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ELECTROCHEMICAL REDUCTION OF Cr^{6+} TO Cr^{3+} USING PACKED BED ELECTROLYSERS

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ABSTRACT

Hexavalent chormium in the effluent from plating/metal finishing industries has been known to be the major toxic pollutant, which necessitates removal of the same as a measure of environmental pollution control. Treatment of such effluent has been mainly oriented towards reduction of Cr^{6+} to Cr^{3+} followed by removal of the same by precipitation. The present paper deals with the investigations carried out in a packed bed reactor of flow-by configuration on electrochemical reduction of Cr^{6+} to Cr^{3+} starting with an initial concentration of 200 ppm Cr^{6+} and at pH 1.5 and flow rates ranging from 6 to 15 l/hr. It has been observed that 100% conversion could be achieved by electrolysis.

Key words: Reduction of Cr^{6+}, packed bed electrolyser, Mass transfer coefficient

INTRODUCTION

Most of the industrial effluents contain metal ions which are toxic to plant and animal life even at low concentrations. One such metal ion is hexavalent chromium ion present in the plating and metal finishing industrial waste water. Chromium when reduced to trivalent state becomes less toxic and hence methods of treatment of plating industry wastes chiefly involve the reduction of Cr^{6+} to Cr^{3+} followed by precipitation of $Cr(OH)_3$. Earlier studies have been made on a bench scale on the electrochemical reduction of Cr^{6+} to Cr^{3+} [1] and it has been found that under optimum conditions nearly 100% conversion could be achieved. In recent years there has been greater interest on the use of packed bed reactors for treatment of industrial waste water [2-5]. The packed bed electrode because of its large surface area is well known to have high space-time yield with respect to electrochemical reactions. The reduction reaction has been studied extensively in dilute solutions and the kinetics and mechanism of the reduction of Cr^{6+} to Cr^{3+} have been reported in literature [6-9]. The influence of cations on the reduction of Cr^{6+} to Cr^{3+} has also been investigated [10]. With a view to study the reduction of Cr^{6+} in a packed bed reactor, the present investigations have been carried out.

EXPERIMENTAL

Investigations have been carried out using single packed bed electrode reactor which is shown schematically in fig. 1. The cell system comprises of a packed bed working electrode made up of 3 mm size graphite particles and a planar graphite counter electrode in a divided compartment system with sintered PVC diaphragm in between. The complete cell system has been fabricated out of PVC with appropriate provisions for electrical contact for the two electrodes and also for the flow of the electrolyte through the anode and cathode chambers. The working electrode has a volume of approximately 70 cc with 41% porosity. Uniform flow of electrolyte through the compartments is achieved through use of distributors situated at the bottom and top of the cell. The cell belongs to flow by configuration which is known to be more efficient than flow through configuration. The electrolyte was flown through anode chamber and then to the cathode chamber where it gets reduced. The flow of electrolyte was by gravity and the flow rate was adjusted by suitable valves on the line. Potassium dichromate solution containing 200 ppm of Cr^{6+} mixed with H_2SO_4 was used as the electrolyte. The pH of the solution was maintained at 1.5. The current voltage characteristics was determined for different flow rates up to a maximum applied voltage of 90 V. Based on the observations the voltage for further experiments on electrolysis was selected.

The electrolysis was carried out at a constant applied voltage of 30 V and the flow rate was varied from 6 to 15 l/hr. The concentration of the unreduced Cr^{6+} was estimated spectrophotometrically using the diphenyl carbazide method [11]. Initially experiments were carried out for 6 hrs. Based on the results the optimum flow rate was fixed and a continuous trial was carried out at this flow rate to find the maximum extent of reduction possible. The current efficiency for the reduction was calculated at different levels of electrolysis for different flow rates.

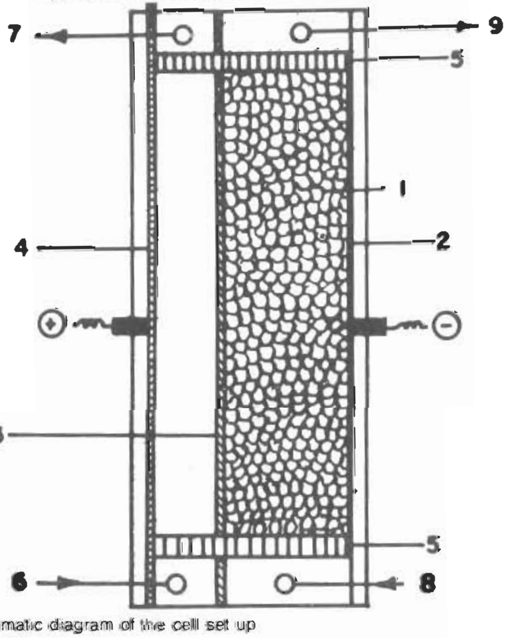

Fig. 1 : Schematic diagram of the cell set up

RESULTS AND DISCUSSION

The results are presented in figures 2 to 6 and Table I. Figure 2 shows the current voltage characteristics for the system. The current increases with increase in voltage at all flow rates under study. The curve shows more or less a linear behaviour. It was observed beyond 30-35 volts the gas evolution was considerably increased and heating of the electrolyte was also observed and hence for further experiments, the voltage was fixed at 30 V for this particular cell configuration.

Variation of concentration of the unreduced Cr^{6+} with time of electrolysis at different flow rate is presented in fig. 3. At all flow rates, the concentration decreases exponentially with time. It has also been observed that there is not much difference in variation of concentration within the range of flow rates studied.

Variation of current efficiency with concentration of Cr^{6+} is shown in fig. 4. As can be expected current efficiency is low at low concentrations.

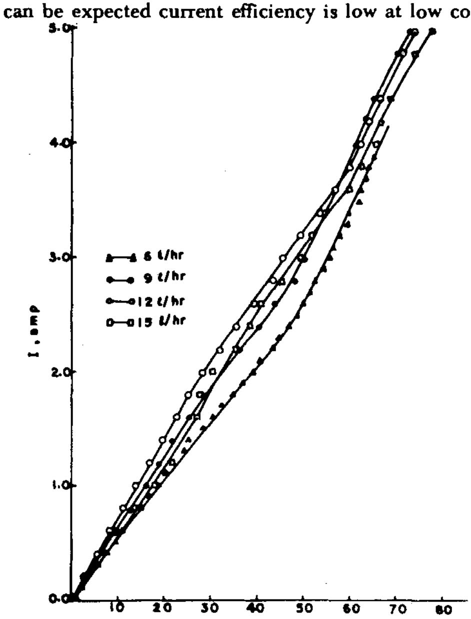

Fig. 2 : i-E relationship at different flow rates

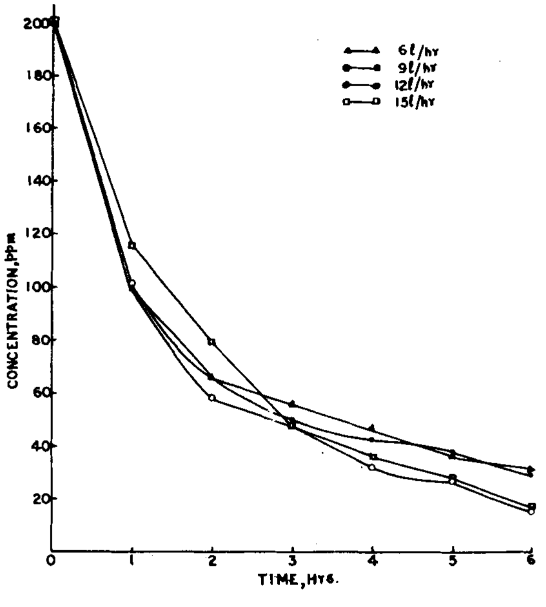

Fig. 3 : Variation of concentration of unreduced Cr^{6+} with time of electrolysis at different flow rates

A maximum current efficiency of 50% has been obtained at 6 l/hr whereas on increasing flow rate up to 12 l/hr has yielded a current efficiency of 40% and on further increase there is a still lowering of current efficiency to 30% at a Cr^{6+} concentration of 200 ppm. At concentrations below 100 ppm, the current efficiency is less than 20% and towards the end current efficiency is of the order of 3 to 5%.

The value of K the mass transfer coefficient was calculated at different flow rates from the slope of ln Ct/Co vs t plots and are given Table I. From the Table, as expected, K increases with flow rate. It is also seen that the increase in flow rate improves the conversion efficiency while the overall current efficiency is a bit lowered.

In the light of the above observations, a flow rate of 12 l/hr has been found to be the optimum condition for electrolysis and a continous electrolysis was carried out at this flow rate in order to find out the maximum extent of reduction possible. Fig. 5 shows the variation of current and concentration of hexavalent chromium during electrolysis. As can be seen from the figure, within first 2 hrs the concentration of Cr^{6+} drops down to 58 ppm and thereafter the decrease is more or less linear with time. In 8 hrs of electrolysis the final concentration reached is nearly zero ppm within the limits of detection by Spectrophotometry which is specified as 0.02 ppm. Since the electrolysis was carried out at constant voltage, variation of current is also recorded with respect to time. The current initially falls from 2.8 Amp to 2 Amp and thereafter remains more or less constant at 1.75 ±0.1 Amp.

Table I: Results obtained with packed bed electrolyzer in the electrochemical reduction of Cr^{6+} to Cr^{3+}

Sl. No.	Flow rate l/hr	Average current (amp) at 30 V	Concentration ppm Initial	Final after 6 hours electrolysis	Overall current efficiency %	Conversion efficiency %	Mass transfer coefficient $K \times 10^4$ cmsec^{-}
1.	6	1.4	200	31	15.56	84.5	7.26
2.	9	1.7	200	29	12.96	85.5	8.43
3.	12	1.8	200	12	13.46	94.0	9.28
4.	15	1.9	200	16	12.48	92.0	10.50

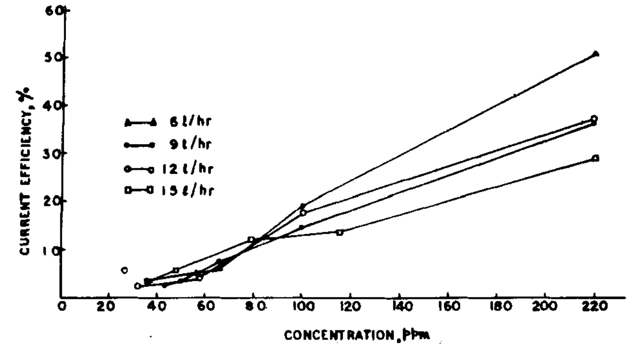

Fig. 4 : Variation of current efficiency with concentration of Cr^{6+} at different flow rates

In fig. 6 logarithmic plot of mass transfer coefficient K and Reynolds number R_e is given. Within the range of flow rates studied K increases with R_e and the values for the constants a and b in the equation $K = a R_e^b$ have been calculated from the figure. The values for a and b are 2.9525×10^{-5} and 0.410 respectively.

During electrolysis the following reactions occur at the cathode; $Cr^{6+} + 3e^- \rightarrow Cr^{3+}$ (1) and simultaneously part of the current is utilized for electrolysis of water liberating H_2.$2H^+ + 2e^- \rightarrow H_2$ (2). Within the concentration range under study, both these reactions occur side by side. As the concentration of Cr^{6+} decreases, the reaction involving H$^+$ ions becomes predominant and most of the current goes only towards hydrogen evolution reaction as is evident from very low current efficiencies for the reduction reaction. In this investigation the electrolyte from the reservoir was flown through the anode chamber and then subsequently through cathode chamber. From the cathode chamber the solution returns back to the reservoir. In the anode chamber there is a partial oxidation of Cr^{3+} back to Cr^{6+} during recycle. This may also result in lowering of current efficiency in this case. Hence it is felt that a three dimensional electrode system with divided flow may be more suitable than with single continuous flow system.

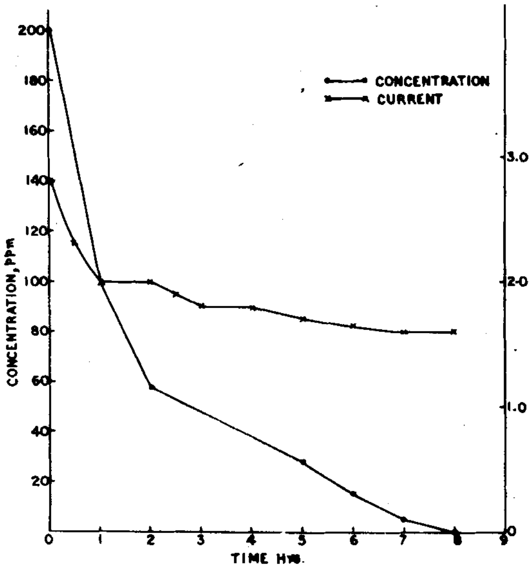

Fig. 5: Variation of concentration of Cr^{6+} and current with time during continuous electrolysis

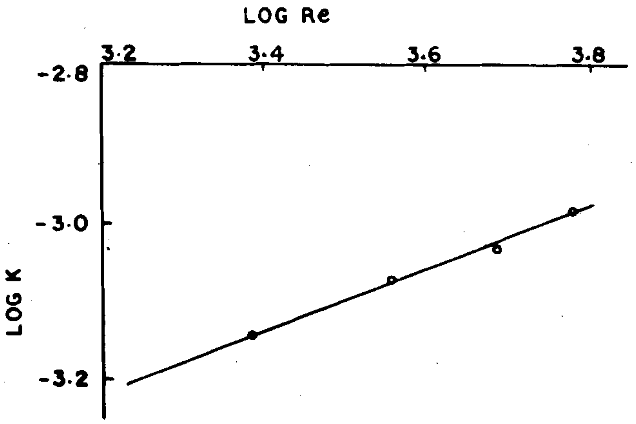

Fig. 6: Plot of log K vs log Re

In a packed bed, the reaction comes under diffusion control because of low concentration of electrolyte. The effect of activation and mixed control can be ignored. The packed bed then behaves as a plug flow reactor [12]. The equations relating the concentration factors and mass transfer properties have been discussed elsewhere [13].

Calculated values of K from the depletion experiment are given in Table I. The good agreement of values calculated for b supports this model in this present case.

CONCLUSION

In conclusion, it has been observed that it has been possible to convert the hexavalent chromium ion to trivalent chromium effectively in a packed bed reactor. Though the reaction proceeds with very low current efficiencies, nearly 100% conversion is possible on prolonged electrolysis. As stated above with a divided flow system, it may be even possible to improve the reduction efficiency.

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