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# Removal of Cr<sup>3+</sup> by electrocoagulation with multiple electrodes: Bipolar and monopolar configurations

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#### Abstract

Removal of  $Cr^{3+}$  from aqueous solutions by electrocoagulation (EC) with multiple electrodes was studied with both bipolar and monopolar configurations. The influence of chloride ions, pH, initial  $Cr^{3+}$  concentration and cell current on removal performance was investigated in a batch stirred cell. It was noted that, the enhancement of solubility of  $Cr(OH)_3$  and co-precipitated [Cr, Fe](OH)\_3 in presence of chloride ions results in reduction of removal efficiency. Removal of  $Cr^{3+}$  improved at higher pH due to combined effect of precipitation, co-precipitation as solid solution like species, adsorption, cathodic reduction and sweep coagulation. The maximum  $Cr^{3+}$  removal per unit charge loading was found to be increasing with increase in initial  $Cr^{3+}$  concentration. The cell current efficiency was less than that predicted from Faraday's law of electrolysis for both configurations. The operating cost was estimated from the power cost and cost of electrode material. The former was 40% and the later was 43% higher for bipolar configuration compared to monopolar configuration for achieving final chromium discharge limit of 2.0 mg/l.

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Keywords: Electrocoagulation; Bipolar; Monopolar; Electrode configuration; Current efficiency

# 1. Introduction

The derivatives of trivalent chromium are extensively used as chrome tanning agent in leather treatment, as fungcides in wood preservation, as electroplating agents in the metal finishing industry, mordants in the textile industry, etc. These are also utilized as component of inorganic pigments and in the photographic industry. Aqueous effluents from these processes contain substantial quantity of chromium. Leather industry in particular, generates large quantity of polluting wastewater from tanning of animal hides and skins. Chromium basic sulfate or basic chrome sulfate (BCS) is most widely used for tanning of animal hides and skins in the conventional single bath chrome tanning process. The wastewater streams generated contain about 30-35% of the initial tanning salt [1]. It is therefore essential to treat this effluent prior to discharge into the environment and meet the environmental regulations. Indian standard for discharge of total chromium containing wastewater is 2.0 mg/l [2].

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Reduction of  $Cr^{6+}$  to  $Cr^{3+}$  and subsequent lime precipitation is most popular method for removal of chromium from wastewater [3]. Due to poor sedimentation characteristics of the precipitated particles, higher settling time and larger thickener area is generally required. Adsorption is often used to remove the heavy metals from wastewater. But the known shortcoming of the process is the difficulty to regenerate the adsorbents and the process performance is equilibrium limited [4]. The advanced treatment technologies like membrane separation [5] and ion exchange [6] have disadvantages of high removal cost. Recently electrocoagulation (EC) has received considerable attention for treatment of wastewater from various industrial processes. Iron is employed as electrode material and dissolution of the same generates  $Fe^{2+}(aq)$  ions. The ferrous ions transform to  $Fe^{3+}(aq)$  at proper pH range. Ferric ions generate various monomeric and/or polymeric amorphous metal oxy-hydroxides such as Fe(OH)<sub>3</sub>,  $Fe(OH)_4^-$ ,  $Fe(H_2O)_3(OH)_3^0$ ,  $Fe(H_2O)_6^{3+}$ ,  $Fe(H_2O)_5(OH)^{2+}$ ,  $Fe(H_2O)_4(OH)^{2+}$ ,  $Fe_2(H_2O)_8(OH)_2^{4+}$ ,  $Fe(H_2O)_6(OH)_4^{4+}$ , etc. [7] and co-precipitate as [Cr, Fe](OH)<sub>3</sub> [8]. Moreover with progress of EC, the soluble metal hydroxides formed increase the solution pH. At elevated pH  $Cr^{3+}$  ion is precipitated as  $Cr(OH)_3$ , Cr(OH)<sub>4</sub> [9].

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Electrocoagulation of wastewater containing coloring materials [10–12] suspensions of ultra-fine particles [13], boron [14], nitrite [15], fluoride [16], arsenic [17], chemical mechanical polishing (CMP) wastewater [18], tannery effluents [19], laundry wastewater [20], etc. have proved successful. Remarkable removal of heavy metals from wastewater containing heavy metals (Cr, Pb, Zn, etc.) also has been reported by EC [21–23]. Electrocoagulated sludge contains less bound water and is therefore readily settleable. The supernatant contains less total dissolved solids compared to the chemical coagulation. In case of EC using a pair of electrodes, only on the one side of an electrode is effective. Both sides of an electrode except the end electrodes are effective when the electrodes are connected in monopolar and as well as in bipolar arrangements.

No literature could be found on treating of effluent generated from chrome tanning process by EC. It was therefore thought prudent to investigate removal of  $Cr^{3+}$  from wastewater by EC using multiple electrodes. Effect of operating parameters such as cell current, pH and conductivity of the solution, etc. has been studied on  $Cr^{3+}$  removal performance. The operating cost of electric power and the cost due to electrode consumption in bipolar and monopolar electrode arrangements were investigated.

### 2. Experimentations

#### 2.1. Chemicals

One liter (8000 mg/l) stock solution of  $Cr^{3+}$  was prepared with distilled water by dissolving about 60 g of basic chrome sulfate (BCS) of tanning use quality procured from M/s Chandni Chemical Pvt. Ltd., Kanpur, India. BCS solutions of desired concentrations were prepared by appropriate dilution of the stock solution. Initial pH of solution was adjusted prior to each experiment with either 0.1(N) NaOH and/or HNO<sub>3</sub>. The change in pH was noted with progress of EC. Sodium chloride was added to have Cl<sup>-</sup> concentration close to the order of the same present in the effluent streams from chrome tanning process. Solution conductivity and the solubility of chromium hydroxides are considerably affected by presence of chloride ions [9]. Fig. 1 depicts



Fig. 1. Influence of pH on solubility of  $Cr(OH)_3$  in presence of chloride ions [9].

the solubility of  $Cr^{3+}$  in aqueous solution not containing  $Cl^{-}$  and in presence of  $Cl^{-}$  at different pH values. Any point below the solid and dashed line in the solubility curve indicates that  $Cr^{3+}$ is only present in dissolved states without  $Cl^{-}$  and in presence of  $Cl^{-}$  respectively.

## 2.2. Quantitative analysis

Samples were drawn periodically during the EC experiments. These were centrifuged at 5000 rpm to get the clear liquid and settled sludge for quick separation, minimizing any further removal due to post EC contact between sludge and solution. Atomic absorption spectrophotometer (Analyst-700 Perkin-Elmer, USA) was used for determination of the chromium and iron contents in solution and in sludge with air–acetylene flame at 357.9 and 248.3 nm wavelengths, respectively. The pH of solutions and/or supernatants was measured using a pH meter (Type CL-46, Toshniwal Instruments, India). A digital conductivity meter (Model 611E, EI products, India) was used to measure the ionic conductivity of aqueous phase.



Fig. 2. Schematic electrodes configurations in the reactor.

#### 2.3. Electrode configurations

The electrodes are made of mild steel (MS) sheets placed parallel to each other inside the reactor containing the solution of basic chrome sulfate. The electrode configuration scheme is presented in Fig. 2. The arrangements illustrated in the figure differ in the manner of electrical connection to the DC power source. In monopolar configuration, alternative electrodes were joined to the power supply terminals of opposite polarity, giving a number of individual reactor units of monopolar electrode arrangement. In this system each unit operates at the same voltage and the total current in the reactor (cell current) is the sum of the individual unit currents.

In bipolar arrangement, only the extreme electrodes are connected to the power source. Every electrode excluding the electrodes at the end acts as an anode on one side and cathode on the other side. Each adjacent electrode pair acts as single unit. The total voltage drop in the system is the sum of the individual unit voltages [15].

#### 2.4. Experimental procedure

Mild steel electrodes each having the dimensions of  $130 \text{ mm} \times 58 \text{ mm} \times 0.5 \text{ mm}$  with submerged surface area of 30.74 cm<sup>2</sup> were used. Electrodes were sanded and cleaned with dilute H<sub>2</sub>SO<sub>4</sub> before each experiment to remove passive oxides layer from electrode surfaces. All inter electrodes distance were 22 mm. The reactor was a rectangular Perspex container containing the 800 ml BCS solutions. The electrodes were spaced by a slotted support at the side of the reactor. Enough clearance was given at the bottom for the stirrer bar to rotate at the centre of the bottom of the reactor and agitate the solution. The contents in the electrocoagulator were agitated at 450 rpm to get a homogenous suspension. A magnetic stirrer, make Tarsons India Ltd., Model-MC02 was used for this purpose. Constant current during EC was maintained by appropriately adjusting the impressed cell voltage from a regulated (Aplab Model-7145) DC power supply. All experiments were conducted at around 30 °C.

## 3. Results and discussion

Various parameters of EC were investigated and the results are presented in this section.

#### 3.1. Electrodes—monopolar and bipolar arrangements

The cell current determines the coagulant generation rate, the rate of bubble production, its size and distribution in the reactor with different electrode configurations [15]. The operating conditions of the experiments are shown in Table 1. Fig. 3 depicts the cumulative % removal of Cr<sup>3+</sup> with time of EC with both electrode arrangements.

Different regions of  $Cr^{3+}$  removal can be seen with both electrode configurations during EC as shown in the figure. During electro-coagulation many processes of  $Cr^{3+}$  removal can take place simultaneously: precipitation, sweep coagulation, co-precipitation as  $[Cr_xFe_{1-x}](OH)_3$ , cathodic reduction, and

Table 1

	perating	conditions	parameters
_			

ananalan	
onopolar	Bipolar
00	1000
33.3	1000
10.84	32.52
30.74	30.74
22	22
4	4
00	800
00	1700
20	1820
3.4	3.4
5.5	6.0
	000 00 33.3 10.84 30.74 22 4 00 00 20 3.4 5.5

adsorption. Cathodic reduction (metal is formed and deposited on cathodes) contributes to remove a fraction of  $Cr^{3+}$  from solution mainly at the start of the experiment.

In case of bipolar electrode configuration, three regions can be distinguished. In the initial period (from 0 to 5 min) sluggish rate of Cr<sup>3+</sup> removal is observed. During this period pH rises from 3.4 to 3.8. In this pH range,  $Cr^{3+}$  is significantly soluble (Fig. 1) and low rate of removal is observed mainly due to cathodic reduction and co-precipitation. In second part from 5 to 40 min, Cr<sup>3+</sup> gets removed at a relatively higher rate while solution pH increases from 3.8 to 5.5. In fact a point of inflexion is observed at the junction of these two phases of removal rate. The pH at this point of inflexion is close to 3.8. At this pH the solubility of  $Cr^{3+}$  is close to 1700 mg/l, which is the  $Cr^{3+}$  content of the solution. Solubility of Cr<sup>3+</sup> has logarithmic relationship with pH, and further increase of pH brings out a substantial reduction of solubility leading to a high rate of  $Cr^{3+}$  removal in this zone. After 40 min of EC, cumulative removal of Cr<sup>3+</sup> remains steady as most of Cr<sup>3+</sup> gets removed and the removal efficiency falling due to already low concentration of  $Cr^{3+}$ .



Fig. 3. Removal of Cr<sup>3+</sup> with time of EC for different electrode configurations.



Fig. 4. Solution pH with time of treatment corresponding to Fig. 3.

In case of monopolar arrangement the initial sluggish removal rate period continues up to 20 min when the pH rises from 3.4 to 4.5 with similar explanation as in case of bipolar electrodes. The initial period is longer due to lower individual unit current. The electrodes were noticed to be more fouled in monopolar configuration. The second region continues up to 60 min as the removal rate is lower compared to bipolar arrangement. In 20 min about 18.8% of Cr<sup>3+</sup> is removed with monopolar electrode arrangements whereas the bipolar electrode arrangement takes only 8.5 min to achieve the same removal level. Generation of coagulant iron hydroxides is higher for bipolar arrangement of electrodes. Cr<sup>3+</sup> is removed at a faster rate due to such higher coagulant generation rate and the faster removal region is quickly achieved in case of bipolar electrode configurations. Concentration of residual iron hydroxides is always higher with bipolar arrangement of electrodes and this result in higher solution pH. Fig. 4 corroborates this. Higher pH with bipolar electrode arrangement helps in precipitating Cr<sup>3+</sup> as insoluble chromic hydroxide, which is a favorable factor in improving the % removal of  $Cr^{3+}$ . After 50 min of EC more or less complete removal (99.9%) of Cr<sup>3+</sup> was noted in case of bipolar arrangement but the removal was only 81.5% in case of monopolar electrode arrangement. After 60 min the removal figure for monopolar arrangements improved only to about 94.4%. More bubbles are generated at higher current and in case of bipolar configuration, as this improves the mixing and the removal. This effect may not be appreciable as the system is already agitated.

Complete removal of  $Cr^{3+}$  was achieved around pH 6.0, though at this pH, chromium and iron are partly in the form of  $Cr(OH)^{2+}$  and Fe(OH)<sup>2+</sup> which are soluble. Formation of solid solution like species [Fe or Cr](OH)<sub>3</sub> by co-precipitation and due to formation insoluble chromic hydroxide, high removal (about 99.9%) is noted in case of bipolar configuration [9]. It may be mentioned here that XRD analysis of electrocoagulated sludge generated showed amorphous nature and agrees with the observation made by Saas and Rai [8]. Fig. 4 shows the variation of pH during EC. Initially the solution pH increases at high rate and later the rate falls. This is attributed to increase in molar OH/Fe ratio as polymeric hydroxides of Fe<sup>3+</sup> are formed [24].

# 3.2. Role of Cl<sup>-</sup> ions

The effect of extraneous ions during EC of Cr<sup>3+</sup> has been studied in presence of chlorides ions. Effluents from chrome tanning operations contain about 2000 mg/l Cl<sup>-</sup> ions [1]. About 3000 mg/l NaCl was added to the solution to increase its conductivity for minimizing the energy consumption. This corresponds to Cl<sup>-</sup> concentration of 1820 mg/l. The effect of chloride ions on removal of Cr<sup>3+</sup> by EC is studied with 1700 mg/l initial Cr<sup>3+</sup> concentration, 3.4 initial pH, 500 mA cell current, 450 stirrer rpm, 22 mm electrode spacing and 30.74 cm<sup>2</sup> effective electrode area with both bipolar and monopolar electrode configurations. Addition of NaCl increased the solution conductivity by about 67% i.e. from 5.95 to 9.94 m mho/cm. During EC of Cr<sup>3+</sup> solutions with MS electrode the electrode surfaces get covered with metal oxides or hydroxides that are mainly a mixture of hydrated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> of low solubility [9].

Chloride ions catalyze the dissolution of the electrode material by the pitting corrosion phenomenon, which is a type of localized corrosion caused by a high chloride concentration in the solution [25]. Localized corrosion of iron, aluminum and other similar metals [26–29] takes place through: (i) adsorption of the aggressive anions such as  $Cl^-$  on the oxide layer due to ion–ion force of interaction; (ii) chemical reaction of the adsorbed  $Cl^-$  with the ion in the oxide layer; (iii) dissolution or thinning of the layer; (iv) direct attack of the exposed metal and start intense localized dissolution (localized corrosion). Therefore it was expected that, EC in presence of NaCl might improve the removal efficiency of  $Cr^{3+}$  by increasing the available metal coagulant in solution due to reduction the blan-



Fig. 5. Effect of chloride ions on removal of  $Cr^{3+}$  with the time of EC for different electrode configurations.

keting oxides layer and enhancement of the anodic dissolution of the electrode material whereas the contrary is seen in Fig. 5. The figure shows that presence of Cl<sup>-</sup> ions decrease the removal of  $Cr^{3+}$  during the experiment by about 3.6% with both electrode arrangements. At same pH of solution, presence of Cl<sup>-</sup> ions increases the solubility of  $Cr^{3+}$  ions is higher as can be seen in Fig. 1. This explains lower removal of  $Cr^{3+}$  in presence of Cl<sup>-</sup> ions as observed. Partial conversion of Fe(OH)<sub>3</sub> to soluble FeCl<sub>3</sub> species may be another possible reason for lower removal of  $Cr^{3+}$  in presence of Cl<sup>-</sup> ions.

# 3.3. Effect of pH

The solubility of Cr<sup>3+</sup> is affected by several factors, one of which is the pH of the solution.  $Cr^{3+}$  in aqueous phase forms chromic hydroxides and the solubility of chromic hydroxides as a function of pH is already shown in Fig. 1. It can be seen that  $Cr^{3+}$  is increasingly soluble at both low and high pH. Minimum solubility of  $Cr^{3+}$  is in the pH range of 5.8–9.3 in solutions not containing chloride ions. Animal hides and skins are generally tanned at pH close to 3.5 [30] in single bath chrome tanning operation. The effect of pH on removal of Cr<sup>3+</sup> is therefore investigated at two different initial pH values of 3.4 and 5.0 with both types of electrode arrangements. EC experiments were conducted with 1700 mg/l initial  $Cr^{3+}$  concentration, 1820 mg/l of Cl<sup>-</sup> concentration, 450 stirrer rpm, 22 mm electrode spacing and  $30.74 \,\mathrm{cm}^2$  effective electrodes area. The cumulative progress of  $Cr^{3+}$  removal in these cases with both electrode arrangements is shown in Fig. 6.

With bipolar electrode arrangement, after 20 min of EC, 8% more  $Cr^{3+}$  was removed when the initial pH was 5.0 instead of 3.4 (Fig. 6). Increase of pH during the run precipitates  $Cr^{3+}$  as insoluble  $Cr(OH)_3$ . At higher pH both the chromium and iron co-precipitate leading to low residual concentration of  $Cr^{3+}$  and  $Fe^{2+}/Fe^{3+}$ . With bipolar electrode arrangement after 25 min of EC the rate of chromium removal becomes nearly constant with initial pH of 5.0.



Fig. 6. Effect of initial pH on removal  $Cr^{3+}$  with time of EC.



Fig. 7. Residual iron concentration with progress of treatment with bipolar mode of EC corresponding to Fig. 6.

It can be seen from Fig. 6 that in monopolar electrode configuration the effect of pH on removal efficiency is not as dominating as with bipolar arrangement. After 60 min of EC, compared to 14.6% increase in case of bipolar arrangement, the increase is only 5.6% when the initial pH is 5.0 in place of 3.4. The final pH of the solutions increase to 5.4 and 5.2 after 60 min of EC from initial of 5.0 with bipolar and monopolar electrode configurations. More  $Cr^{3+}$  is readily precipitated as hydroxides with higher pH (after 60 min) with bipolar arrangement and this explains the higher removal of  $Cr^{3+}$  with bipolar electrode arrangement compared to monopolar electrode configuration.

Fig. 7 shows the changing concentration of iron in solution during EC with bipolar electrode configuration. The iron concentration in the solution falls when the initial pH is increased from 3.4 to 5.0. After 60 min of EC, the iron concentrations in solution were 595 and 550 mg/l for the initial pH values of 5.0 and 3.4, respectively. Similar result was obtained in case of monopolar electrode configuration but is not shown here.

#### 3.4. Effect of cell current

The effect of the cell current on removal of  $Cr^{3+}$  was studied at 500 and 1000 mA total cell current levels. These experiments were conducted with 1700 mg/l initial  $Cr^{3+}$  concentration, 3.4 initial pH, 1820 mg/l Cl<sup>-</sup> concentration, 450 stirrer rpm, 22 mm electrodes spacing and 30.74 cm<sup>2</sup> effective electrode area. Fig. 8 shows the experimental results for both electrode arrangements. It is seen that at lower cell current (500 mA) with monopolar electrode arrangement, the nature of progress of  $Cr^{3+}$  removal is distinctly different from other three cases. In this case with low individual cell current (~167 mA), the iron hydroxides generation is lowest. Much of this remains close to the electrode surfaces, contributing to electrode passivation effect. Also the electrodes were found visually more fouled up. Therefore the amount of the iron hydroxides available in solution to form com-



Fig. 8. Effect cell current on removal of  $Cr^{3+}$  with the time of EC for different electrode configurations.

plexes and precipitate  $Cr^{3+}$  is low. This explains the comparative low removal of  $Cr^{3+}$  with 500 mA cell current and monopolar electrode configuration. It is evident from the Fig. 8 that for reducing  $Cr^{3+}$  to low level (99%+ removal) within 50–60 min, 1000 mA cell current is suitable with bipolar arrangement of electrodes.

Often the objective of EC is to achieve the discharge limit of  $Cr^{3+}$  concentration in the supernatant. Fig. 9 shows the time required time to reach the CPCB (India) framed maximum discharge concentration (2.0 mg/l) starting from 1700 mg/l initial Cr concentration in varying individual unit current in bipolar and monopolar electrode arrangements. Others conditions are: 3.4 initial pH, 1820 mg/l Cl<sup>-</sup> concentration, 450 stirrer rpm, 22 mm electrode spacing and 30.74 cm<sup>2</sup> effective electrode area. In fact the total cell currents were 1000, 1500 and 2000 mA, which have then corresponding unit currents plotted in abscissa. The final pH of the solution when the limiting concentration of  $Cr^{3+}$  is achieved is shown in Table 2.



Fig. 9. Time to meet the Cr<sup>3+</sup> discharge limit (mg/l) with different individual unit current.

Table 2	
Final pH of the solution when the limiting concentration of $Cr^{3+}$ is achieved	ł

Cell current (mA)	pH			
	Monopolar configuration	Bipolar configuration		
1000	5.61	5.91		
1500	6.08	6.55		
2000	6.27	6.69		

The time required to achieve the concentration limit for same (total) cell current is higher for monopolar electrode arrangement compared to bipolar arrangement as expected. On doubling total cell current from 1000 to 2000 mA, the time required to achieve the limit is reduced from 66.4 to 42.7 min with monopolar arrangement. The bipolar arrangement has shown lower cell efficiency than the monopolar arrangement of electrodes. Fractional cell current efficiency was calculated from the equation: current efficiency,  $\eta_i = m_{\text{expt}}/m_{\text{f}}$ ; where,  $m_{\text{expt}}$  is actual amount of metal dissolution and  $m_{\rm f}$  is based on Faraday's law.  $m_{\rm expt}$  was calculated from the concentration of Fe in solution and sludge. Now  $m_f = MNIt/2F$ , where, I is individual unit current (A), t (s) the time of EC, M the molecular weight of iron (g/mol), F the Faraday's constant (C/mol) and N the number of individual electrolysis cell, which is 3 for the present work. The current efficiency with 500 mA (total) cell current was about 64.5% and 91.7% for bipolar and monopolar electrodes configurations. These were the average  $\eta$  calculated from the values of the same after 20, 40 and 60 min of EC. At the same total cell current the current efficiency of the cell is considerably lower with bipolar arrangement of electrodes. Individual unit current in case of bipolar configuration is three times the monopolar case. At higher cell current the over-potential of the cell is high and the cell current efficiency falls due to competitive reactions such as decomposition of water.



Fig. 10. Effect of initial  $Cr^{3+}$  concentration on removal of  $Cr^{3+}$  with the time of EC for bipolar electrode configurations.

Initial Cr <sup>3+</sup> concentration (mg/l)	mg Cr <sup>3+</sup> removed/charge loading (C)	Time (min)	Concentration of Cr <sup>3+</sup> in solution (mg/)	% removal of Cr <sup>3+</sup>
1700	0.684	19.1	671	60.0
2250	0.710	21.3	1003	52.0
3000	0.770	24.5	1580	47.2

Table 3Peak values corresponding to Fig. 10

# 3.5. Effect of initial $Cr^{3+}$ concentration on EC

Cumulative removal of Cr<sup>3+</sup> from solution progresses with EC. The removal effected (mg of  $Cr^{3+}$ ) per unit charge loading (C) is shown against different % cumulative removal of  $Cr^{3+}$ in Fig. 10 for bipolar arrangement of electrode with 1000 mA cell current, 3.4 initial pH, 1820 mg/l Cl-, 450 stirrer rpm, 22 mm inter electrode distance and 30.74 cm<sup>2</sup> effective electrode area. Each curve for an initial concentration shows a peak, signifying fall in removal per unit charge loading. As the  $Cr^{3+}$ concentration in the solution falls, less Cr<sup>3+</sup> join the sludge even though EC continues. For 1700 mg/l initial Cr<sup>3+</sup> loading the solution is almost exhausted of  $Cr^{3+}$  and the fall is very sharp. With higher Cr<sup>3+</sup> loading the fall is less sharp as relatively more Cr<sup>3+</sup> still remain in solution. With initial Cr<sup>3+</sup> concentration of 3000 mg/l, the Cr<sup>3+</sup> removed (mg)/charge loading (C) increases for cumulative removal up to about 40%. It signifies that the amount of  $Cr^{3+}$  removal increases more rapidly than the amount of electricity consumption (in term of charge loading) mainly due to pH increase during EC as already discussed in Section 3.1. From 40 to 60% of cumulative removal the ratio reaches a plateau and it decreases beyond that range. While the ratio remains steady, it corroborates that the amount of Cr<sup>3+</sup> removal increase as fast as the amount of electricity consumed. The inevitable decreasing zone follows with the concentration of  $Cr^{3+}$  in solution falling as the cumulative removal % going high.

For different initial  $Cr^{3+}$  concentrations: (i) the peak values of  $Cr^{3+}$  (mg) removal per unit charge loading; (ii) the time; (iii)  $Cr^{3+}$  solution concentration at which it occurs is shown in Table 3. It also contains the % removal at those points.

Though the residual concentration of  $Cr^{3+}$  are substantially different, the time to achieve the said peak remain around 20–25 min. Higher initial  $Cr^{3+}$  concentration therefore affects the  $Cr^{3+}$  removal efficiency in an adverse way, for which probably the reason being a higher concentration of  $Cr^{3+}$  compared to the amount of iron hydroxides generated/available for coagulation of the same.

Fig. 11 shows the same parameters with monopolar electrode arrangement. In this case the plots show similar nature considering the fact that EC was carried to a lesser extent (lower % removal of  $Cr^{3+}$ ).

## 3.6. Operating cost

EC is considered to reduce  $Cr^{3+}$  concentration to CPCB permitted a maximum level of 2 mg/l. The major cost components for EC are (i) power cost; (ii) electrode cost; (iii) sludge



Fig. 11. Effect of initial  $Cr^{3+}$  concentration on removal of  $Cr^{3+}$  with the time of EC for monopolar electrode configurations.

disposal cost. Dry sludge from EC contained about 29-45% chromium and has potential for use in metallurgical industries and its disposal cost is not considered. The costs of treating each m<sup>3</sup> solution to final Cr<sup>3+</sup> concentration of 2 mg/l are shown in Figs. 12 and 13 for monopolar and bipolar electrode arrangements. In each case the initial Cr<sup>3+</sup> concentration is 1700 mg/l, initial pH 3.4, Cl<sup>-</sup> concentration 1820 mg/l, 4 nos. of electrodes, 22 mm electrode gap, 450 stirrer rpm and 30.74 cm<sup>2</sup> effective



Fig. 12. Operating cost with different cell current for monopolar electrode arrangement.



Fig. 13. Operating cost with different cell current for bipolar electrode arrangement.

electrode area. The unit cost of power and electrode are considered to be US\$ 0.1/KWh and US\$ 0.8/Kg. It is noted that in the range of investigation the costs vary practically linearly with cell current with both bipolar and monopolar configurations electrodes.

#### 4. Conclusions

Removal of  $Cr^{3+}$  by EC from aqueous solution with both monopolar and bipolar electrode configurations is a feasible process. Almost complete removal (99.9%) of Cr<sup>3+</sup> is noted after 50 min of EC in case of bipolar electrode arrangement at 1000 mA cell current against 81.5% removal for monopolar electrode configuration. In presence of 1820 mg/l Cl<sup>-</sup> ions about 3.6% decrease in Cr<sup>3+</sup> removal is found with both electrode configurations. EC with bipolar electrode configuration significantly improves the removal of Cr<sup>3+</sup> at higher pH due to combined effect of chemical precipitation, co-precipitation, adsorption, cathodic reduction and sweep coagulation. This effect is felt to a lesser extent in case of monopolar configuration. Current efficiency based on Fe dissolution was found to be about 64.5% and 91.7% for bipolar and monopolar configuration. The mass of  $Cr^{3+}$  removed per unit charge loading shows a peak between 20 and 25 min of EC. The power cost and cost of electrode material was 40% and 43% higher in case of bipolar configuration compared to monopolar configuration for achieving the discharge limit.

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