



## Removal of Cr<sup>3+</sup> by electrocoagulation from simulated wastewater

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**Abstract:** Trivalent chromium (Cr<sup>3+</sup>) removal from aqueous solution by electrocoagulation using iron electrodes material was investigated in this paper. Effects of current density, initial concentration of Cr<sup>3+</sup>, operating time, pH, electrode distance, and operating cost have been investigated. At higher current density and solution pH, remarkable removal of Cr<sup>3+</sup> was observed. Experiments have been show that the maximum removal percentage of the Cr<sup>3+</sup> 99.89% was at initial concentration 1000 mg/L, current density 9.34 mA/cm<sup>2</sup> and reaction time 1 hours. Energy consumption was calculated for Cr<sup>3+</sup> removal at different time. The method is observed to be very effective in the removal Cr<sup>3+</sup> ion from aqueous solution. Electrocoagulation process need simple equipment, designable any size, use any chemical substances and low operating cost.

**Keywords:** Electrocoagulation; current density; trivalent chromium; wastewater

### INTRODUCTION

The industries of tannery, textile and other industries generate a lot of pollutants. Chromium is one of the major sources of environmental pollution. In the environment, chromium occurs mainly in trivalent and hexavalent forms. The hexavalent chromium Cr (VI) is toxic and carcinogenic while the element in its trivalent state Cr(III) is an essential nutrient for plant and animals metabolism in trace amounts [1]. However, Cr(III) has also been shown to be a potential hazard, especially in the aquatic environment. Conventional chromium removal methods include adsorption [2], chemical precipitation [3], biological degradation [4], ion exchange [5], solvent extraction [6], biosorption [7], membrane separation [8] and electrochemical methods [9]. In recent years, electrocoagulation has been successfully used to treat a variety of industrial wastewater. Chrome tanning process use basic chrome sulfate (BCS) [Cr(OH)SO<sub>4</sub>] solution for tanning of animal skins/hides.

The EC process using iron electrodes generate low concentration non-toxic iron oxides and/or hydroxide species in the aqueous media by the electrochemical dissolution of electrode material [10, 11].

With iron as electrode materials the reactions are

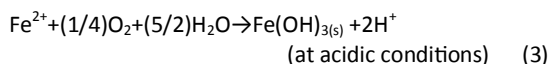
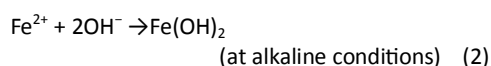
On the anodic electrode surface:



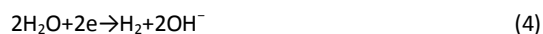
At the vicinity of the electrode:

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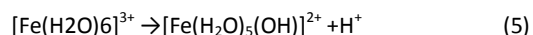
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On the cathodic electrode surface:

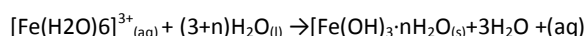
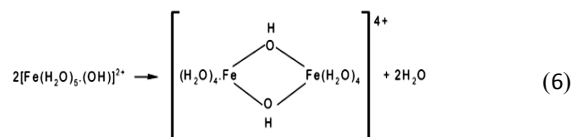


Depending on pH, Fe<sup>3+</sup> and/or Fe<sup>2+</sup> ions form various monomeric and/or polymeric metal hydroxides complexes. The most common complex is the hydrated ion [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>. The complex tends to hydrolyze forming yellowish solutions in the pH range 2–3



In the pH range 4–5 the hydroxo - complexes reorient to a binuclear iron complex species having a high surface charge

In aqueous solutions having pH > 4, the octahedral



hexaaquaions, [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, gives a red-brownish gelatinous precipitate of hydrous oxide.

In the presence of dissolved iron, trivalent chromium is coprecipitated with ferric iron to form the solid

solution of  $[\text{Cr}, \text{Fe}](\text{OH})_3$  which has lower solubility than  $\text{Cr}(\text{OH})_3(\text{s})$  [12]. At higher pH,  $\text{Cr}^{3+}$  is readily precipitated as  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  and the solubility is low between 6.5 and 10. Minimum solubility is at pH 8.5 in solutions containing chloride ions. Bigger aggregates/flocs are formed due to sequential interaction of the hydroxides. The settled sludge/floc phase is easily removed from aqueous phase.

This work focuses on removal of BCS by electrocoagulation using mild steel as electrode material. The process parameters investigated include: operating time, current density, pH, initial  $\text{Cr}^{3+}$  concentration, inter electrode distance and operating cost. In Mongolia wastewater treatment plant used manganese sulfate in order to simultaneously precipitate chromium and sulfide. This method suffer from some drawbacks such as high capital and operating costs, large input of chemicals and incomplete removal. Cheap and effective tannery wastewater treatment method is needed. Electrocoagulation can be compared as an alternative treatment method with many advantages as simple equipment, easy operation and automation, a short retention time, low sludge production and no chemical requirement.

## EXPERIMENTAL

**Chemicals:** Tannery wastewater effluents contain 1000–2000, even up to 3000 mg/l  $\text{Cr}^{3+}$ . Simulated wastewater 1000mg/l Cr(III) solution was prepared from basic chrome sulfate (BCS) ( $[\text{Cr}(\text{OH})\text{SO}_4]$ ) in demonized water and the pH was adjusted using 0.01 M HCl or 0.01 M NaOH. The pH was not controlled during electrocoagulation, but the final pH was recorded. Sodium chloride (1000 mg/L) as supportive electrolyte was added to increase the ionic conductivity of the solution.

**Chemical analysis:** UV– visible spectrophotometer (1,5-diphenyl carbazide method) for the determination of the total chromium content in tannery wastewater after complete conversion of trivalent chromium to hexavalent chromium.

**Experimental procedure:** Mild steel electrode dimension 68mm×62mm×0.2mm having submerged surface area of 89.52cm<sup>2</sup> were used for the batch electrocoagulation studies. Electrodes were sanded and cleaned with dilute  $\text{H}_2\text{SO}_4$  before each experiment to remove passive oxides layer from electrode surfaces. All inter electrodes distance 3.0 cm. The reactor was chemical beaker container containing the 400 ml BCS solutions. The solution was agitated during EC with a Teflon coated magnetic stirrer. All experiments were conducted at around 25°C. Figure 1 shows the schematic representation of the experimental setup.

## RESULTS AND DISCUSSIONS

**Effect of current density and operating time:** In any

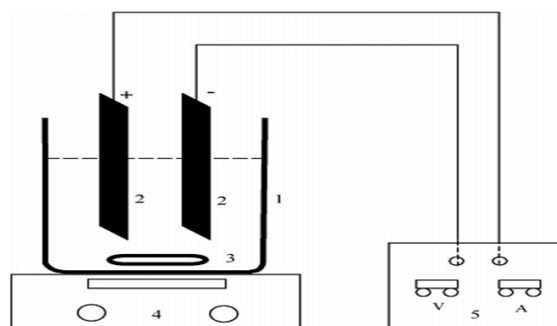


Fig. 1. Schematic process arrangement.

(1) Chemical beaker ; (2) mild steel electrode pair; (3) magnetic stirrer bar; (4) magnetic stirrer; (5) dc power supply (V, voltage regulator and A, current regulator)

EC process current density ( $\text{A}/\text{m}^2$ ) and time of electrolysis are important operational parameters setting the ultimate removal and defining the electrical energy and power consumption so eventually the ultimate operating cost for the process. Current density during EC experiments were varied by changing cell current and as well as electrodes area. Figure 2 showed the effect of current density on EC at constant electrodes surface area (89.52 cm<sup>2</sup>). Each of

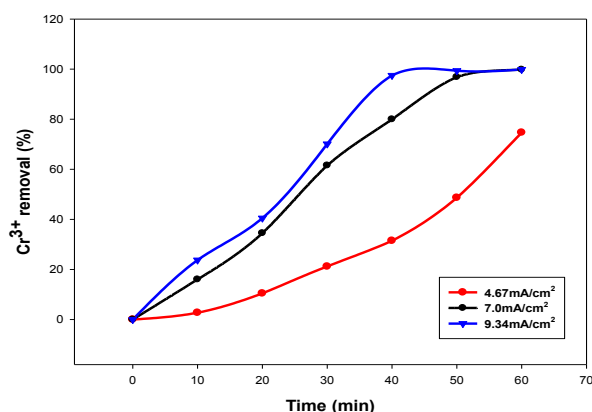


Fig. 2.  $\text{Cr}^{3+}$  removal for different current density operations (1000 mg/L initial  $\text{Cr}^{3+}$  concentration, initial pH 3.4, 85.65 cm<sup>2</sup> electrode area, 1000 mg/l NaCl)

these experiments was conducted with same initial concentration of 918.3 mg/l of Cr. After 60 min of EC, 74.66, 99.82 and 99.89%  $\text{Cr}^{3+}$  from the liquid phase was found to be transferred to sludge phase at current densities of 4.67, 7.0 and 9.34 mA/cm<sup>2</sup>, respectively. Therefore, effective removal of  $\text{Cr}^{3+}$  from the supernatant by electrocoagulation is observed at higher current densities. Higher dissolution of electrode material (Faraday's law) with high rate of formation of monomeric and/or polymeric iron hydroxides result in significant improvement in  $\text{Cr}^{3+}$  removal mainly due to co-precipitation forming solid solution like species. This effect is solely dominant at the beginning of the experiments as  $\text{Cr}(\text{OH})$  is significantly soluble at this pH (at the initial stage) and

[Cr, Fe](OH) has lower solubility than Cr(OH) (s) [12]. Due to elevated dissolution rate of anode, more sludge from the metal electrodes is generated. This boosts the Cr<sup>3+</sup> removal due to sweep coagulation at higher solids loading [15]. More bubbles are generated at higher current and this improves the mixing and the removal [16].

**Effect of initial Cr<sup>3+</sup> concentration:** A range of initial concentrations, from 1000 to 3000mg/L, were treated using Fe electrodes, applied current density of 9.34 mA/cm<sup>2</sup> and pH value of 3.4.

Variations of percentage removal of Cr<sup>3+</sup> are shown in Figure 3. It is seen from the figure that the percentage removal increases with time. 1000mg /L concentration of chromium solution reduction by electrocoagulation 99.5% was removed after 40 minutes. It is well obvious after 100 minute initial concentration of Cr<sup>3+</sup> increases from 2000 to 3000

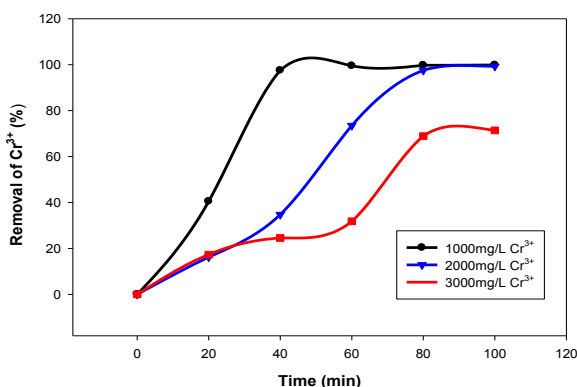


Fig. 3. Variation of extent of Cr<sup>3+</sup> removal with time for different initial Cr<sup>3+</sup> concentrations. Inter electrode distance: 3cm, current density: 9.34mA/cm<sup>2</sup>, supportive electrolyte 1000 mg/L NaCl.

mg/L, the % removal of Cr<sup>3+</sup> decreases from 99.3% to 71.4% respectively. Initial concentration of pollutants increases at a fixed current density, the adsorption capacity of the Fe(OH)<sub>n</sub> is consumed rapidly and as a result the % removal decreases consequently.

**Effect of inter electrode distance:** Variation of percentage removal of Cr<sup>3+</sup> with inter electrode distance is shown in Figure 4. It may be observed from the figure that with the increase of inter electrode distance, percentage removal of Cr<sup>3+</sup> decreases. For Cr<sup>3+</sup>, removal efficiency decrease from 52.3% at 0.5cm electrode distances to 47.6% at 3cm electrode distances. It is well known that, during the electrocoagulation as the potential is applied to the electrodes initially, the anodic oxidation is started. Now as the time proceeds a very fine film of metal hydroxides would get formed on the anode generating an extra resistance that even increases with increasing inter electrode distance [17].

Therefore, as a result, after some time of the operation current falls down. To maintain a constant current, applied potential has to be increased.

Now it is very much clear that current is remained constant but the resistance is increased. Therefore, the ohmic loss (IR resistance) increases which in turn inhibits the rate of anodic oxidation. As the rate of

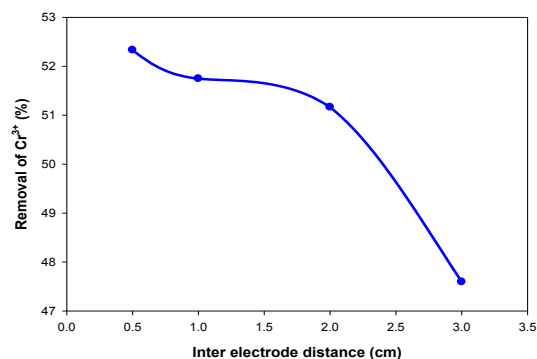


Fig. 4. Effect of inter electrode distance on the Cr<sup>3+</sup> removal. Current density 9.34mA/cm<sup>2</sup>, initial Cr<sup>3+</sup> concentration 1000mg/L, time 20 minute, pH 3.54.

anodic oxidation becomes lower, numbers of cations at anode also decreases. These cations are responsible for the formation of coagulant. Therefore, at higher inter electrode distance, rate of aggregation of suspended particles as well as adsorption of contaminants would be low. This may be the reason behind the lower removal efficiency at higher inter electrode distance. The decrease of removal efficiency also results from decreasing ions density via hydroxide polymers and it leads to the decrease of electrostatic attraction [17].

**Effect of pH:** The pH is one of the main factor for electrocoagulation process. Vik (1984) noted that pH has a considerable effect on the efficiency of the electrocoagulation process. In addition pH changes during the process dependent on the anode material and the initial pH value of the treated solution. The effect of pH on removal of Cr<sup>3+</sup> is therefore investigated at three different initial pH values of 2.07, 3.4 and 4.91 with mild steel electrodes. olution pH was adjusted by alkali/acid addition and the agitated solution. EC experiments were conducted with 1000 mg/L initial Cr<sup>3+</sup> concentration, 30min EC time, 2.0 cm electrode spacing and 9.34 mA/cm<sup>2</sup> current density. It shows that after 30 min of EC with initial of pH 2.07, 3.4 and 4.91 about 19.0, 75.9 and 96.9% of Cr<sup>3+</sup> is removed from aqueous phase. It is well known that the solubility of Cr(OH)<sub>3</sub> decreases with the increase of pH and the minimum solubility of Cr(OH)<sub>3</sub> occurs at pH 8.5, in the solution containing chloride ions, whereas Fe(OH)<sub>3</sub> is least soluble at pH 8 [9].

It may be concluded that as pH increases, the tendency for Cr<sup>3+</sup> chemical precipitation and co-precipitation increases, in addition the formation of Fe(OH)<sub>n</sub> precipitate increases, which facilitates Cr<sup>3+</sup> removal by sweep coagulation and adsorption.

**Operation cost:** One of the most important parameters that affect the application of any method

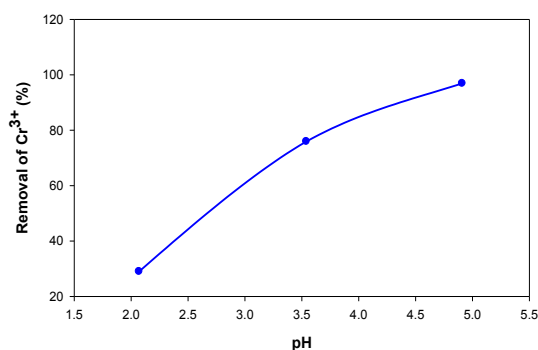


Fig. 5. Effect of inter pH on the Cr<sup>3+</sup> removal. Current density 9.34 mA/cm<sup>2</sup>, initial Cr<sup>3+</sup> concentration 1000mg/L, time 30 minute.

of wastewater treatment greatly is the cost. The major cost components for EC are (I) power cost; (II) electrode cost; (III) sludge 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. Cost due to electrical energy (kWh/m<sup>3</sup> Cr<sup>3+</sup> solution) is calculated as Where:

$$C_{\text{energy}} = \frac{U \times I \times t_{ec}}{V} \quad (8)$$

$t_{ec}$  - the time of electrolysis (s) and  $V$  - the volume (m<sup>3</sup>) of Cr<sup>3+</sup> solution.

Cost for electrode (kg Al/m<sup>3</sup> Cr<sup>3+</sup> solution) is calculated by the following equation by Faraday's Law. Where:

$I$  - current (A);  
 $t$  - time of electrolysis (s);

$$C_{\text{electrode}} = \frac{I \times t \times M_w}{z \times F \times V} \quad (9)$$

$M_w$  - molecular mass of iron (55,84 g/mol);  
 $z$  - number of electron transferred ( $z=2$ );  
 $F$  - Faraday's constant (96487 C/mol); and  
 $V$  - volume (m<sup>3</sup>) of Cr<sup>3+</sup> solution [13].

Where:

$C_{\text{energy}}$  (kWh/m<sup>3</sup> of Cr<sup>3+</sup> solution) and

$$\text{Operating cost} = a C_{\text{energy}} + b C_{\text{electrode}} \quad (10)$$

$C_{\text{electrode}}$  (kg Fe/m<sup>3</sup> of Cr<sup>3+</sup> solution) are consumption quantities for the Fe(II) removal, which are obtained experimentally.

$a$  - electrical energy price 105 ₮/kWh;  
 $b$  - electrode material price 150 ₮/kg Fe.

In the case initial Cr<sup>3+</sup> concentration is 1000mg/L, initial pH 3.54, 2.0 cm electrode distance and 9.34mA/cm<sup>2</sup> current density.

It is noted that in the range of investigation the costs vary practically linearly with time.

## CONCLUSIONS

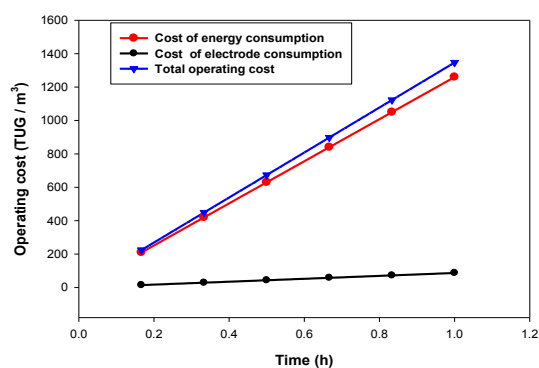


Fig. 6. Operating cost with different time

Variation of percentage removal of Cr<sup>3+</sup> with different operating parameters such as, current density, initial concentration of Cr<sup>3+</sup> and operating time, inter electrode distance, effect of pH were studied in detail. Electrocoagulation was carried out for 60 min for Cr<sup>3+</sup> concentration 1000 mg/L and satisfactory removal of 99.89% was obtained. As current density (4.67-9.34 mA/cm<sup>2</sup>) increases, Cr<sup>3+</sup> removal efficient (74.66-99.89%) increases. The initial concentration of Cr<sup>3+</sup> ions increases, Cr<sup>3+</sup> removal efficient decreases. The setup of electrode assembly is very important for required effective surface area of electrode and inter electrode distance. Increase of inter electrode distance (0.5-3.0cm), percentage removal of Cr<sup>3+</sup> decreases (52.3-47.6%). On adjusting initial pH of solution (1000 mg/L Cr<sup>3+</sup>) to 5, in 30 min about 96.9% of Cr<sup>3+</sup> gets removed. In our country treatment of tannery wastewater by EC, low operating cost which is a suitable.

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