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ELECTROCHEMICAL OXIDATION AS A TOOL FOR POLLUTION CONTROL : VII– DESTRUCTION OF CYANIDE USING STACK REACTOR SYSTEM

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The plating and metal finishing industries are the major sources of cyanide pollution. Cyanide concentration in effluents varies from 50 to 100 ppm as against tolerance limit of 0.01 ppm for inland surface water. The results of investigation on electrochemical oxidation of cyanide in a packed bed reactor with flow by configuration are reported.

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

INTRODUCTION

The problem of pollution pertaining to electroplating and metal finishing industries mainly concerns with disposal of cyanide bearing effluents. Cyanide waste is generally treated with chlorine, sodium hypochlorite, ozone, hydrogen peroxide etc. In recent years, methods, based on electrochemical oxidation, have been investigated for this purpose. Since the conductivity of cyanide containing effluent is low, the current efficiency is also found to be low, in the case of direct oxidation. Then attempt has been made to combine the principles of well known processes of alkaline chlorination and electrolytic oxidation. By this, it has been proved that it is possible to obtain more effective treatment for cyanide waste. The processes of electrochemical oxidation of cyanide through insitu formation of hypochlorite was first reported as early as 1958 [1]. Subsequently there are numerous papers describing cyanide destruction based on interaction with hypochlorite formed during electrolysis of cyanide containing water in the presence of dissolved chloride [2-6]. The recent developments involve in the use of three dimensional electrodes such as fluidized bed [7], trickle tower [8] and packed bed [9-11] electrodes. Since packed bed electrodes, characterised by high specific surface area per unit volume, are known to result in high mass transfer rates, they are investigated for use in such effluent treatment processes. The selection and standardisation of the proper reactor design as well as the optimisation of conditions of reaction play an important role in obtaining good efficiencies for the treatment. Most of the studies on packed bed electrodes have so far emphasized the theoretical analysis of the electrodes which are assumed to operate in the state of either activation polarization or limiting current alone [12]. Investigations were carried out earlier to study the various parameters for the electrolytic destruction of very low concentration of cyanide using porous packed bed electrodes [13-15].

In the present paper, the results of investigation on electro-oxidative destruction of cyanide in a stack reactor system are reported with the objective of arriving at conditions for scale up of the process of oxidation.

EXPERIMENTAL

Initial experiments were carried out with a central packed bed anode with two packed bed cathodes placed on either side of the anode. The construction of the packed bed electrode has been described elsewhere [15]. Experiments were carried out at four different flow rates from 60 to 240 $l \cdot h^{-1}$ at a constant applied voltage of 30V as done earlier. The electrolyte was synthetic effluent made from sodium cyanide and sodium chloride. Initial concentration of cyanide was kept at 200 ppm in a supporting electrolyte of 5 gpl sodium chloride. Batch recirculation type electrolyser system was used in the study.

Further investigations were carried out in a stack reactor system consisting of two packed bed anodes with three packed bed cathodes interleaving with anodes. The electrode construction was the same as described earlier. The cell system is represented schematically in Fig. 1. The flow of electrolyte was in series through

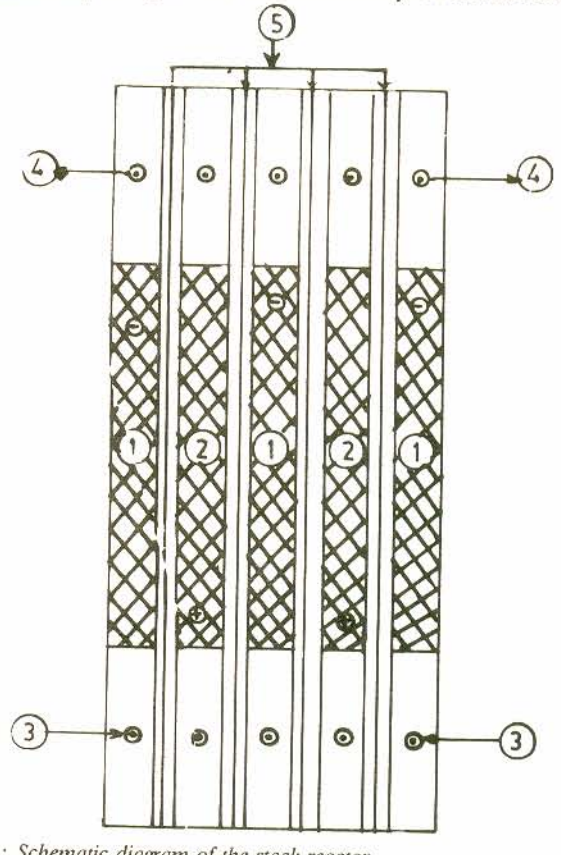

Fig. 1: Schematic diagram of the stack reactor
(1) Cathodes (2) Anodes (3) Electrolyte inlet (4) Outlet (5) Perforated PVC separator

all the chambers and the batch recirculation system was adopted in this case also. Experiments were carried out at four different flow rates from 60 to 240 $l \cdot h^{-1}$ at a constant applied voltage of 10V. Unlike the single packed bed cell, excessive heating was observed due to heavy current flow when the voltage was raised beyond 10V. Hence the applied voltage was restricted to 10V for the stack reactor system. Samples were drawn at 15 minute intervals and unreacted cyanide was estimated potentiometrically.

RESULTS AND DISCUSSION

Results are presented in Figs. 2 to 7 and Table I. Figure 2 represents the variation of concentration with time using central packed bed reactor. At all flow rates under study, the concentration varies more or less linearly with time upto about 60 ppm of cyanide and thereafter the concentration decreases exponentially with time and the cyanide concentration reaching zero (within the limits of detection by potentiometry) in three hours.

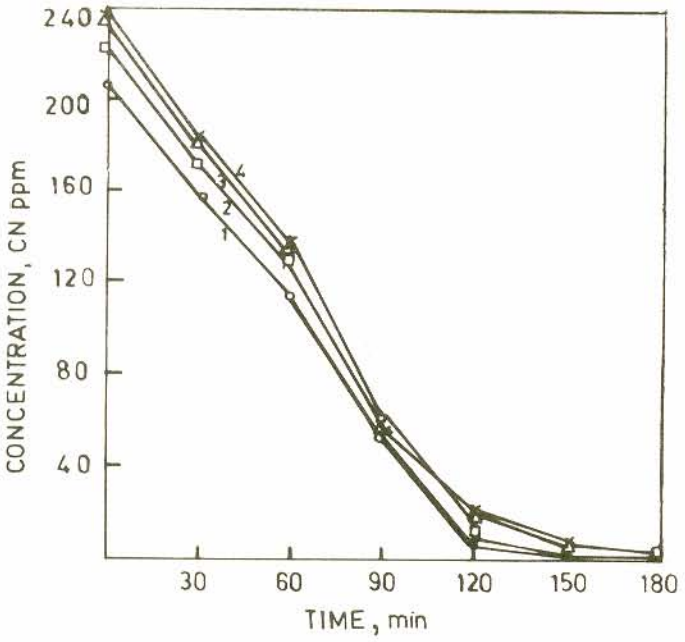

Fig. 2: Variation of concentration with time for central packed bed reactor (1) 60 $l \cdot h^{-1}$ (2) 120 $l \cdot h^{-1}$ (3) 180 $l \cdot h^{-1}$ (4) 240 $l \cdot h^{-1}$

Figure 3 shows the variation of current efficiency with percentage conversion. Current efficiency was found to be around 25% in the case of central packed bed reactor. Beyond 90% conversion(concentration of cyanide:approx: 20 ppm) the efficiency falls.

Figure 4 shows the variation of concentration with time using stack reactor system. In this case also, concentration decreases linearly with time upto a concentration of 60 ppm after which it falls exponentially with time. Figure 5 shows the plot of current efficiency vs percentage conversion. In this case also, current efficiency vs percentage conversion shows the same trend as in the central packed bed reactor, but generally the current efficiency is found to be higher in this reactor.

The current voltage characteristics of the three reactors are shown in Fig. 6. It is evident that the stack system with parallel connections for the electrode chambers has resulted in considerable reduction in internal cell resistance as indicated by high current values even at lower voltage as compared with the other reactors.

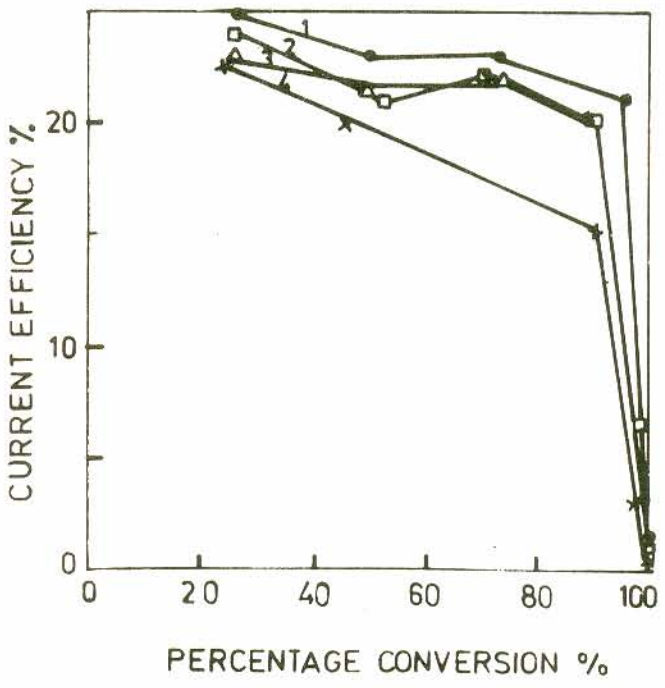

Fig. 3: Variation of current efficiency with percentage conversion (1) 60 $l \cdot h^{-1}$ (2) 120 $l \cdot h^{-1}$ (3) 180 $l \cdot h^{-1}$ (4) 240 $l \cdot h^{-1}$

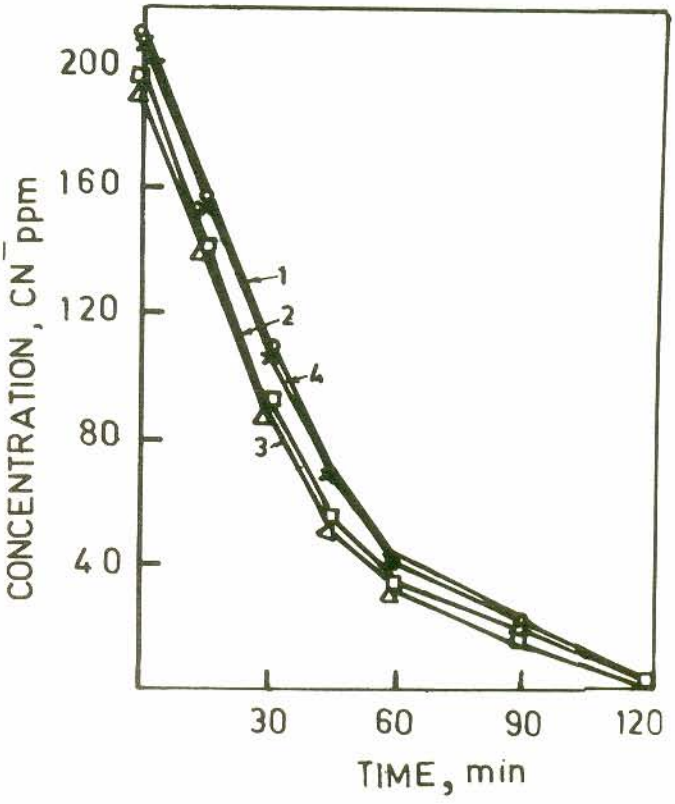

Fig. 4: Variation of concentration with time using stack reactor system (1) 60 $l \cdot h^{-1}$ (2) 120 $l \cdot h^{-1}$ (3) 180 $l \cdot h^{-1}$ (4) 240 $l \cdot h^{-1}$

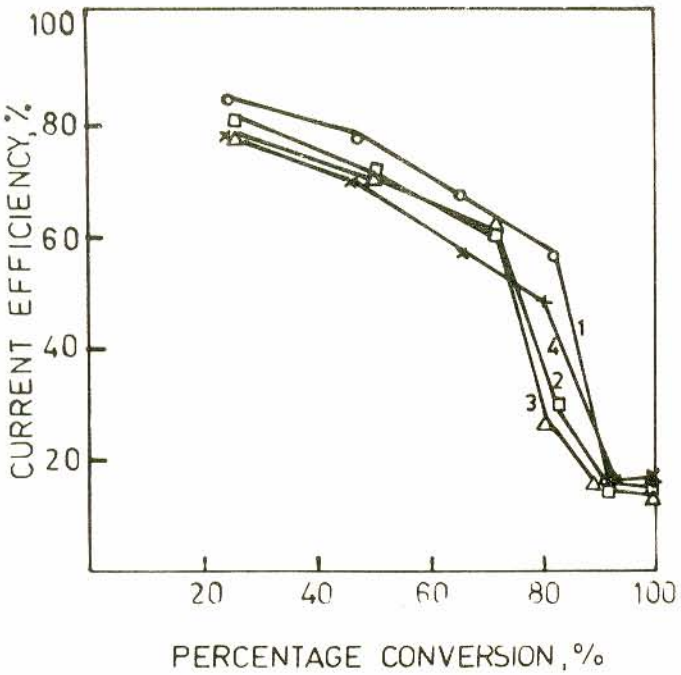

Fig. 5: Variation of current efficiency with percentage conversion (1) 60 l · h^{-1} (2) 120 l · h^{-1} (3) 180 l · h^{-1} (4) 240 l · h^{-1}

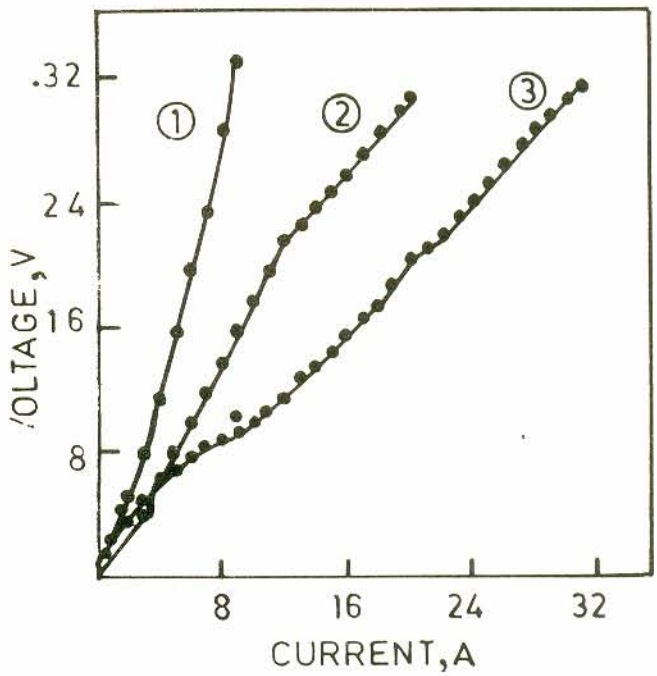

Fig. 6: Current-voltage characteristics of three reactors. Flow rate: 180 l·h^{-1}: (1) CPB with planar cathodes (2) CPB with packed cathodes (3) Stack reactor

Figure 7 shows the comparison of behaviour of three reactors with reference to the removal of cyanide. As can be seen from the figure, the rate of decomposition of cyanide is considerably high in the stack system and the total time required for complete destruction of cyanide to two-thirds of that required with a central packed bed reactor. It is also observed that most of the current in reactors type 1 and 2 has dissipated mostly as heat, as indicated by a temperature rise of 20K in three hours.

The results are summarised in Table I giving the overall current efficiency for the four different reactor systems along with the mass transfer coefficient(K) values calculated for the same. Though there is a decrease in K, there is an improvement in overall current efficiency observed in the stack reactor system. This has to be taken advantage of while scaling up the electrolyser.

CONCLUSION

It is concluded from the investigations that the oxidative destruction of cyanide can be carried out more effectively by using the stack reactor system.

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TABLE-I: Comparison of mass transfer coefficient K and current efficiencies among various reactors

Reactor	Mass transfer coefficient, K							
	60 l · h^{-1} (× 10^{-3})		120 l · h^{-1} (× 10^{-3})		180 l · h^{-1} (× 10^{-3})		240l.h^{-1} (× 10^{-3})	
	K	CE (%)	K	CE (%)	K	CE (%)	K	CE (%)
1. CPB with planar cathode*	1.73	22.6	2.63	22.8	3.4	23.7	3.1	22.5
2. DPB*	1.13	27.3	1.63	31.8	2.23	31.1	0.84	29.2
3. CPB with packed cathodes	2.93	19.4	2.99	19.7	3.2	18.2	2.66	18.6
4. Stack	2.33	51.9	2.66	44.3	2.82	43.4	2.33	46.7

*Results have been taken from Ref. 15 and 16 for comparison

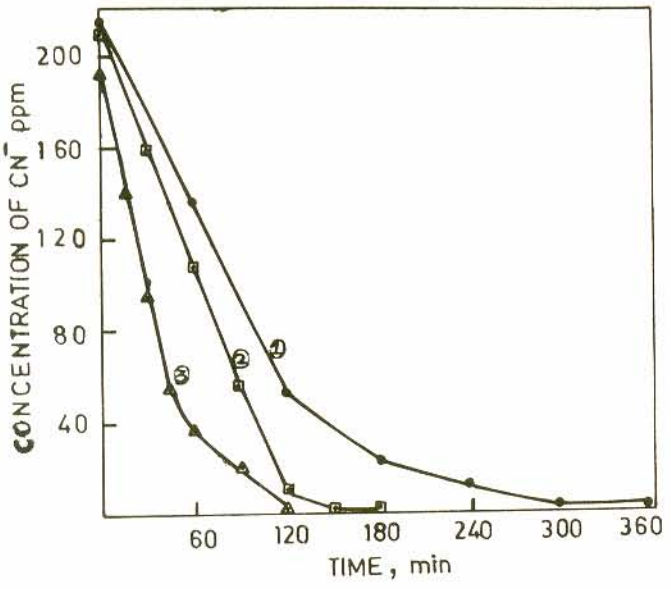

Fig. 7 : Comparison of three reactors. Flow rate: 180 $l \cdot h^{-1}$
(1) CPB with planar cathodes (current 7.9A) (2) CPB with packed cathodes(Current 19.4A) (3) Stack reactor (Current 11.0A)

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