# Investigations on recovery of heavy metals from plating effluents

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The electroplating industry is one of the major industries, which generate a large amount of wastewater containing heavy metals. Even though chemical treatment processes are suitable for treatment of this kind of wastewater, the high concentration of heavy metals necessitates more treatment before discharge into natural resources, as heavy metals are important sources of environmental pollution and they can form compounds, which are toxic even in very low concentrations. The only way to remove the metals is to change their chemical states by oxidation/reduction and precipitation, and recover them in an acceptable form. In the present paper studies have been carried out by ethylenediaminetetraacetic acid complexation of effluents, using cyclic voltammetry.

Keywords: Recovery, Heavy metals, Effluents, Complexing, Cyclic voltammetry

## Introduction

Metals are used in a broad range of industrial processes and products. Because of toxicity of heavy metals, metal containing wastewater must be adequately treated. Measurement of effluents is a very important activity on the metal finishing industry and has become more vital with setting up of regulatory boards. Effluent treatment can be done using chemical and electrochemical methods.

Most of the effluents can be neutralised by chemical treatment. The main idea of chemical treatment is to remove the pollutants in the form as present in wastewater or by conversion into easily separable non-toxic material. The various chemical methods used are:

  (i)   coagulation
  (ii)  flocculation
  (iii) adsorption
  (iv)  neutralisation
  (v)   oxidation by chlorination
  (vi)  reduction and
  (vii) double decomposition.

The electrochemical methods are based on the known principles of electrochemical reactions, such as anodic oxidation, cathodic reduction and electrodeposition. The main advantages of electrochemical methods are that they do not add to the mineralisation of water and do not result in secondary pollution. Also there is no excess wastage of water, which is a significant factor, as many industries require large quantities of water. Sundaram has discussed on recycling a never ending source of metals.[1] The use of complexing agents such as ethylenediaminetetraacetic acid (EDTA) and NTA for effective ion exchange separation of Co (II)/Ni (II) from aqueous solutions has been studied by Juang and Wang.[2] An investigation on the removal of nickel from industrial process liquids has been carried by Koene et al.[3] Alternatives to the use of sodium dimethyldithiocarbamate for the removal of dissolved heavy metals from wastewater was suggested by Erven.[4]

It is known that chelating resins bind certain transitional metal ions such as $Cu^{2+}$, $Fe^{3+}$ very lightly but not lighter metals such as sodium, calcium and magnesium. Ethylenediaminetetraacetic acid forms stable, soluble, stochiometric 1 : 1 complexes with most metals, with some selectivity obtainable because of difference in stability constants (pH).

In order to understand the electroactivity of the compounds and associated chemical reactions, cyclic voltammetric studies were carried out on effluents obtained from process baths, with the aim of recovery and regeneration of plating chemicals, to maximise useful life, and to characterise the electrochemical system. In the present paper, results of cyclic voltammetric studies of plating effluents containing individually and in combination, common cations copper, nickel and zinc in the absence and presence of EDTA, and the surface morphology pictures of electrodeposits obtained from the effluents are presented.

## Experimental
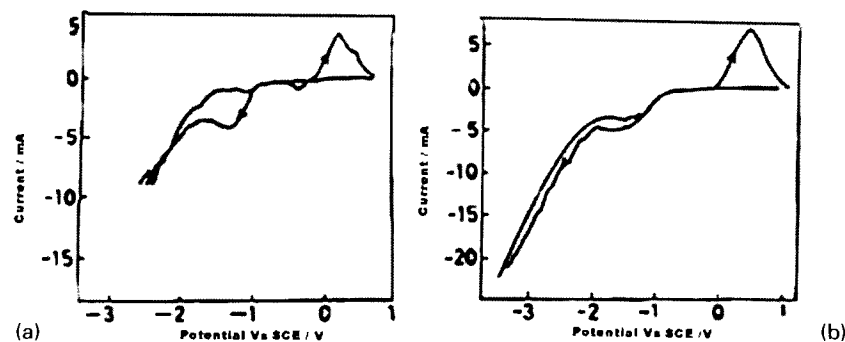
### Preparation of synthetic effluents

Table 1 gives the bath compositions and operating conditions of the plating solutions used. Synthetic effluents were prepared for these studies by diluting 2 mL of the respective plating baths to 100 mL using distilled water.
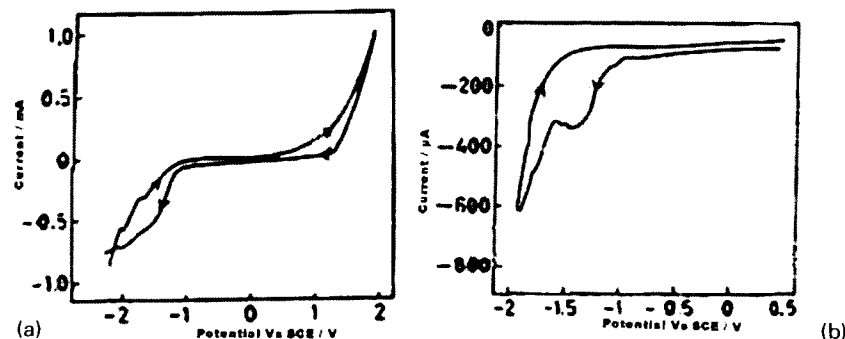
### Cyclic voltammetry

Cyclic voltammetry was carried out using the Thales Impedance Analyzer, using a conventional three electrode cell assembly comprising of glassy carbon ($0.2$ $cm^{-2}$) as the working electrode, platinum as the counter electrode and saturated calomel as the reference electrode. The temperature of the cell was kept at 30°C; the pH values of the solutions were adjusted using a digital pH meter ($\pm 0.1$ accuracy). A scan rate of 25 mV $s^{-1}$ was applied for all the studies.

### Surface morphology

Scanning electron microscopy (SEM) pictures of electrodeposits produced from synthetic effluents in

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**1 Cyclic voltammograms for** *a* **copper and** *b* **Cu+EDTA**



**2 Cyclic voltammograms for** *a* **nickel and** *b* **nickel+EDTA**

combinations of two metals from copper, nickel and zinc, in the absence and presence of EDTA, were taken using SEM Model Hitachi 3000H to study the nature of crystal growth.

## Results

### Electrochemical behaviour of copper effluent

Figure 1*a* presents the cyclic voltammograms obtained in Cu (II) ions solutions. When polarised from 1000 to −2500 mV, the forward scan exhibited zero current crossing potential (ZCCP) at 60 mV followed by the appearance of cathodic peaks at −340 and −1280 mV which was followed by hydrogen evolution. While reversing the scan the ZCCP was at −120m V and an anodic peak was seen at 240 mV.

Introduction of EDTA disodium salt modified the voltammogram. During the forward scan, ZCCP did not occur and a cathodic peak was seen at −1500 mV. While reversing the scan the ZCCP occurred at −120 mV and an anodic peak appeared at +500 mV (Fig. 1*b*).

### Electrochemical behaviour in nickel effluent

Figure 2*a* presents the cyclic voltammogram obtained in nickel (II) ions solutions. When polarised from 0 to

**Table 1 Compositions used for preparing synthetic effluents**

| Series No. | Plating bath | Constituents, g L⁻¹ | pH |
|---|---|---|---|
| 1 | Copper | $CuSO_4$: 200<br>$H_2SO_4$: 100 | 2·0 |
| 2 | Nickel | $NiSO_4$: 240<br>$NiCl_2$: 40<br>$H_3BO_3$: 30 | 4·8 |
| 3 | Zinc | $ZnSO_4$: 240<br>$CH_3COONa$: 30<br>$Al_2 (SO_4)_3$: 30 | 3·7 |

−2000 mV, the forward scan did not exhibit a ZCCP. A cathodic peak appeared at −1500 mV, which was followed by hydrogen evolution.

While reversing the scan the ZCCP was seen at +380 mV, and anodic peak appeared at −500 mV. Figure 2*b* shows the cyclic voltammogram with the introduction of EDTA. The electrochemical behaviour is modified. During the forward scan the appearance of cathodic peaks at −1400 and −1545 mV is seen. The reverse scan exhibited an anodic peak at −75 mV.

### Electrochemical behaviour in zinc effluent

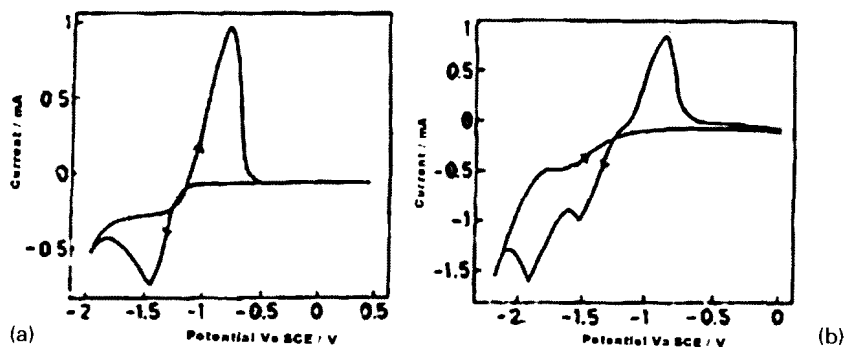Figure 3*a* presents the cyclic voltammograms obtained in Zn (II) ions solutions.

When polarised from 500 to −2000 mV, the forward scan exhibited no ZCCP. A cathodic peak was seen at −1460 mV. The reverse scan exhibited an anodic peak at −750 mV. Introduction of EDTA in the solution gave a cyclic voltammogram with ZCCP at −1350 mV followed by the appearance of a cathodic peak at −1550 mV (Fig. 3*b*). On reversing the scan, an anodic peak was seen at −950 mV.

### Electrochemical behaviour of copper, nickel and zinc present in combination in effluent
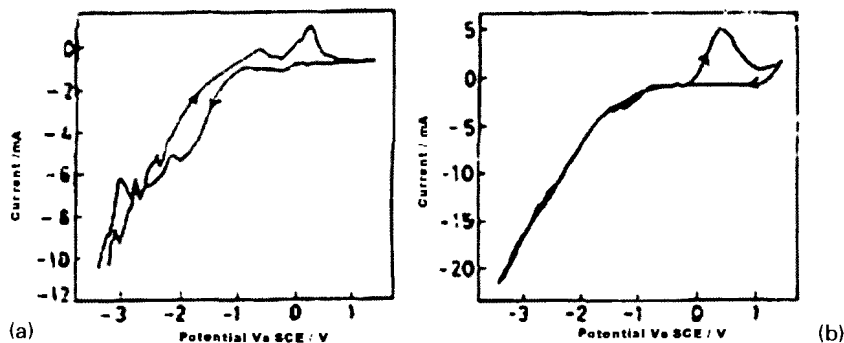
Figure 4*a* presents the cyclic voltammogram obtained in solutions containing 2 mL/100 mL of Cu, Ni and Zn ions. When polarised from +1000 to −3000 mV the forward scan exhibited no ZCCP. Cathodic peaks were seen at −2000 and at −2500 and −2800 mV. The reverse scan exhibited ZCCP at 100 mV, and anodic peaks at −700, −550 and +300 mV. Introduction of EDTA solution modified the spectrum slightly (Fig. 4*b*). The ZCCP occurred at −550 mV in the forward scan and a clear cathodic peak was exhibited at −1200 mV suggesting the reduction of the metal ion complex. The ZCCP in the reverse scan occurred at 0 mV and anodic peaks were observed at −700, −550 and −300 mV.

**3 Cyclic voltammograms for *a* zinc and *b* zinc + EDTA**



**4 Cyclic voltammograms for *a* copper + nickel + zinc and *b* copper + nickel + zinc + EDTA**

## Discussion

### Dissolution behaviour

The deposition reaction of copper is slow due to stabilisation on complex formation with EDTA, and the dissolution of the copper + EDTA complex is prominent. For the nickel effluent, during the scan in cathodic direction, the current rise at $-1\cdot2$ V is due to nickel deposition which is followed by hydrogen evolution. The wide separation of the peaks indicates that the reaction is irreversible.

In the presence of EDTA, in the case of nickel, the current is reduced. That means it has an adverse effect on the reaction and thereby, on the deposition. In the case of zinc, the reaction with EDTA is faster. In the case of the effluent containing all three metals, only copper is apparently deposited. The quantitative deposition seems to be less in this case, though it was the fastest among all the cases.

Table 2 summarises the parameters derived from cyclic voltammograms at scan rate 25 mV s$^{-1}$ for plain and EDTA complexed effluents.

Table 3 gives the ZCCP and anodic peak intersection potentials of the effluents.

The ZCCP, which is the corrosion potential of the metal film on the medium, varied with the metal complexes. Zinc had the tendency to form complexes more easily compared with nickel and copper. The more positive the value of ZCCP the less the tendency to dissolve. In presence of EDTA copper had the least tendency to dissolve. The first anodic peak was used for analysis. Extrapolation of the linear segment of the portion of the anodic peak to zero current would give the reversible potential of the metal/metal complex reaction. Zinc + EDTA complex had a value of $-1000$ mV, which is more active compared with $-250$ mV for nickel + EDTA and $-200$ mV for copper + EDTA. It is known that at potentials more positive than the reversible potentials, the metal will dissolve. In the solution containing Cu, Ni and Zn present in mixed form, the nickel + EDTA complex seems to be the more stable

one as is evident from the low anodic peak current (Fig. 4b). This was followed by Zn + EDTA, and lastly Cu + EDTA with respect to the stability.

### Surface morphology

Scanning electron micrographs obtained for copper–nickel, copper–zinc and zinc–nickel alloy deposits obtained from the synthetic effluents containing the respective two ions, in the absence and presence of EDTA are given in Fig. 5a–f. A non-uniform surface with pits can be seen in all of the three cations combinations in the absence of EDTA, whereas in the presence of EDTA relatively uniform distribution of particles with fewer clusters can be observed, with the particles merged together to form larger clusters. The porosity is also reduced and the particle sizes are smaller in the latter case. Ethylenediaminetetraacetic acid helps to produce a smooth surface by refining the grains.

### Conclusions

In the case of the copper effluent, with the addition of EDTA the cathodic peak shifts to a more negative value,

**Table 2 Parameters derived from cyclic voltammograms at scan rate 25 mV s$^{-1}$**

| Metal | $E_{p,c}$, mV | $I_{p,c}$, mA | $E_{p,a}$, mV | $I_{p,a}$, mA |
|---|---|---|---|---|
|  | $-320$ | $-100$ |  |  |
| Copper | $-1280$ | $-430$ | $+240$ | $+350$ |
| Cu/EDTA | $-1500$ | $-550$ | $+500$ | $+660$ |
| Nickel | $-1500$ | $-500$ | $-600$ | 25 |
| Ni/EDTA | $-1545$ | $-330$ | $-75$ | $-50$ µA |
| Zinc | $-1460$ | $-780$ | $-750$ | 925 |
| Zn/EDTA | $-1525$ | $-1000$ | $-975$ | 88 |
|  | $-2000$ | 540 | $-760$ | $-580$ |
| Cu + Ni + Zn | $-2500$ | 660 | $-670$ | $-400$ |
|  | $-2800$ | 760 | $+300$ | $+100$ |
|  |  |  | $-700$ | 0 |
| Cu + Ni + Zn/EDTA | $-1200$ | $-350$ | $-550$ | 0 |
|  |  |  | $-300$ | 0 |
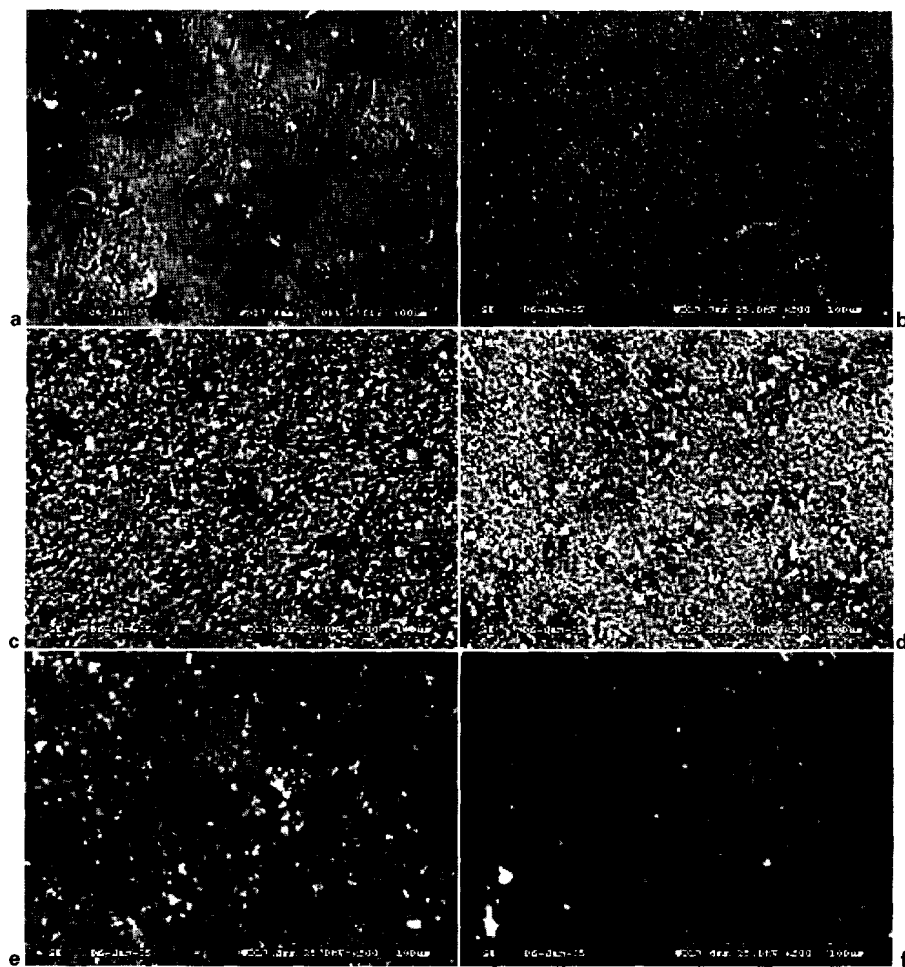
*a* Cu and Ni; *b* Cu and Ni, in presence of EDTA; *c* Cu and Zn; *d* Cu and Zn, in presence of EDTA; *e* Zn and Ni; *f* Zn and Ni, in presence of EDTA

**5 Scanning electron micrographs of deposits obtained from synthetic effluents**

**Table 3 Zero current crossing potential and anodic peak potential, mV**

| | Without EDTA | | With EDTA | |
|---|---|---|---|---|
| Metal | ZCCP | First anodic peak intersection potential | ZCCP | First anodic peak intersection potential |
| Copper | −120 | −50 | −120 | +30 |
| Nickel | +380 | −250 | – | −150 |
| Zinc | −1150 | −1100 | −1350 | −1150 |
| Cu+Ni+Zn | +100 | +100 | 0 | +200 |

indicating that deposition is favoured. The two peaks that appeared in the EDTA free effluent appear very close together. Beyond −1900 mV there is hydrogen evolution. The two anodic peaks appearing at +240 and +500 mV are seen to have been merged into a single peak at +500 mV in the effluent containing EDTA.

In the case of the nickel effluent, deposition is seen clearly favoured in the presence of EDTA and the anodic peak potentials also shifting to more positive values indicate that dissolution of nickel is facilitated.

As for the zinc effluent with EDTA, deposition is favoured as indicated by the $E_{p,c}$ becoming active, but dissolution is slightly hindered. For effluent containing copper, nickel and zinc in combination complexed with EDTA, the dissolution of copper is apparently predominant. Of all the metals zinc dissolves most with

lowest ZCCP and most negative anodic potential when complexed with EDTA solutions. Further investigations will have to be carried out at narrow range of potentials to get information on the deposition of specific metals from the effluents.

Scanning electron microscope studies on these deposits showed that the presence of the complexant EDTA in the effluent favoured the formation of uniform crystallites covering the surface.

# References

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