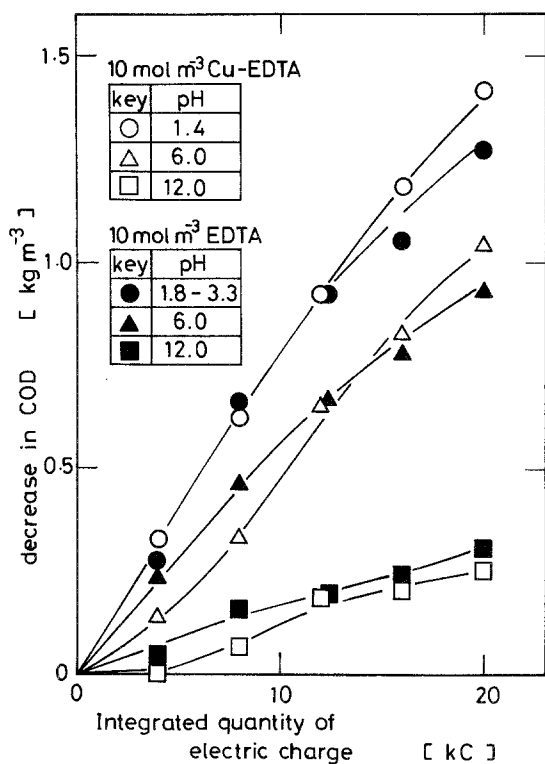


Fig. 6. Effects of pH and complex formation on decrease in COD. Cathode packings: graphite particles. Catholyte: 0.01M Cu-EDTA + 0.5M Na<sub>2</sub>SO<sub>4</sub>, pH uncontrolled. Anode packings: Pt-Ti pellets. Anolyte: 0.01 M EDTA or Cu-EDTA + 0.5M Na<sub>2</sub>SO<sub>4</sub>. COD (initial) = 2.2 kg m<sup>-3</sup>. Current, 1 A.

Fig. 7 shows the concentration change of EDTA, NTA, IDA and glycine with a current of 1 A. The electrolysis was carried out independently with each reactant whose initial concentration was 0.01 M. The concentration of NTA as well as EDTA was reduced below 0.001 M after the passage of 10 kC, while IDA and glycine were resistant to the electro-oxidation.

From the above results, the reaction schemes for EDTA are summarized in Fig. 8. Regardless of the pathways A and B, EDTA is oxidized to NTA, IDA, glycine and oxalic acid. The decomposition rates of NTA to IDA and of oxalic acid to CO<sub>2</sub> are relatively fast. The oxidation of EDTA also proceeds by radical mechanisms.

Fig. 7 also shows the change of COD. The current efficiency related to the elimination of COD,  $\eta_{\text{COD}}$ , is defined as follows.

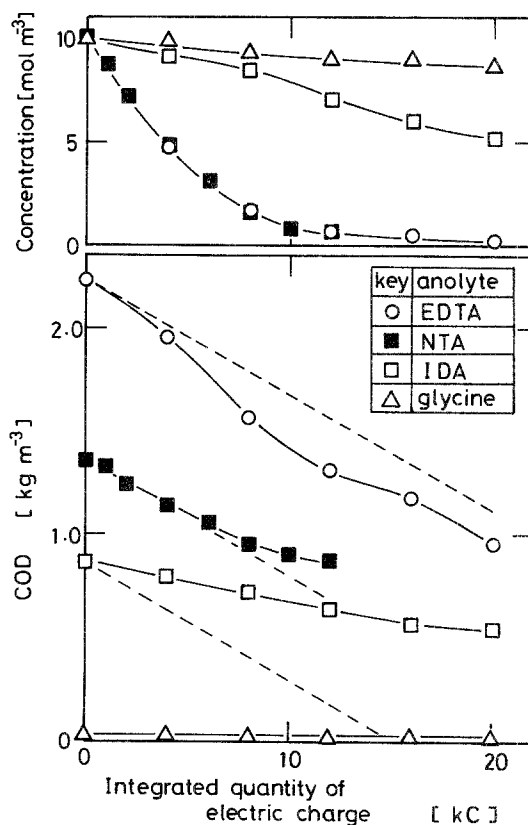


Fig. 7. Change of concentration and COD with integrated quantity of electric charge. Cathode packings: graphite particles. Catholyte: 0.01 M Cu-complex + 0.5M Na<sub>2</sub>SO<sub>4</sub>, pH uncontrolled. Anode packings: Pt-Ti pellets. Anolyte: 0.01 M chelating agent corresponding to catholyte + 0.5M Na<sub>2</sub>SO<sub>4</sub>, pH 3. Current, 1 A.

$$\eta_{\text{COD}} =$$

$$\frac{(\text{Decrease in COD}) (\text{Volume of solution})}{(\text{Mass of oxygen equivalent to electricity})}$$

$$= \frac{2F\Delta C_{\text{COD}}V}{16Q} \quad (7)$$

where  $F$  is Faraday's constant,  $\Delta C_{\text{COD}}$  is the decrease in COD mass concentration,  $V$  is the volume of solution, and  $Q$  is the quantity of electricity. The broken lines in Fig. 7 indicate  $\eta_{\text{COD}} = 1$ , while the average values of  $\eta_{\text{COD}}$  for EDTA, NTA and IDA were 1.4, 0.7 and 0.32, respectively, in the range 0–12 kC. Glycine is produced during the oxidation of EDTA, but is hardly detected by the KMnO<sub>4</sub> method as indicated in Table 1 and Fig. 7. This is the main reason why the value of  $\eta_{\text{COD}}$  for EDTA exceeds unity.

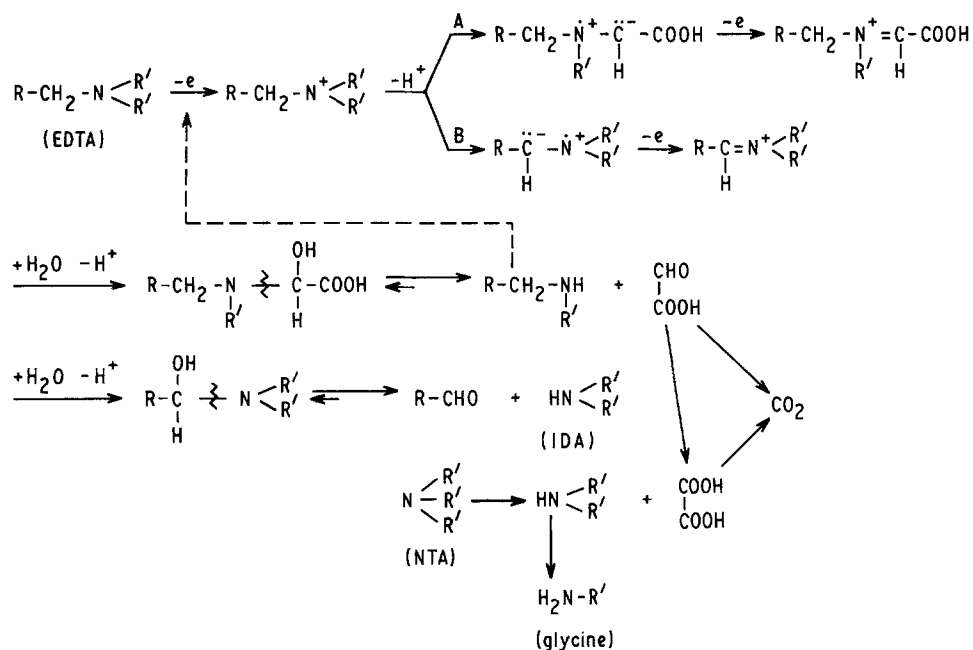


Fig. 8. Reaction schemes for electro-oxidation of EDTA.  $R \equiv -CH_2N(CH_2COOH)_2$ ,  $R' \equiv -CH_2COOH$ .

#### 4. Conclusion

Packed bed electrodes were successfully applied to the treatment of waste water containing both copper ions and chelating agents. Electrowinning of copper and the removal of COD were simultaneously achieved in the cathodic and anodic chamber, respectively. As cathode packing, the graphite felt was superior to the pulverized graphite particles because of the large surface area of the felt. The Pt-Ti pellets and the  $\beta$ -PbO<sub>2</sub> particles were comparable as anodic packings in their suitability for COD removal.

Table 1. Comparison between calculated and experimental COD values

	Calc. COD* (kg m <sup>-3</sup> )	Exp. COD† (kg m <sup>-3</sup> )	Exp. COD/ calc. COD
EDTA	2.72	2.20	0.81
NTA	1.44	1.35	0.94
IDA	0.96	0.86	0.90
Glycine	0.48	0.03	0.07

The initial concentration of each reagent is 0.01 M.

\* Amount of added oxygen theoretically needed in the reactions  $N \rightarrow NH_3$ ,  $H \rightarrow H_2O$  and  $C \rightarrow CO_2$ . Hydrogen and oxygen atoms originally contained in the organic substance should be preferentially consumed.

† KMnO<sub>4</sub> method (JIS K0101).

EDTA and NTA were oxidized with high current efficiencies, but IDA and glycine were resistant to the electro-oxidation.

The cell voltage of packed-bed electrode cells was 15–45% lower than that of a conventional flat plate cell.

#### Acknowledgements

Electrodes (Pt-Ti plates and Pt-Ti pellets) were provided by Permelec Electrode Ltd, Fujisawa, Japan. The authors gratefully acknowledge this support. They also thank Dr Makoto Takagi (Department of Organic Synthesis, Kyushu University), Dr Kazuaki Isomura (Laboratory for Waste Water Treatment, Kyushu University) and Mr Kazuhiko Hirao (Permelec Electrode Ltd) for helpful discussion.

#### References

- [1] R. M. Spearot and J. V. Peck, *Environ. Progress* **3** (1984) 124.
- [2] C. Lestrade, P. Y. Guyoma and M. Astruc, *Environ. Tech. Letters* **2** (1981) 409.
- [3] B. M. Kim and J. L. Weininger, *Environ. Progress* **1** (1982) 121.
- [4] D. W. Kirk and F. R. Foulkes, *J. Electrochem. Soc.* **131** (1984) 760.
- [5] B. G. Ateya, A. A. Ateya and M. E. El-Shakre, *J. Appl. Electrochem.* **14** (1984) 357.
- [6] D. Simonsson, *ibid.* **14** (1984) 595.