ELECTROCHEMICAL OXIDATION AS A TOOL FOR POLLUTION CONTROL – PART IV STUDIES ON DOUBLE PACKED BED REACTOR FOR THE DESTRUCTION OF CYANIDE

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ABSTRACT

Treatment of cyanide bearing effluent has been a matter of great concern, especially with reference to plating and metal finishing industries. Earlier investigations have been carried out on electrochemical oxidation of cyanide in effluents. In this paper, results of the investigation using a double packed bed reactor using graphite particle with flow by configuration in presence of NaCl are reported. Trials were run with an initial concentration of 200 ppm cyanide and at flow rates varying in 30 to 40 litres per hour. The concentration of cyanide could be brought down to zero level.

Key words : Electrochemical oxidation, double packed bed reactor, cyanide destruction

INTRODUCTION

Plating and metal finishing industries are the major source for cyanide pollution. Treatment of the effluent from these industries requires a special attention, since even small doses will cause serious health hazards in living organisms. Cyanide concentration in the effluent ranges from 50 to 1000 ppm as against the tolerance limit of 0.01 ppm for inland surface waters [1]. Cyanides in effluents can be destroyed either by chemical or electrochemical oxidation. Electrooxidative destruction of cyanide by direct or through in situ formation of hypochlorite have been found to be fairly successful.

The process of electrochlorination was first reported in 1958 [2]. Various electrochemical reactors such as flowing systems [3-7], packed bed [8], trickle tower [9] and bipolar rotating electrode system [10] have been tried for direct and indirect oxidation of cyanide.

Earlier, investigations have been carried out with single packed bed electrolyser with flow-through configurations for the anode oxidation of cyanide [11]. The cyanide concentration could be successfully brought down to zero level from an initial concentration of 200 ppm. Investigations had also been carried out to compare various reactors having different configurations and it has been found that reactors having flow-by configuration serve better than those of flow-through configuration [12].

In this paper results of investigation on the oxidation of cyanide in a double packed bed reactor with flow-by configuration are reported.

EXPERIMENTAL

Figure 1 shows the schematic representation of the reactor used in this study. The cell consisted of two packed bed electrodes, one being anode and the other being cathode separated by a perforated PVC separator. The packed bed electrodes consisted of graphite particles of approximately 3 mm size, the volume being approximately 83 cm^3 with 41 % porosity. Thickness of the bed was 1.2 cm and height 9 cm. The capacity of the cell was 140 cc and that of reservoir 10 dm^3. The cell was fabricated out of PVC with appropriate provisions for electrical contact to the electrodes and also for uniform flow of electrolyte through both the chambers. The electrolyte was flown from the bottom and the outflow was recirculated.

The electrolyte was prepared using AR NaCN and NaCl and the initial composition was fixed at 200 ppm cyanide and 5 gpl NaCl. Initially the experiments were carried out by varying only the flow rate from 60 to 240 l/h
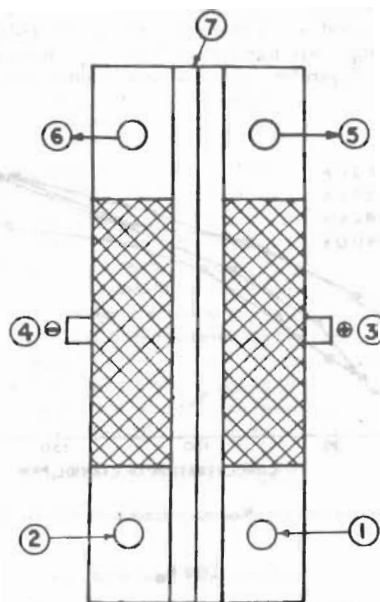
Fig. 1 : Schematic diagram of the cell set up

for 6 hrs at a constant applied voltage of 30 V. Based on the results obtained continuous electrolysis was carried out to determine the maximum extent of oxidation. The concentration of cyanide during electrolysis was estimated by drawing samples from the reservoir at one one hour interval, using potentiometric titration method.

RESULTS AND DISCUSSION

The results are presented in Figs. 2 to 5. Fig. 2 shows the variation of concentration with time during 6 hr electrolysis at different flow rates. The concentration varies exponentially with time at all the flow rates. However, it is observed that the optimum flow rate is 180 l/hr. The variation of current efficiency with concentration of cyanide is given in fig. 3. It has been observed that the efficiency is around 40 % within the cyanide concentration
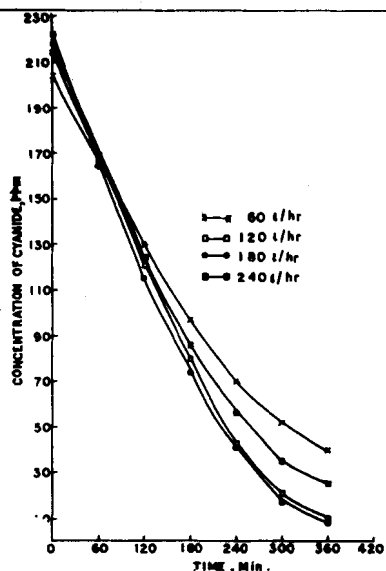
Fig. 2 : Effect of flow rate on the oxidation of cyanide

The results are summarised in Table I. The average current obtained at an applied voltage of 30 V increases up to 180 1/h whereafter there is no significant improvement in the current. Overall current efficiency under the optimum conditions is 31.08% at a conversion efficiency of 91.2%. During 6 hours electrolysis with a flow rate of 180 1/h, the minimum cyanide concentration obtained has been found to be 8.2 ppm.

From the above results it has been concluded that flow rate of 180 1/h yields the best results under the conditions of study. Hence, a continuous electrolysis was carried out to find out the minimum attainable level for cyanide in solution. Fig. 5 shows the variation of concentration with time during continuous electrolysis. The concentration reaches nearly zero (within limit of experimental detection by potentiometry) after 9 hours electrolysis and the value extrapolated to zero level.

Table I : Summary of results obtained in the anodic oxidation of cyanide

Flow rate Q l/h	Initial concentration of cyanide ppm	Concentration of cyanide after 6 hrs. ppm	Average current A	Overall current efficiency %	Conversion efficiency %	Mass transfer coefficient $K \times 10^3$ cm sec^{-1}
60	203.7	39.1	5.00	27.3	80.8	1.126
120	214.0	10.3	5.30	31.8	95.2	1.793
180	218.1	8.2	5.68	31.1	96.2	2.298
240	222.3	24.7	5.60	29.2	88.9	0.841

range of 100 to 200 ppm under all conditions. Fig. 4 shows the logarithmic plot of mass transfer coefficient K and Reynolds No. Re. The mass transfer coefficient increases with Reynolds No. up to a value corresponding to flow rate of 180 1/h beyond which there is a precipitous fall of coefficient. Constants correlating mass transfer coefficient and Reynolds No. were calculated from this logarithmic plot [12] and found to be 2.2×10^{-5} and 0.65 respectively.
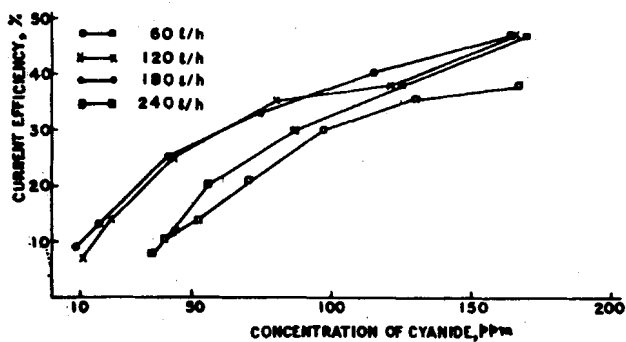

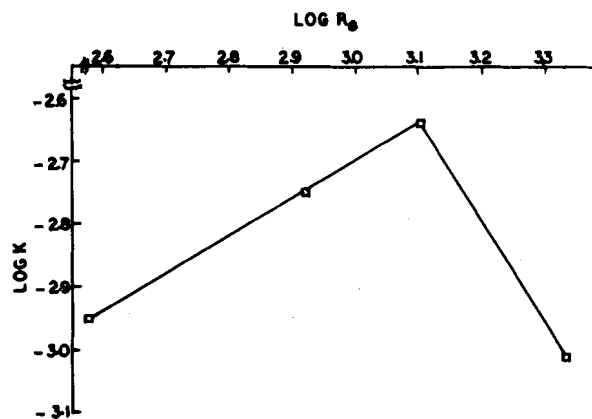Fig. 3 : Relationship between current efficiency and concentration of cyanide at different flow rates
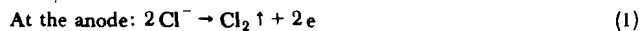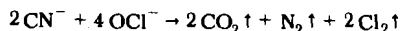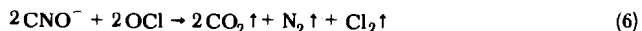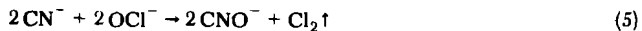

Fig. 4 : Plot of log K vs log Re

Fig. 5 : Variation of concentration of cyanide with time during during continuous electrolysis

It is known that in a packed bed the reaction comes under diffusion control because of low concentration of electrolytes. The effect of activation and mixed control can be ignored in such condition and the packed bed then behaves as a plug flow reactor. The equations relating the concentration factors and mass transfer properties have been discussed elsewhere [12]. The value of the constant b correlating the mass transfer coefficient and the Reynolds No. based on this model agrees well with those obtained experimentally, thereby confirming the validity of this model.
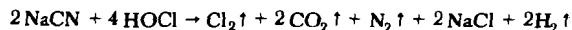
During electrolysis the following reactions occur in the cell. Chlorine is formed insitu in the anode chamber and further oxidation of cyanide occurs according to the equations given below:

At the anode: $2\,Cl^- \rightarrow Cl_2 \uparrow + 2\,e$ (1)

At the cathode: $2\,H_2O + 2\,e \rightarrow H_2 \uparrow + 2OH^-$ (2)

In the bulk: $H_2O + Cl_2 \uparrow \rightarrow HCl + HOCl$ (3)

$HOC \rightleftharpoons H^+ + OCl^-$ (4)

reaction with CN^-

$2\,CN^- + 2\,OCl^- \rightarrow 2\,CNO^- + Cl_2 \uparrow$ (5)

$2\,CNO^- + 2\,OCl^- \rightarrow 2\,CO_2 \uparrow + N_2 \uparrow + Cl_2 \uparrow$ (6)

$2\,CN^- + 4\,OCl^- \rightarrow 2\,CO_2 \uparrow + N_2 \uparrow + 2\,Cl_2 \uparrow$
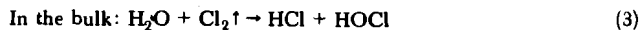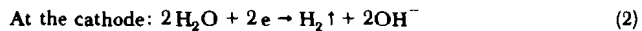
Overall reaction of NaCN and HOCl can be written as

$2\,NaCN + 4\,HOCl \rightarrow Cl_2 \uparrow + 2\,CO_2 \uparrow + N_2 \uparrow + 2\,NaCl + 2H_2 \uparrow$

The exact reaction mechanism is yet to be confirmed.

From these it is very clear that both the reactions, viz. cyanide oxidation and chlorine evolution occur at the anode. Depending on the cyanide ion availability either of the two reactions occurs predominantly. In the present case the range of concentration of cyanide taken up for investigation falls at very low level as compared with excessive chloride ion present as supporting electrolyte. Current efficiency for the cyanide oxidation is considerably low since the majority of the current is used up for the chlorine evolution than for the cyanide oxidation.

In conclusion, the double packed bed electrode, because of its large surface area and high mass transfer rate, seems to be suitable for cyanide destruction.

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