REMOVAL OF COPPER FROM DILUTE STREAMS – EFFECT OF INDUCED ROUGHNESS ON ROTATING CYLINDER ELECTRODE

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ABSTRACT

As part of the programme on removal/recovery of toxic and valuable metals from dilute solutions, the removal of copper has been studied using a rotating cylinder electrode. Amongst the techniques like fluidised bed electrode, porous flow through electrode etc. rotating cylinder electrode is simpler in that it offers a high mass transfer at low speeds caused by increased turbulence and is adaptable in a cascade system for continuous usage.

Use of a rotating cylinder electrode with induced roughness caused by a wire mesh wrapped round the cathode has been investigated for removal of copper from solutions of concentrations 100 ppm and less. The results obtained bring out the effects of current density, rotation rate, temperature and surface roughness on the removal of copper. The benefits of increased surface roughness are shown as increased current efficiency and possibility of reducing the copper concentration down to 1 ppm.

Key words: Rotating cylinder electrode, induced roughness, copper removal, dilute streams of solutions

INTRODUCTION

The importance of removal of heavy metal ions from waste waters of metal finishing industry has been appreciated in recent times. The worldwide concern in this regard is seen from the attempts to evolve suitable techniques to reduce the metallic content of effluents to safe levels. Though a variety of chemical and physical methods like hydroxide and sulphide precipitation, ion exchange and reverse osmosis are available, electrochemical method has the unique advantage of enabling the recovery of the constituents in metallic form. Among the electrochemical procedures, the rotating cylinder electrode is attractive from the following considerations. It is capable of giving high mass transfer rates at low rotation speeds, equipotential conditions on the surface enabling potentiostatic control, relatively simple design and adaptability of continuous cascade mode of operation. Though the principle of rotating electrode is well known, the improvement of its performance is presently engaging attention of electrochemists. One way of achieving this is by inducing roughness on the cylindrical surface. In the present work, removal of copper from solutions of 100 to 1000 ppm concentration was investigated making use of rotating cylinder electrode with roughness caused by wrapping wire mesh round the electrode.

EXPERIMENTAL

The rotating cylinder electrode (RCE) reactor consisted of a stainless steel sleeve fitted tighly over a PVC cylinder which in turn was attached to a centrally located PVC shaft. The PVC shaft was coupled to a metallic (brass) shaft mounted vertically on bearings. The metal shaft was driven by means of a variable speed motor. The speed of rotation was monitored by the use of magnetic pick up RPM counter. Mercury contact was used for d.c. electrical connection to the metal shaft and the S.S. cylinder electrode was connected by an external strip. S.S. wire meshes of 8 (0.7 mm wire dia), 12 (0.53 mm) and 20 (0.25 mm) sizes were used to induce roughness. The RCE was placed in a container of 5 litre volume with a cylindrical anode made of lead silver alloy fixed to the wall of the container. Baffle strips were attached to the inner side of the anode. The RCE used in all experiments was 10 cm dia and 13 cm ht. Three litres of solution were used in each experiment. The results are based on galvanostatic studies carried out with a rectifier of 20 amp, the current being controlled through appropriate resistance. The quantum of metal removal was computed from analysing the solution using atomic absorption spectrophotometer. The deposit of copper was dissolved chemically and fresh S.S. surface was made available for each experiment.

RESULTS AND DISCUSSION

In the initial experiments, removal of copper was done starting from 1000 ppm till a concentration of 1 ppm is reached, splitting the range into four stages viz. 1000-500, 500-100, 100-50 and 50-1 ppm. The influence of apparent current density was found separately for each stage and is shown in fig. 1. The fall in efficiency with current density is very steep for the low concentration range showing that the limiting current density is exceeded.

The increased rate of rotation normally gives rise to increased turbulence, leading to higher mass transfer. The performance of the reactor with rotational speeds up to 400 rpm corresponding to a linear velocity of 210 cm sec^{-1} is shown in fig. 2.

The effect of surface roughness was investigated by varying the size of the mesh and the performance compared with that of smooth cylinder mechanically and electrochemically polished. The surface roughness is given as the ratio of the diameter of cylinder to the height of the protruding surface (d/ε). A threefold increase in current efficiency was observed between smooth cylinder and that wrapped with 20 mesh. Further improvement could not be obtained by the use of meshes with greater wire diameter and hence greater roughness.

It has been shown [1-3] that the deposit on to an RCE with solutions less than 1 gm dm^{-3}, becomes powdery with passage of time resulting in an increased surface area as well as roughness. The increase of the limiting current (i_L) was found to be almost tenfold [3] for a constant concentration and 3 to 4 times [4] for declining concentration. Just as the increased rate of rotation brings about an enhancement of mass transfer, surface roughness also helps in the same way by providing greater hydrodynamic shear at the electrode. Hence in the case of RCE, the surface roughness developed due to powdery deposit is an additional benefit for increasing the limiting current which is essential for working with dilute solutions. However, in case of continued metal deposition or starting with initially rough surface, the active surface area is naturally higher than in smooth cylinder. Hence enhancement of mass transfer in such cases is due both to an increase in
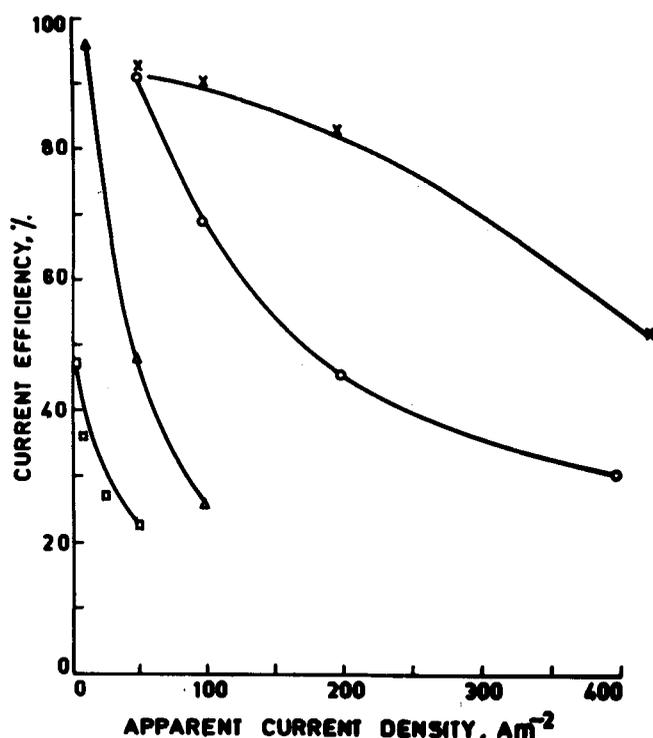
Fig. 1 : Current efficiency as a function of current density for various concentration
ranges: Copper concentration (mg dm^{-3}) : —

-X-1000-500 ; -0-500-100 ; -Δ-100-50 ; -□-.50-1

Conditions : 0.5 M H$_2$SO$_4$; 100 rpm ;

Cylinder diameter : 10 cm ; Mesh employed : 12
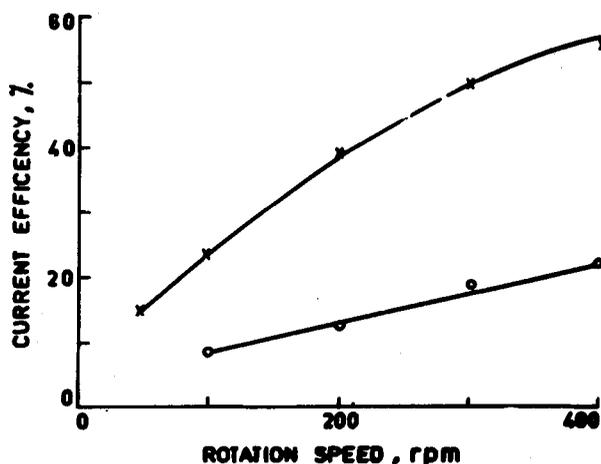
Fig. 2 : Current efficiency as a function of rotational velocity for smooth and rough
cylinders : Copper concentration : 100 mg dm^{-3}

0.5 M H$_2$SO$_4$; Apparent current density : 100 Am^{-2} ;

Cylinder diameter : 10 cm ; -0- Smooth ; -X- Rough ; Mesh employed : 12

active area and improved turbulence due to rough surface. The relation
between the limiting current enhancement and speed of rotation in the form
of a power law has been proposed [2] in which the effect of roughness is
introduced as a variable power of the speed.

$$I_L = KCU^x$$

where

I_L = limiting current

C = concentration of metal ion

U = Linear velocity of RCE

Index x = 0.7 for smooth cylinder

x = 0.9 for rough cylinder

The intermediate values between 0.7 and 0.9 for 'x' are for varying
degrees of roughness which is given by the ratio of the diameter of RCE to
the fin height. Machined knurled cylinders have been used [4] to give
different roughness (d/ε) since the roughness induced by powdery deposit of
metal could not be characterised. The limiting current was found to increase
as the (d/ε) value decreases, which was confirmed with two different sizes of
cylinders.

In the present study, the roughness factor is varied by wrapping the
RCE with meshes having different wire thickness. The results of current
efficiency are presented in Table I.

Table I : Effect of surface roughness on current efficiency

Cu^{++} 100 mg dm^{-3} C.D. 100 A.m^{-2} Duration : 8 min

H$_2$SO$_4$ 50 g dm^{-3} RPM 100   Amp-hrs 0.5

S. No.	Nature of surface roughness	d/ε	Final copper concentration (mg dm^{-3})	Current efficiency (%)
1.	Mechanically polished cylinder	...	83	8
2.	Electropolished cylinder	...	83	8
3.	Cylinder with 20 mesh	400	37	30
4.	Cylinder with 12 mesh	189	37	29
5.	Cylinder with 8 mesh	143	41	28

Though the apparent area of mesh wrapped RCE could show an increase as
the mesh size is reduced from 8 to 20, the current efficiency does not
improve. As regards the roughness, it decreases as the mesh size is reduced
owing to the lesser thickness of the wire. This indicates that the contribution
for the improved performance of RCE with induced roughness is probably
more due to increased roughness than to increased surface area of the
electrode. However, this needs further investigation. The absence of
improvement with reduced mesh size (8-20 mesh) for which roughness is
higher, shows that the saturated roughness could have been reached or the
current density has already exceeded the limiting current as seen from the
simultaneous hydrogen evolution.

The concentration decay of copper in the solution was obtained for
different rotation rates and is shown in figs. 3a and 3b for initial
concentration of 100 and 50 ppm respectively. An experimental fall of
concentration obeying the following first order rate law is observed :

$$C_t = Co \exp^{(-kt)}$$

$$k - \text{First order rate constant} = \frac{K_L A}{V_R}$$

where

K_L = mass transfer coefficient, A = active surface area, V_R = reactor
volume. The rate of decay shows an increase as the mass transfer coefficient
increases as seen from Table II.

The increase of temperature of electrolysis was found to be beneficial as
shown in fig. 4. The fluid properties are altered at high temperatures leading
to higher mass transfer coefficient.

With a view to effect additional improvement, the RCE was fitted with
an integral stirrer at the bottom so as to create circulatory motion of the
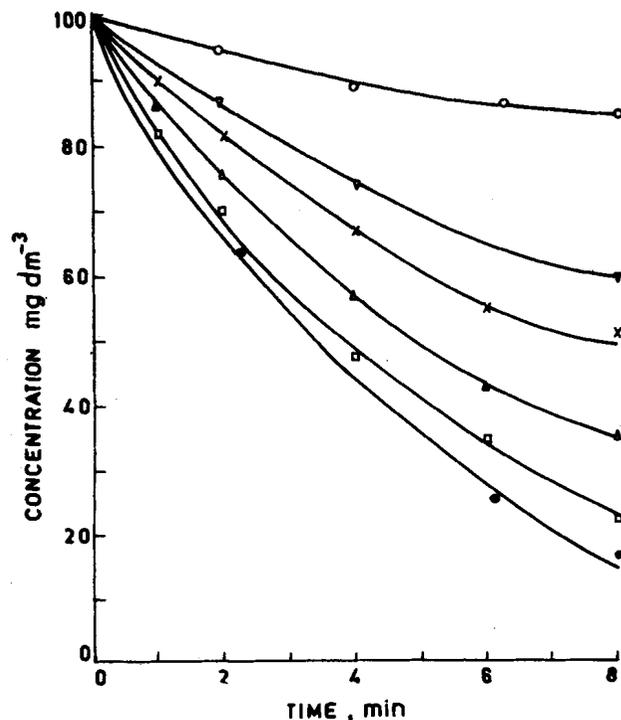
Fig. 3a.: Concentration decay for various rotational velocity with rough cylinder

Copper concentration $100 \, mg \, dm^{-3}$; Apparent C.D. $100 \, Am^{-2}$; $0.5 \, M \, H_2SO_4$; Cylinder dia. 10 cm; Mesh employed: 12; Rotational velocity (rpm): -0-100 (smooth); $-\nabla$-400 (Smo⌣.h); -X-100 (Rough); -Δ-200 (Rough) □-300 (Rough); -0-400 (Rough)

Table II: Variation of mass transfer coefficient with rotation

Conditions same as in Table I except rpm of RCE

S. No.	Rotation speed (rpm)	Rate constant 'k' $sec^{-1} \times 10^{-3}$	Mass transfer $K_L \, cm \, sec.^{-1} \times 10^{-2}$
1.	100	1.688	1.24
2.	200	2.33	1.72
3.	300	3.11	2.34
4.	400	3.64	2.73

Table III: Influence of additional agitation measures on current efficiency

Conditions same as in Table I except the mesh employed 12 mesh

S. No.	Stirring condition	Final concentration $(mg \, dm^{-3})$	Current efficiency (%)
1.	Rotation alone	60	26
2.	Rotation with integral stirrer	56	26
3.	Rotation with air agitation	52	24

liquid in addition to the shear due to rotation. This was not found to yield any improvement though the agitation of the liquid in the cell was visually observed to be appreciably greater (Table III).
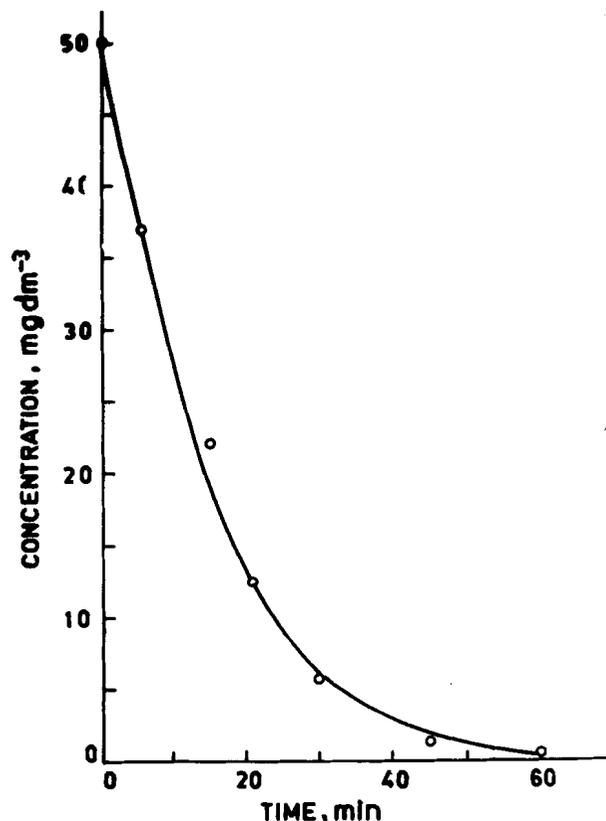
Fig. 3b: Concentration decay with rough cylinder: Copper concentration: $50 \, mg \, dm^{-3}$ $0.5 \, M \, H_2SO_4$; 100 rpm; Apparent C.D: $100 \, Am^{-2}$ Cylinder diameter: 10 cm; Mesh employed: 12

By combining axial flow of solution with rotation of RCE it has been reported [5] that axial flow does not result in further enhancement of mass transfer. Also superimposing air agitation in the bulk of the liquid along with rotation of cathode was not found to give any additional benefit. These observations show that the hydro-dynamic conditions prevailing at the interface between the liquid and the moving surface of RCE is influenced very little by external agitation whereas roughness to the extent of $(d/\varepsilon)400$ could bring about a marked improvement in the limiting current and hence the current efficiency.

The distribution of current between the cylinder and the mesh was found from the quantity of metal deposited for different apparent current densities taking into account the geometrical area of cylinder alone. The results are given in Table IV. As the current density is increased the share of current taken up by the mesh increases till a maximum is reached and remains the same thereafter.

Table IV: Distribution of current between cylinder and mesh

Conditions same as in Table 1 except current density

S. No.	Apparent current density $(A.m^{-2})$	% of copper deposited on cylinder	% of copper deposited on mesh
1.	25	57	43
2.	50	45	55
3.	200	33	67
4.	300	35	65

RESULTS AND DISCUSSIONS

The variation of photosensitivity with time is well brought out in the figure 4. Although various percentages of addition of CdSO$_4$ to the sensitized powder were tried, the addition of 2% and 3% of CdSO$_4$ gave R$_D$/R$_L$ values in the useful range (since the CdS required for photovoltaic work should not only have a low-resistance but R$_D$/R$_L$ value tending to 1). As is shown in the figure the sensitivity is maximum for 40 minutes sintering time for 2% CdSO$_4$ as well as 3% CdSO$_4$. During sintering, the cadmium chloride melts at 585°C and CdS dissolves in the molten cadmium chloride to initiate recrystallisation. Beyond optimized time and temperature, CdCl$_2$ volatilizes away.
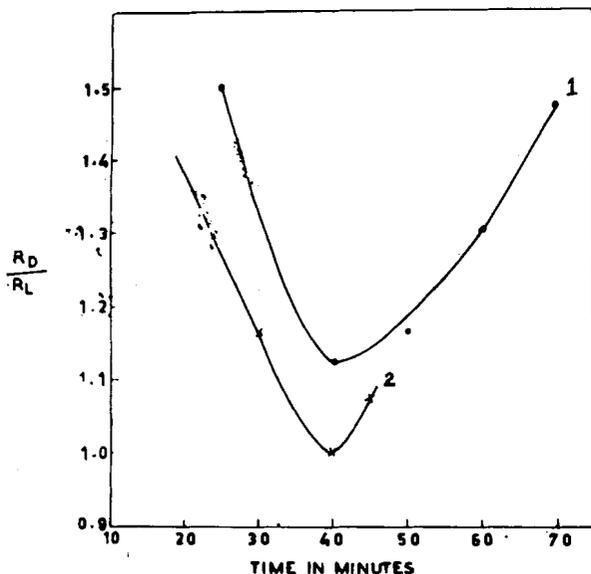
Fig. 4: Effect of sintering on CdS layer resistance:

1) 2% CdSO$_4$ and 2) 3% CdSO$_4$

Effect of cadmium sulphate on the resistance of CdS

The addition of CdSO$_4$ brings about an increase in Cd^{++}/S^{--} ratio as revealed by the reactions

$$CdS + CdSO_4 \rightarrow 2Cd^{++} + 2SO_2\uparrow$$

$$(1-x)\,CdS + xCd^{++} \rightarrow CdS_{1-x}$$
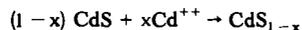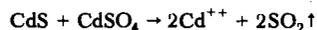
CdS reacts with CdSO$_4$ to form more Cd^{++} ions and the evolution of SO$_2$ from the lattice creates more sulphur vacancy. As a result, Cd^{++}/S^{--} ratio increases which is reponsible for the lower resistance of the layer. Above 3%, CdSO$_4$ remains as such in the lattice and this being an insulator does increase the resistance. Below 3% CdSO$_4$ sufficient Cd^{++}/S^{--} ratio is not built for want of CdSO$_4$. Hence the high resistance.

Role of cadmium chloride

Figure 4 shows a decrease in the values of R$_d$/R$_L$ with time up to 40 minutes and then a rise, which is due to the fact that more and more chloride ions are getting incorporated into the lattice giving rise to more donor levels. Above the sintering time of 40 minutes, more and more of chloride ions begin to get out of the lattice gradually thereby decreasing the donor concentration.

Even though Mo substrate is the best choice with spherical grain structure for maximum efficiency [11] followed by stainless steel substrate, the cost, short circuiting and peeling-off of the layers after Cu$_2$S formation are the unfavourable factors, when low cost cells with reasonable conversion efficiency are aimed.

The V$_{oc}$ and I$_{sc}$ of the final cell with varied parameters are given in Table I.

Table I: Properties of Cu$_2$S—CdS Solar cells

Cell No.	Deposition time (sec)	Sheet resistance of Cu$_{2-x}$S (ohms per sq.)	Time of heat treatment (minutes)	V$_{oc}$ (mV)	I$_{sc}$ (mA/cm^2)
1	10	120	5	397	0.60
37	5	140	10	425	1.17
61	10	160	12	240	2.50
62	10	200	14	370	6.00
64	10	140	15	340	1.78

Maximum I$_{sc}$ was obtained for the cell No. 62 whose Cu$_2$S sheet resistance is maximum. When the post heat-treatment time was increased from 5 to 14 minutes, the Cu$_2$S sheet resistance also increased from 120 ohms to 200 ohms/square. This may be due to the diffusion of cadmium ions into the Cu$_2$S lattice. The Cu$_2$S being p-type, cadmium ion entering the lattice as donors brings about an increase in resistance [2]. However, the resistance decreases when post heat treatment time exceeds 14 minutes. This may perhaps be attributed to the number of copper ions entering the CdS lattice exceeding the number of cadmium ions entering the Cu$_2$S lattice. Thus a post heat treatment of 14 minutes tends to form the chalcocite phase of the Cu$_2$S layer which absorbs most of the incident solar radiation [13] for current generation. Also a recent work [14] on the physicochemical properties confirms the observation that the resistivity is more when the Cu content in the Cu$_x$S layer increases and is maximum for Cu$_2$S.

CONCLUSION

The addition of 3% CdSO$_4$ is necessary to obtain low-resistance, sintered CdS layers and thereby increasing the cell output.

Further investigations are being continued to increase the sheet resistance of the cuprous sulphide layer and optimize the conditions for chalcocite (near Cu$_2$S) formation for getting maximum output.

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