

ELECTROCHEMICAL REMOVAL OF ZINC FROM INDUSTRIAL EFFLUENTS

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ABSTRACT

Zinc is well known for its toxic effects, when present in excess in the environment and every effort has to be made to remove the same from industrial effluents before discharging into the environment. Simple neutralisation and sludge disposal lead to secondary pollution which is still more difficult to be tackled. Electrolytic removal coupled with recovery and recycling of metal values can be the only possible solution to this problem. Towards this goal, experiments have been carried out for the treatment of rayon industry effluent using a bipolar disc electrolyser and the results are reported in this paper.

NOMENCLATURE OF SYMBOLS USED

A	-	Electrode area
A _e	-	Electrode area per unit volume
C	-	Bulk zinc concentration
C ₀	-	Initial zinc ion concentration
C _m	-	Minimum concentration
C _t	-	Concentration of zinc ion at time t
CSTR	-	Continuous Stirred Tank Reactor
F	-	Faraday
I _L	-	Limiting current
K _L	-	Mass transfer coefficient
Q	-	Volumetric flow rate
t	-	Time
T	-	Space time of reservoir
V _e	-	Electrode volume
V _m	-	Volume of the reservoir
z	-	Number of e- transferred

1. INTRODUCTION

Pollution by toxic metal including Cadmium, Copper, Chromium, lead, mercury, nickel and zinc generated by a wide range of manufacturing industries such as mining, metal finishing, plating, chemical, electronics, semiconductor and printed circuit board manufacturing as well as several other industries that have metal treatment as a part of their overall manufacturing processes has been a matter of serious concern in recent years. Waste management practice in these industries vary widely. In

some cases effluent streams are simply diluted to meet regulatory limit but more commonly a chemical process is used where caustic soda, lime or sulphide is added to the waste stream to convert the dissolved metal into a semisolid sludge and dewatering the metal sludge before being dumped into a land disposal site.

There is now indisputable evidence¹ that such land disposal of toxic wastes is only a temporary solution to the problem. All of these storage or disposal site containing many toxic species find their way into natural water courses and subsequently into the biological food chain. There are strong trends seeking on-site - zero discharge - resource - recovery technology^{2, 3}. There are many environmental waste management problems where electrochemistry is able to offer effective solution²⁻⁵. Removal of heavy metals through hydrometallurgical separation process⁶ solvent impregnated ion exchange method⁷ adsorption on activated sludge⁸ activated carbon⁹ vermiculite¹⁰ have also been reported followed by regeneration. Leaching with mineral acids followed by electrolysis or chemical displacement has been used for the recovery of heavy metals from mixtures¹¹. Removal of zinc from effluent using a packed bed reactor has been reported earlier¹².

The purpose of this attempt is to investigate the problem of electrolytic removal coupled with recovery and recycle of zinc value contained in rayon industry effluent using a bipolar disc electrolyzer. Reactor performance is investigated using mass transfer controlled deposition of zinc from lean solution in a batch recycle operation. Particular attention is paid to low initial concentration of dissolved zinc and the achievement of very low final concentration.

2. EXPERIMENTAL

The electrochemical cell with its associated electrical and electrolytic flow circuits is described in detail elsewhere¹³ and the flow cell is shown schematically in Fig. 1. The cell stack consists of two end PVC frames. In between these frames, a cylindrical perspex tube is placed, inner diameter of which is 10 cm and the height of the cell is 11 cm. This bipolar cell consisted of eleven graphite discs of 9 cm diameter and 0.6 cm thick of which two discs have been fixed on to the two end frames of the cell. These two electrodes act as feeder electrodes and remaining 9 discs are stacked in between these two discs. The electrodes are kept 4 mm apart from each other by polypropylene spacers. Feeder electrode at the top acts as anode and that at the bottom acts as cathode. The electrode stack has a central

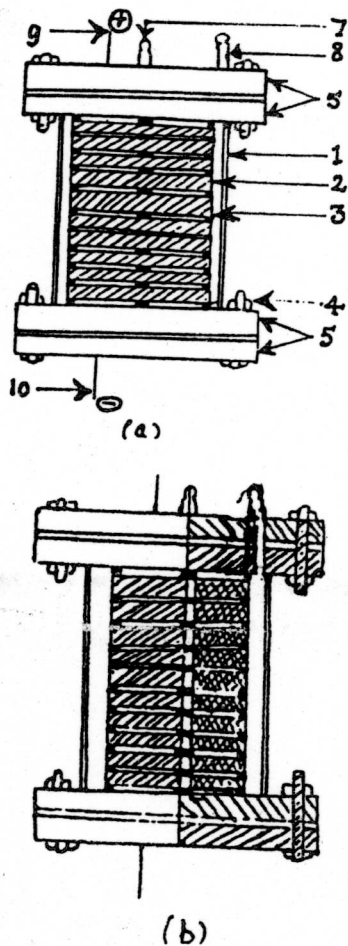


Fig. 1. (a) Schematic Diagram of the cell set up
 (b) Half sectional view of the cell set up
 (1) Cell container (2) Graphite Disc (3) Insulator (4) Coupling Bolts (5) Flanges (6) Gasket (7) Inlet (8) Outlet (9) Anode lead (10) Cathode lead

bore through which the electrolyte is flown and the overflow is collected from the top and is recirculated.

Provisions for electrolyte inlet and outlet have been made at the top of the reactor. Each of the disc between the feeder electrodes act both as anode and cathode i.e. top surface of each disc electrode acts as cathode and bottom surface of the same acts as anode. By this way the reactor functions as a stack of 10 unit cells. Area of each disc is 0.636 dm^2 . Therefore total area of cathode for a 10 unit cell is 6.36 dm^2 .

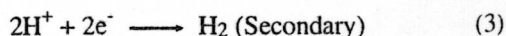
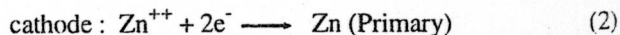
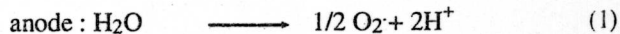
The total cell volume without disc electrode is approximately 780 cm^3 and with electrodes is approximately 370 cm^3 . The free volume of electrolyzer is approximately 400 cm^3 and the reservoir capacity is 2.0 liters.

The electrolyte was made from ZnO/ZnCO_3 sludge obtained from chemical industry. Stock solution was prepared by dissolving 20 gm of sludge in dil. sulphuric acid. The pH was adjusted to 2.5- 3.0 by adding excess sulphuric acid. The exact concentration of solutions were prepared by dilution of this stock solution. Three concentrations namely 50 ppm, 500 ppm and 5000 ppm of zinc were used for the experiment.

Electrolysis was carried out in batch recirculation. The total volume of the solution was 2 litres and this was recirculated for electrolysis. Electrolysis was carried out at a constant current of 1 ampere. Experiments were carried out by varying flow rate of electrolyte from 10 l/hr to 80 l/hr. The depletion in zinc concentration was estimated by analysing the sample drawn from the reservoir at regular intervals using AAS.

3. THEORY

The primary cathode reaction within the bipolar disc reactor is removal of zinc ion through electrodeposition. The main secondary cathode reaction is hydrogen evolution. The anode process is oxygen evolution.



In the present studies, the electrode potential and the electrolysis condition due to lean solution of metal ions are so-fixed such that the removal of zinc is completely under mass transfer control. The disc cathode then operates at its maximum duty, corresponding to limiting current I_L which

may be expressed in terms of mass transfer coefficient, k_L , the electrode area, A , and the bulk zinc concentration, C .

$$I_L = K_L A z F C \tag{4}$$

It is assumed that the entire cathode surface is active eq. (4) may be written

$$I_L = K_L A_e V_e z F C \tag{5}$$

which A_e is the electrode area per unit volume of the electrode and V_e is the electrode volume.

The reactor performance is characterized by the factor $k_L A_e$ which may be determined by direct measurement of the limiting current at a known concentration followed by application of a rearranged form of eqn (5).

$$K_L A_e = I_L / V_e z F C \tag{6}$$

or via the assumption of a mathematical model to describe conversion in the reactor system.

In the batch recycle mode operation, the reactor can be assumed to be CSTR under full mass transfer control.

Then the expression for variation of concentration of zinc ion in the reservoir with respect to time is given by,

$$\frac{C_t}{C_o} = \exp \left[\frac{-t}{\tau} \left(\frac{K_L A_e / Q}{1 + K_L A_e / Q} \right) \right] \tag{7}$$

where C_o is the initial zinc ion concentration

Q is the volumetric flow rate

τ is the space time of reservoir (V_m/Q)

V_m is the volume of the reservoir

C_t is the concentration of zinc ion at time t .

Eqn. (7) may be rewritten in terms of the logarithm.

$$\ln \frac{C_t}{C_o} = \left\{ \frac{-t}{\tau} \left(\frac{K_L A_e / Q}{1 + K_L A_e / Q} \right) \right\} \tag{8}$$

$K_L A_e$ may be found from the plot of $\ln(C_t/C_o)$ Vs t .

4. RESULTS AND DISCUSSION

The results are presented in Figs. 2 - 4 and Table I. The variation of concentration of zinc during electrolysis with time have been plotted for two concentration ranges namely $C_o = 45 \pm 5$ ppm and 5000 ± 250 ppm in Figs. 2a and 2b respectively. The plots show an exponential variation of concentration with time at all flow rates under study. Minor

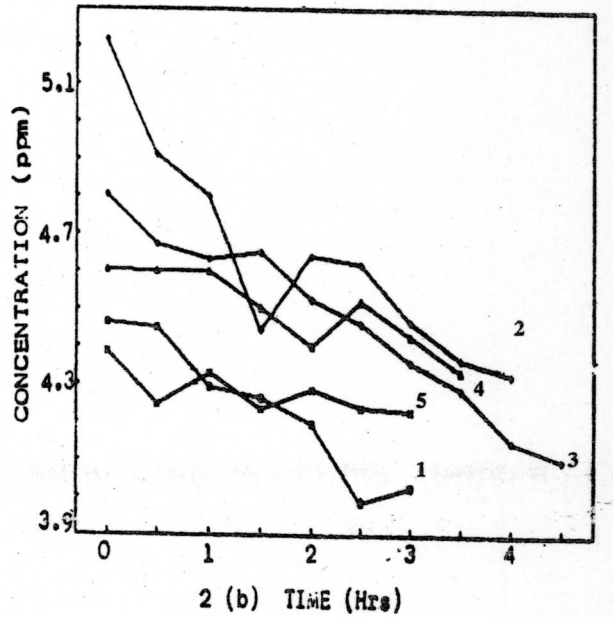
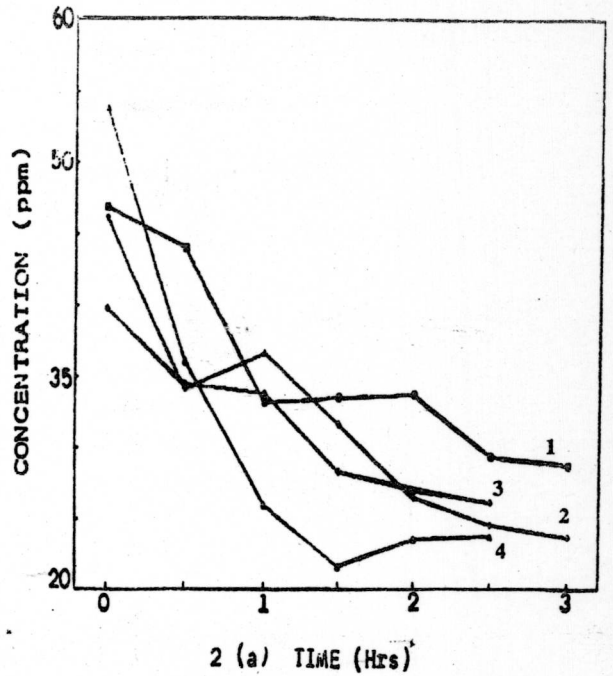


Fig. 2 Variation of Concentration with time
 2(a) (1) 10 l/Hr (2) 14 l/Hr (3) 20 l/Hr (4) 30 l/Hr
 2(b) (1) 19 l/Hr (2) 29 l/Hr (3) 43 l/Hr (4) 60 l/Hr
 (5) 80 l/Hr

variations in concentration have been observed possibly due to dislodging of the deposited zinc powder which might have undergone redissolution in the electrolyte.

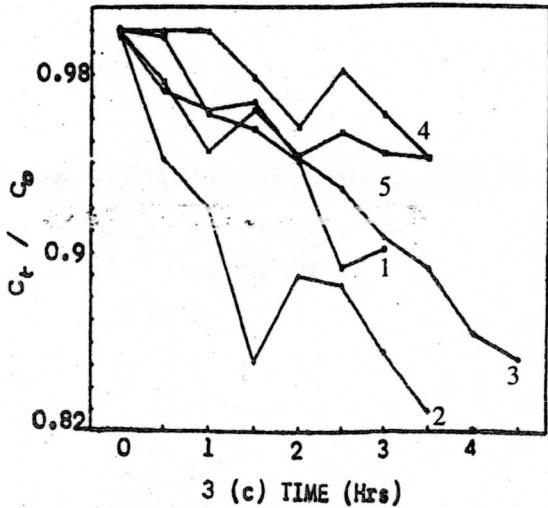
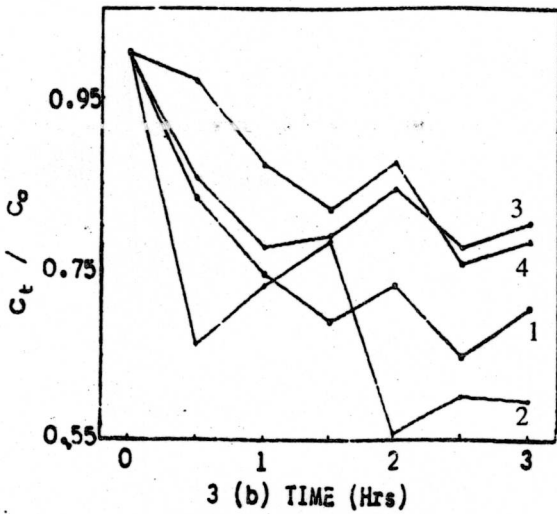
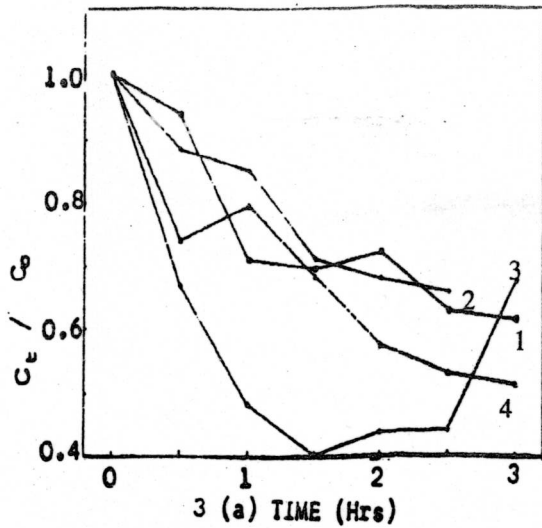


Fig. 3 Variation of C_t / C_0 with time
 3(a) (1) 10 l/Hr (2) 14 l/Hr (3) 20 l/Hr (4) 30 l/Hr
 3(b) (1) 10 l/Hr (2) 14 l/Hr (3) 20 l/Hr (4) 24 l/Hr
 3(c) (1) 19 l/Hr (2) 29 l/Hr (3) 43 l/Hr (5) 60 l/Hr (5) 80 l/Hr

TABLE 1.				
Initial Conc. (ppm)	Minimum conc. (ppm)	Duration of electrolysis (hrs)	Volume Flow rate (Q) (l/hr)	$k_L A_e$ (l/sec)
46.92	28.80	3.00	10	1.0065×10^{-4}
39.84	26.16	2.30	15	1.1227×10^{-4}
53.88	21.60	1.30	20	3.3440×10^{-4}
46.2	24.60	2.30	30	1.4150×10^{-4}
341.5	222.0	2.30	10	1.3923×10^{-4}
508.0	283.0	2.00	15	1.4286×10^{-4}
263.0	203.5	2.30	20	6.2548×10^{-5}
682.5	515.0	2.30	25	6.5030×10^{-5}
4464.01	3988.98	2.30	19	1.4080×10^{-5}
5216.76	4325.78	4.00	29	3.5990×10^{-3}
4804.77	4098.62	4.30	43	1.8510×10^{-5}
4603.56	4332.26	3.30	60	8.3110×10^{-6}
4401.20	4228.81	3.30	80	1.1110×10^{-5}

In Figs. 3a - 3c the ratio of C_t / C_0 with time for the three different concentration ranges at different flow rates are presented. At low concentration (Fig. 3a) the variation shows an exponential behaviour whereas at increasing concentration range there is a slight variation in the behaviour especially at 500 ppm. At low flow rates (10 and 14 l/hr) the plot shows an exponential variation (Fig. 3b) whereas on increasing flow rate there is an initial decrease and after that there is an increase due to possible redissolution of the deposited metal. On further increasing the concentration the exponential behaviour is observed. It is to be noted even at very fast flow rates the concentration variation shows a downward trend only. This is quite possible since even after three and a half hours of electrolysis, the concentration still remains in the high range i.e., 4000 ppm (Fig. 3c).

Fig. 4 shows the plot of C_t / C_0 Vs time for an initial concentration of 100 ppm on continuous electrolysis carried out in order to find out the lowest zinc concentration attainable under the optimum flow rate namely 30 l/hr. The plot indicates a minimum limit of 30% of the initial concentration, in other words, maximum removal efficiency of 70%. Beyond this, there has been a continuous deposition and redissolution as indicated by an average of

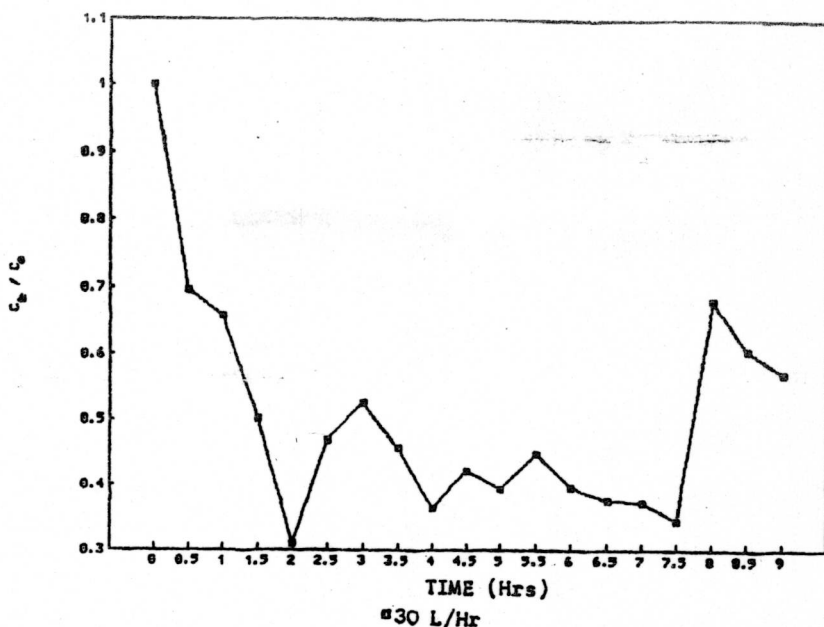


Fig. 4. Variation of C_t / C_0 with time

40% remaining zinc concentration (i.e 60% removal). Beyond seven and a half hours of electrolysis, there is vigorous gassing at the electrode, resulting in the removal of black particles of zinc leading to an increase in concentration, nearly double. The undissolved particles could be observed in the electrolyte.

Following the eqn. (8), $K_L A_e$ was calculated for the system using the plot of $\ln C_t / C_0$ Vs time and the results are summarised in Table I. From the foregoing account it is evident that the rate of removal of zinc, using this reactor has been possible upto a certain limit. Beyond this, the process of dislodging of the fine deposited powder and redissolution of the same hinders further removal of the metal ion from the solution. Under the conditions of study, the current efficiency obtained has been very low, of the order of less than 10% and hence the rest of the current has been utilised for the main side reaction, namely water electrolysis. The low metal ion concentration involved in the process, very narrow gaps between the electrodes and vigorous gassing due to low current efficiency for deposition have led to fluctuation of dissolved zinc concentration in the solution and inefficient removal of the metal ion. Hence we concluded that this system of arrangement may not be very conducive for use, for recovery of such metals capable of undergoing quick dissolution in the acid medium is not very encouraging.

5. CONCLUSION

Electrolytic removal of zinc from effluent by electro-deposition using capillary gap cell over a concentration

range upto 5000 ppm has been found to be possible only upto a certain limit. The results indicate that the particular type of electrolyser may not be very much suited for metals like zinc especially from acid media. The high dissolution rate in such cases has been earlier reported to be due to very high activity of freshly deposited metal powder.

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