

**ROTATING CYLINDRICAL ELECTRODE REACTOR FOR CONTINUOUS COPPER REMOVAL***V NANDAKUMAR, P ADAIKKALAM, J A M ABDUL DADER and R SRINIVASAN*

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Rotating cylindrical electrode reactor has been employed as a continuously stirred tank reactor for the removal of copper from dilute solutions. The mass transfer performance is enhanced by the use of mesh wound over the cylinder. The operation of the reactor in a batchwise manner treating a fixed volume of the metal bearing solution and with continuous flow of solution through the reactor is described. The average rate of removal in batchwise as well as continuous processing is arrived at. The overall efficiency of metal removal is higher for stagewise cascading operation than for one step removal.

**Key words:** Copper removal, lean solution, rotating cylindrical electrode reactor

**INTRODUCTION**

The rotating cylindrical electrode (RCE) enjoys the unique advantage of achieving high mass transfer rate with minimum of complexity in design. It has uniform mass transport over the entire surface area of the electrode. The steady increase of mass transport rate with rotational speed is an added advantage. Commercial sized units employing rotating cylindrical electrodes are stated to be available for precious metal recovery from process solutions and in effluent treatment for toxic metals. Though the concept of RCE is sufficiently old, improvements in its performance have been recently proposed by inducing roughness over the cylindrical surface [1-3]. The theory of the RCE in respect of its use as an electrochemical reactor has been refined in recent years. The RCE reactor is essentially a backmix or stirred tank type. It can be operated in batchwise or continuous mode for metal removal adopting single step or multiple stages to effect the desired degree of removal. The present investigation compares the two modes of operation for the case of copper removal from 100 ppm to about 1 ppm.

**EXPERIMENTAL**

The rotating cylindrical electrode reactor consisted of a stainless steel sleeve fitted tightly over a PVC cylinder which was rotated by means of a metal shaft driven by a variable speed motor. Mercury contact was used for d.c. electrical connection. The surface of the cylinder was made rough by wrapping with a single layer of s.s. mesh (20). The RCE was placed in a container of 5 litre volume with a concentric anode made of lead silver alloy. The electrode measured 9.5 cm in diameter and 14 cm in height. In case of batchwise mode of operation, the volume of the solution taken in the cell alone constituted the reactor volume and the electrolysis was continued till the required removal had taken place. The solution was continuously passed through the cell at constant rate, feeding at the bottom and removing from the top in the case of continuous mode of operation. Atomic Absorption Spectrometer

was used for analysis of metal concentration. The deposit of copper was dissolved chemically and fresh s.s. surface was made available for each experiment.

**RESULTS AND DISCUSSIONS****Mass transport studies**

Mass transport measurements were initially done by potentiostatic and potentiodynamic polarisation studies. The polarisation curves obtained did not show a clearly defined plateau for limiting current. The current was steadily rising by the increase of potential and the inflection to show limiting behaviour was not observed. The difficulty of finding out mass transfer coefficient by limiting current measurement with as low a concentration as 100 ppm has been experienced [4]. Considering the RCE reactor as a backmix type under batch conditions, the variation of concentration with time was found to be useful in the estimation of mass transfer coefficient. The variation of concentration with time is given by,

$$C_t = C_o \exp (-K_m At/V) \quad \dots\dots (1)$$

From the slope of the plot of  $\ln (C_o/C_t)$  with time, mass transfer coefficient ( $K_m$ ) is computed. The electrode needs to be operated at limiting current throughout the period, in order that equation (1) is applicable. This implies that the applied current has to be continuously reduced in order that the electrode is always at limiting current. As an approximation, constant potential was applied to obtain the concentration decay history. Potentials from -300 mV to -700 mV with respect to SCE were tried to get the maximum mass transfer coefficient from the relation (1). The variation of concentration decay with the applied potential is shown in Fig. 1. Here it is essential that the potential selected does not lead to hydrogen evolution which will enhance the mass transport rate by creating further turbulence near the electrode surface. The onset

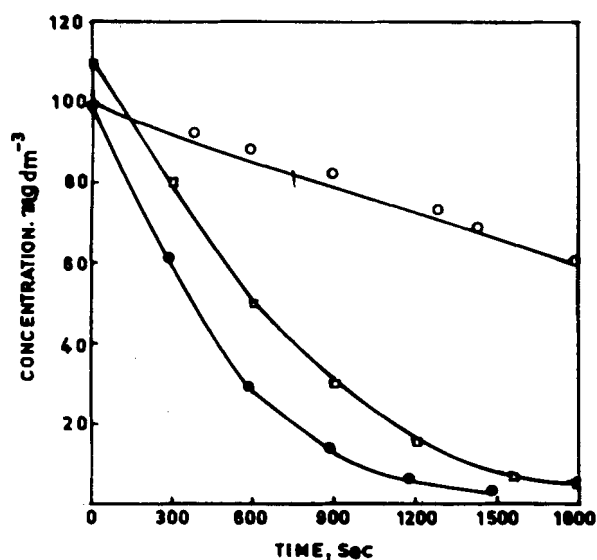


Fig. 1. Concentration decay with different cathode potentials - ● - 300; - □ - 500; - ○ - 700 (mV vs SCE)  
 Conditions : 20 gdm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>; Rotation rate : 400 rpm;  
 Cylinder diameter : 9.5 cm; Reactor volume : 4.5 dm<sup>3</sup>;  
 Temperature : 30°C

of hydrogen evolution is indicated by the more or less steady value of current which will otherwise be falling exponentially if the discharge of metal ion is the only reaction taking place. A potential of -500 mV was found to yield the maximum mass transfer and at the same time without allowing hydrogen to evolve. The mass transfer coefficient as found above was made use of for studies involving the use of RCE as electrochemical reactors.

**DEVELOPMENT OF RCE REACTOR**

**Stirred tank batch reactor**

The RCE reactor can be operated in the batch or continuous mode for practical cases of metal removal. In case of batch operation, a definite volume was taken in the reactor and electrolysis was continued till the desired removal was obtained. Table I shows the performance of the reactor in batch mode at constant current density.

Table I: Data for batch RCE reactor (single stage)  
 Rotation rate : 400 rpm; Temperature : 30°C  
 Reactor volume : 4.5 dm<sup>3</sup>  
 Constant current density : 45 A/m<sup>2</sup>; H<sub>2</sub>SO<sub>4</sub> : 20 gdm<sup>-3</sup>

Time (sec.)	Concentration (mgdm <sup>-3</sup> )	Fractional removal	Current efficiency (%)	Overall space time yield (g hr <sup>-1</sup> dm <sup>-3</sup> )
0	102	0.69	69	
720	33	0.81	59	
1005	19	0.81	59	
1260	12	0.88	51	0.23
1400	10	0.90	48	

Because of the declining concentration of metal ion, the reactor would not be operating at the limiting current. Hence for operating the reactor at limiting current (at which value the current efficiency could be maintained at the maximum), current though the cell has to be reduced continuously. An alternative approach is to accomplish the removal in stages whereby the current value is also reduced in stages. This will enable the individual stages to operate close to limiting current which helps to get maximum current utilisation and a good nature of the metallic deposit as well. The number of stages has to be limited by economic consideration of the investment as well as practical convenience. Also, while an increase in the number of stages is brought about, the condition approaches that prevailing in a plug flow reactor which always results in a higher throughput because of the absence of back mixing.

In the present investigation, removal of copper from 100 ppm to about 1 ppm was done in five stages aiming a fractional removal of 0.6 in each stage. The advantage in effecting the removal in multiple stages can be seen in terms of overall increase in current efficiency (Table II).

Table II: Data for batch RCE reactor (Multiple stages)

Rotation rate : 400 rpm; Temperature : 30°C  
 Reactor volume : 4.5 dm<sup>3</sup>; Duration of each stage : 7 minutes;  
 H<sub>2</sub>SO<sub>4</sub> : 20 gdm<sup>-3</sup>

Stage	Initial copper concentration (mgdm <sup>-3</sup> )	Final copper concentration (mgdm <sup>-3</sup> )	Current density (Am <sup>-2</sup> )	Fractional removal	Current efficiency (%)	Overall space time yield (g hr <sup>-1</sup> dm <sup>-3</sup> )
I	102	43	45	0.58	100	
II	42	16	18	0.61	100	
III	16.5	10.7	7	0.35	65	0.170
IV	7.0	4.9	2.9	0.30	57	
V	2.9	2.6	1.1	0.10	21	

In every stage, the nature of deposit was maintained good by this approach. However, the expected removal was not observed at low concentration ranges. This is probably due to the redissolution of finely divided deposit of metal which may be facilitated by the oxygen evolving at the anode and getting dissolved in the electrolyte.

However, in order to effect the removal down to 1 ppm, applied current density was increased to 2 to 3 times of limiting current for concentration less than 15 ppm. At such high current densities, the accompanying gas evolution results in further enhancement of mass transport. The results are represented in Fig.2. It can be seen that the limit of 1 ppm could be realised by this approach. The nature of deposit need not be of much concern here because the quantum of metal available at such low concentrations will obviously be low.

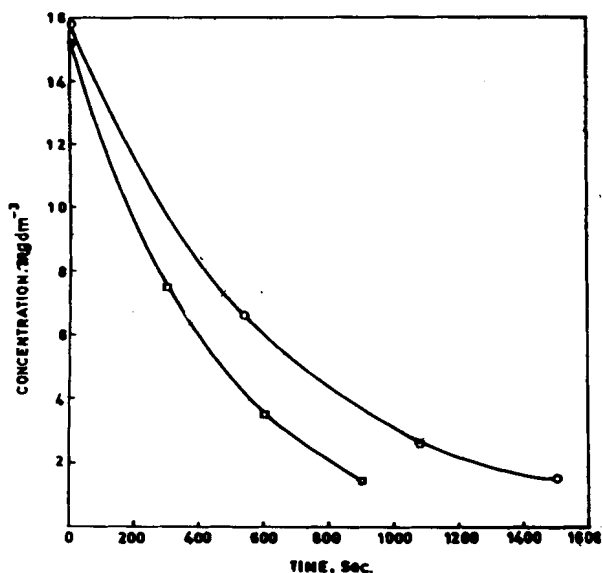


Fig.2: Concentration decay at low concentration with high current densities. - O - 13.6; - □ - 20.4 (Am<sup>-2</sup>); Conditions : 20 gdm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>; Rotation rate : 400 rpm; Cylinder diameter : 9.5 cm; Reactor volume: 4.5 dm<sup>3</sup>; Temperature : 30°C

**Continuous stirred tank reactor (CSTR)**

The RCE reactor could also be operated in a continuous mode with a constant feeding and removal of the solution. The schematic representation of the reactor with single stage as well as with a number of identical units in hydraulic series is shown in Fig.3a and 3b.

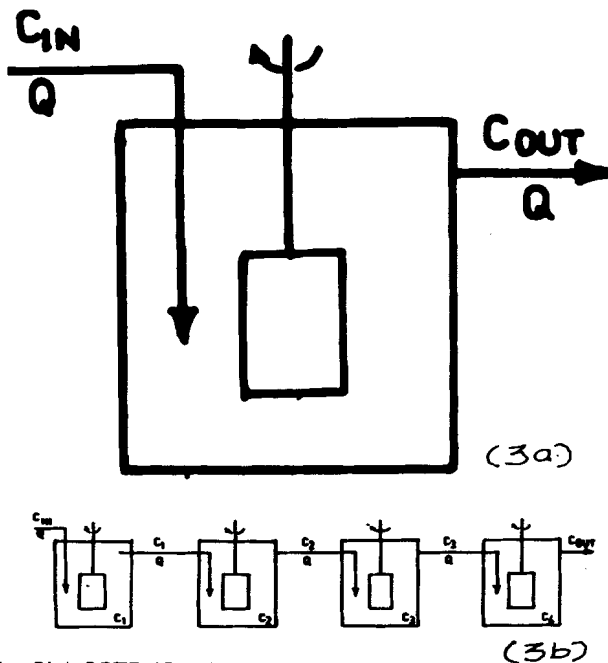


Fig. 3(a) CSTR (Single stage)  
3(b) CSTR (Four Stages)

The basic equation for a CSTR under mass transfer control is,

$$Q(C_{in} - C_{out}) = K_m C_{out} A \quad \dots\dots(2)$$

$$(C_{in} - C_{out}) = (K_m C_{out} A) / Q \quad \dots\dots(3)$$

$$f_R = (C_{in} - C_{out}) / C_{in} \quad \dots\dots(4)$$

$$= 1 - 1 / (1 + \frac{K_m A}{Q}) \quad \dots\dots(5)$$

Fractional removal for 'n' reactors in series,

$$(f_R)_n = 1 - 1 / [(1 + K_m A) / Q]^n \quad \dots\dots(6)$$

Applying mass balance over the individual unit and using Faraday's law, current through each unit can be calculated.

$$\frac{-dm}{dt} = Q(C_{in} - C_{out}) \quad \dots\dots(7)$$

$$\text{Also, } \frac{-dm}{dt} = \frac{IM}{ZF} \quad \dots\dots(8)$$

$$= \frac{I \times 63.54 \times 1000}{2 \times 26.8}$$

$$Q(C_{in} - C_{out}) = 11851$$

$$I = \frac{Q(C_{in} - C_{out})}{1185} \quad \dots\dots(9)$$

The equations (6) and (9) are useful in the design of RCE reactor to perform a given duty (i.e.) handling of a given volumetric rate of flow of solution for achieving a desired conversion when the K<sub>m</sub> value and area of the individual reactor is known. The result of the continuous RCE reactor operated on the above conditions is shown in Table III.

Table III: Data for continuous RCE reactor (CSTR - multiple stage)  
Rotation rate : 400 rpm; Temperature : 30°C  
Reactor volume : 4.5 dm<sup>3</sup>; Solution flow rate : 15 dm<sup>3</sup> hr<sup>-1</sup>  
H<sub>2</sub>SO<sub>4</sub> : 20 gdm<sup>-3</sup>

Stage	Current density (Am <sup>-2</sup> )	Inlet copper concentration (mgdm <sup>-3</sup> )	Outlet copper concentration (mgdm <sup>-3</sup> )	Fractional removal (%)	Current efficiency (%)	Overall space time yield (ghr <sup>-1</sup> dm <sup>-3</sup> )
I	18.5	100	40	0.60	100	
II	7.4	40	22.5	0.43	72	
III	2.9	16	11.0	0.31	51	0.065
IV	1.2	6.5	5.0	0.23	38	
V	0.5	3.25	3.0	0.08	13	

A fractional removal of 60% is envisaged in each unit. However, the fractional removal becomes considerably lower for concentrations less than about 16 ppm which is similar to the observation with the batch mode of operation.

The overall space time yield obtainable with the RCE reactor operating in continuous mode is nearly half compared to batch mode of operation. This is attributed to the back mixing occurring in CSTR whereby the reactor concentration is always equal to that of exit concentration. However, increasing the number of stages and aiming at a lesser fractional removal in each stage will enable the CSTR to approach the batch reactor's performance. But increasing the number of stages would lead to higher investment. In case of batch reactors operating in stages, number of reservoirs needed for a desired conversion will be more and in addition more labour will be involved in transferring the entire volume of solution between the stages. But batch mode of operation allows control of exit concentration precisely and also tolerates variation in feed concentration. The continuous mode will be useful when metal bearing waste waters are generated at a high rate and need to be treated without provision of large storage arrangements. These factors indicate that the selection of batch or continuous mode of operation has to be based on many factors like quantity of solution to be treated, extent of removal, variation in feed concentration etc.

It may also be mentioned that an increase in temperature to 50°C results in an increased mass transfer and this leads to a higher throughput of the reactor which is nearly double. The observation will be useful while handling effluents which are discharged at higher temperatures.

## CONCLUSION

Rotating cylindrical electrode reactor was found to be adaptable for batch as well as continuous modes of operations. When the metal ion removal is accomplished in multiple stages, restricting the fractional removal to 60% in each stage and with progressive reduction in current density, the overall current efficiency for copper removal from 100 ppm to 3 ppm is about 70% which is greater than that obtainable in a single step operation. The throughput of the reactor (space time yield) is considerably greater when the reactor is operated in batch mode under the above conditions.

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