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INVESTIGATIONS ON ELECTROCHEMICAL REDUCTION OF HEXAVALENT CHROMIUM IN INDUSTRIAL EFFLUENTS

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ABSTRACT

Chromium is a potential pollutant in industrial waste waters discharged in both hexavalent as well as trivalent forms. To safeguard the environmental conditions against such toxic pollutants has become a statutory obligation for the industries.

With a view to develop an electrochemical method, experiments were carried out using potassium dichromate plus H_2SO_4 as electrolyte keeping the initial concentration of Cr^{6+} at 200 ppm. The reduction was carried out in a divided cell with sintered PVC as diaphragm using graphite electrodes. The current density was varied from 0.8 to 10 A/dm^2 and the concentration of unreduced Cr^{6+} was determined spectrophotometrically using diphenyl carbazide method as per ISS 2488 (Part II) 1968.

It was observed that the reduction of Cr^{6+} to Cr^{3+} occurs with 40-50% current efficiency at an optimum current density of 5-10 A/dm^2. The concentration of hexavalent chromium could be brought down by electrolysis from an initial value of 200 to zero ppm.

Key words: Cr^{6+} pollutant, pollution control, electro reduction

INTRODUCTION

Chromium in its hexavalent state has been known to be one of the priority pollutants and highly toxic [1]. It is present in chromic acid and chromates. The chromates and dichromates, if ingested, produce serious hazardous effects like skin disorder, nose bleeding and perforation of nasal septum. Prolonged exposure causes liver and kidney diseases and even results in cancer [2]. In the electroplating and metal finishing processes, chromic acid is used in the electropolishing baths, hard chromium plating and for the decorative chromium finishes. Use of chromates as inhibitors is also well known. The extent of chromium content in the waste water depends on various process factors and varies widely from industry to industry, which may be anywhere between 10 and 200 ppm.

Present methods of treatment of hexavalent chromium containing effluents are based on the chemical reduction of Cr^{6+} to Cr^{3+} in acid medium followed by precipitation of the same as $Cr(OH)_3$ in alkaline medium [3] as per the following equations:

$$2\,H_2CrO_4 + 6\,FeSO_4 + 6\,H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 8\,H_2O$$

$$Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 12\,Ca(OH)_2 \rightarrow 2\,Cr(OH)_3 + 6\,Fe(OH)_3 + 12\,CaSO_4$$

The chemical reduction is brought about either by $FeSO_4$ or $NaHSO_3$ or SO_2 in presence of H_2SO_4.

Though the method had been fairly satisfactory, the problem of large consumption of chemicals and also disposal of sludge containing $Cr(OH)_3$ and $Fe(OH)_3$ have been the major disadvantages in the conventional methods. With a view to obviate these difficulties, the electrochemical reduction has been resorted to.

Considerable work has been reported in literature regarding the electrochemical conversion of Cr^{6+} to Cr^{3+} [4]. The major stress had been on the mechanism and kinetics of the electroreduction of chromic acid with a view to understand the mechanism of reactions involved in chromium plating [5-7]. The effects of various anions and cations in high concentration ranges have also been investigated with specific reference to reduction of chromic acid [8,9].

In recent years more attention has been paid to the reduction of Cr^{6+} to Cr^{3+} in very dilute solutions because of the importance with reference to effluent treatment. The Cr^{3+} has been known to be far less toxic than Cr^{6+} and also can be removed easily by precipitation from solutions. Reports are available in literature on the electrochemical reduction of Cr^{6+} using various electrode materials [10, 11] as well as electrochemical reactors [12]. For effluent treatment, it has been reported that the process of electrolytic reduction of chromic acid in presence of $FeSO_4$ using lead electrodes and porous diaphragm has been fairly satisfactory [13]. The reactions involve reduction of chromic acid by $FeSO_4$ in presence of H_2SO_4 and the ferric sulphate is then electrolytically reduced back to Fe^{2+} state with regeneration of H_2SO_4. Consumable iron anodes have also been tried. Though there have been certain attempts made at developing this technique, there are no positive reports of commercial application so far.

With a view to develop the process of electrochemical reduction for application for effluent treatment, the present investigations have been undertaken. The results of a systematic study of the various parameters involved are presented in this paper.

EXPERIMENTAL

Investigations have been carried out on the reduction of Cr^{6+} to Cr^{3+} under galvanostatic conditions using potassium dichromate as the source of hexavalent chromium. The concentration of chromium for investigation was fixed at 200 ppm which is the maximum reported value present in effluents. Preliminary experiments with an undivided cell were unsuccessful and hence a two-compartment cell separated by a porous sintered PVC diaphragm was used for the experiment. Mixture of potassium dichromate (200 ppm Cr^{6+}) and sulphuric acid (200 ppm) was used as the catholyte. In order to avoid diffusion of catholyte into anolyte, the anolyte concentration was maintained at higher level (400 ppm) with sulphuric acid (200 ppm) in all the experiments.

Electrolysis was carried out using plane graphite electrodes at an interelectrode distance of 5 cm. The cathode current density was varied from 0.8 A/dm^2 to 10 A/dm^2 in 5 steps. The cathode potential was measured with reference to SCE. The concentration of the unconverted Cr^{6+} was estimated spectrophotometrically using diphenyl carbazide method [14].

The efficiency for the reaction was calculated assuming that the reaction involves three-electron transfer. In order to find out the maximum extent of conversion possible, experiments were carried out on a continuous basis and the concentration of Cr^{6+} at various intervals was estimated.

RESULTS AND DISCUSSION

The results are presented in Tables I and II and figures 1-3. It can be seen from Table I that the cathode potential increases with current density. With an interelectrode distance of 5 cm, the cell voltage has been found to be fairly high, especially at high current densities. Current efficiency shows an initial decrease with current density from 0.8 to 2 A/dm^2 but on further increase it increases slightly at 5 A/dm^2 which remains fairly the same on doubling the current density.

Table I: Data obtained on the electrochemical reduction of Cr^{6+} to Cr^{3+}

No.	C.d. A/dm^2	Cathode potential V	Cell voltage V	Concentration initial (ppm)	Concentration final (ppm)	Current efficiency %
1.	0.8	1.74	9.9	200	101	48.3
2.	1.0	1.8	11.3	200	121	39.1
3.	2.0	2.18	17.9	200	125	37.6
4.	5.0	2.2	38.3	200	115	42.1
5.	10.0	2.6	67.8	200	111	41.3

Finding that the maximum conversion has been 40-50 % at different current densities under study, the electrolysis was continued aiming towards 100 % conversion of Cr^{6+} to Cr^{3+} by passing excess current over and above the theoretically calculated value based on three-electron transfer for the reaction.

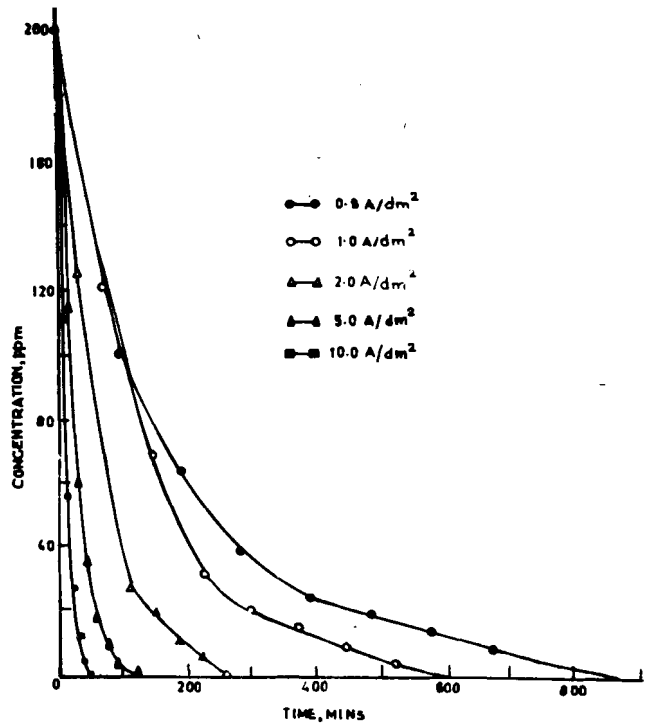

Fig. 1: Variation of concentration with duration of electrolysis

On a continuous trial the variation of concentration of unconverted Cr^{6+} ion with respect of time is presented in fig. 1.

As can be expected, the duration of electrolysis to attain the point of 100 % conversion decreases with increase in current density. The general behaviour seems to be more or less same at all current densities indicating a sharp fall in initial electrolysis followed by a decrease in the rate of conversion at low concentrations of Cr^{6+}.

Fig. 2 shows the variation of concentration with percentage quantity of current for electrolysis at different current densities. Initially there is a very sharp decrease in concentration which shows an almost exponential behaviour with respect to current.

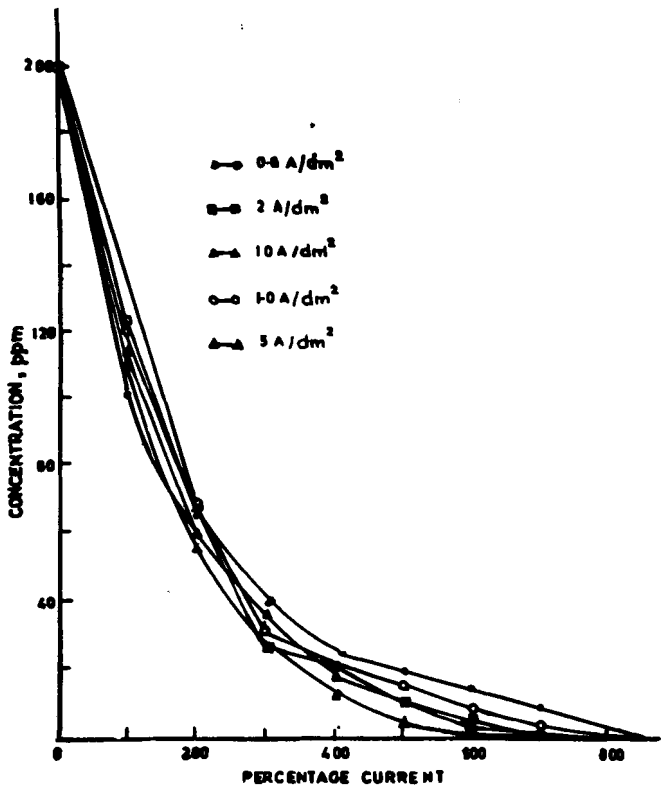

Fig. 2: Variation of concentration with quantity of current

The variation of current efficiency with total quantity of current passed is summarised in Table II.

Table II: Variation of current efficiency (h) at different current densities with total quantity of current passed (Q)

No.	Q (% theoretical)	Current efficiency, % at 0.8	1.0	2.0	5.0	10 A/dm^2
1.	100	48.3	39.1	37.6	42.1	41.3
2.	200	17.6	25.7	28.6	27.2	25.5
3.	300	12.2	19.3	20.6	11.8	13.5
4.	400	7.3	5.4	3.5	8.9	6.9
5.	500	2.9	2.4	5.0	3.9	3.7
6.	600	2.4	3.5	2.5	3.5	1.8
7	700	2.9	2.5	2.5	0.5	–
8.	800	2.4	1.5	–	1.0	–
9.	900	1.5	–	–	–	–

It can be seen that beyond three times the theoretical current the fall in current efficiency is very considerable, and towards the end irrespective of current density, the current efficiency remains very low. It can also be seen from Table II at higher current density, the reduction reaction seems to have been favoured and the point of 100 % conversion of Cr^{6+} to Cr^{3+} is reached much earlier than at low current densities.

Fig. 3 shows the variation of current efficiency with concentration of Cr^{6+} unreduced. Below the concentration of 40 ppm, the efficiency obtained for the conversion reaction is very low (< 10 %) at all current densities. There is not much distinction observed by variation of current density in this region of concentration.

From the above results, it is evident that the two competing reactions at the cathode, namely, reduction of Cr^{6+} ion as well as hydrogen evolution occur simultaneously. Major portion of the current seems to have been used up in the side reactions rather than for the reduction of Cr^{6+}. This is more predominant at lower concentrations of Cr^{6+} than at higher concentrations. The fact that zero concentration of unreacted Cr^{6+} is attained earlier at higher current densities can also be explained on the basis of the fact that the current efficiency remains more or less at 2.5% at low concentrations irrespective of current density employed. Considering all the above factors, an optimum current density of 5 A/dm^2 has been found to be most suitable condition for the reduction of Cr^{6+} to Cr^{3+} ion.

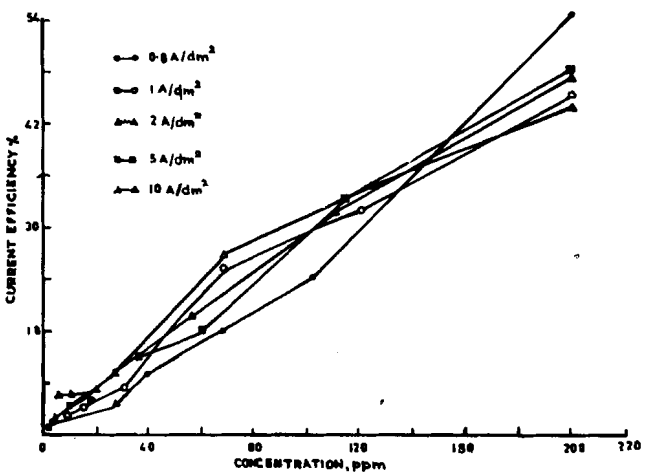

Fig. 3: Variation of current efficiency of reduction with concentration

CONCLUSION

The electrochemical reduction of Cr^{6+} to Cr^{3+} in presence of H_2SO_4 has been found to occur with 40-50 % current efficiency at graphite electrodes at an optimum current density of 5-10 A/dm^2. The concentration of hexavalent chromium was brought down by electrolysis from an initial 200 ppm to zero ppm even though the efficiency below 10 ppm of Cr^{6+} in solution is less than 5 %. It has been planned to use three dimensional electrodes to attain better current and conversion efficiency for the conversion of Cr^{3+} to Cr^{3+} as part of our future programme.

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