Electrocoagulation: A cleaner method for treatment of Cr(VI) from electroplating industrial effluents

Daniel Reddithota\textsuperscript{a}, Anjaneyulu Yerramilli\textsuperscript{b} & Reddithota J Krupadam\textsuperscript{c} \textsuperscript{*}

\textsuperscript{a}Jawaharlal Nehru Technological University, Hyderabad 500 072, India
\textsuperscript{b}Jackson State University, Jackson MS 13972 USA
\textsuperscript{c}National Environmental Engineering Research Institute, Nagpur 440 020, India

Email: rj_krupadam@neeri.res.in

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Chromium contamination in waters are highly toxic even in very low concentrations and need to be completely removed from the effluents before they are discharged into a stream, sewer or on land. Electroplating industry is one of the industrial sectors producing chromium bearing wastewaters, mostly originating from chromium plating, anodizing, electroplating solutions and dip solutions like passivating dips, bright dips, etc. Chromium concentration in the effluents varies from 3 to 50 mg/L depending upon the care with which the plating operations are carried out. The results of this study have shown the applicability of electrocoagulation as a clean method for treatment of Cr(VI) containing wastewaters. The optimum removal of Cr(VI) was attained between $p$H 4-8. Increase in current density enhances the removal rate and the quickest treatment with an effective reduction of Cr(VI) concentrations was achieved below permissible level within 20 min. Iron electrodes were found to be more efficient in removing chromium in comparison to the aluminum and hydrid Al/Fe electrodes. This may be due to the formation of stable Fe-Cr complex which is more stable than Al-Cr complexes. On the other hand, 1 kg of Cr(VI) removal produces only 2.8 kg of sludge against 36 kg of sludge generated from iron sulphate precipitation method. The rate of removal is faster in comparison to the adsorption on activated carbon which is one of the most important requirement for practical application of this treatment method.

**Keywords**: Electrocoagulation, Electroplating effluents, Chromium (VI) treatment

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Electroplating involves the deposition of a thin protective metallic layer onto a prepared metal surface, using electrochemical process. Due to excellent hardness (typically 700-1000 Vickers) bright appearance with no discoulouration, resistance to corrosive environments, easily applicable and low cost, makes chromium plating a preferable option. However, hexavalent chromium plating suffers from low cathode efficiency, poor metal distribution, lack of coverage around holes, and is very difficult to use in barrel plating. From environmental point of view also, it has been found to be environment non-friendly procedure. As mentioned above, chromium bearing wastewaters originate from chromium plating, anodizing, electroplating solutions and dip solutions like passivating dips, bright dips, etc., and small portions arise from rinsing of metals treated with chromate solutions. In general, the plating vats are not discharged. Chromium concentration in the effluents varies from 3 to 50 mg/L, depending upon the care with which the plating operations are carried out. The main sources of chromium in the wastewaters are the drag-out and washing operations. The $p$H of the rinse waters is generally in the neutral range and rarely goes below 5.5. The overall effluent is typically extremely variable (1 to 500 L per m\textsuperscript{2} of surface plated) but usually high in chromium, heavy metals and fluorides, cyanides, and oil and grease.

The hexavalent chromium ions are highly toxic even at very low concentrations and treatment is essential to attain stipulated standards before they are discharged into a stream, sewer or on land. While in many cases disposal of untreated effluents from electroplating industries into municipal sewers, has been prevented by taking several measures, but it has caused a problem of sludge from municipal sewage treatment plants owing to the accumulation of toxic metals in the sludge. For example, it has been estimated that if the existing number of metal finishing industries in the town of Ludhiana, Punjab state in India, do not adequately remove the toxic metals in their effluents before disposal into municipal sewers, the sludge from the proposed sewage treatment plant of the town would contain...
1,850 mg nickel/kg of sludge and 415 mg of chromium/kg of sludge respectively, and be totally unfit for use as manure on agricultural land.

The most effective and economical way of treatment involves, reduction to trivalent state Cr(III), and subsequent precipitation with an alkali. Reduction to trivalent state takes place most effectively in acid solution. Ferrous ion is used to reduce chromate quantitatively in acid solution. Ferrous sulphate along with sulphuric acid is commonly used for this purpose. This reduction takes about one hour. Other reducing agents are sulphur dioxide and sodium bisulphite. Maximum reduction occurs in the pH range 2.0 to 2.5. Sodium metabisulphite is equivalent to 66 per cent sulphur dioxide by mass and is more expensive than sulphur dioxide. In small installations the convenience and the safety of handling sodium salts in powder form make them preferable to sulphur dioxide gas. In large installations the gas is generally more economical. The reduced trivalent chromium is precipitated individually or in combination with other metal wastes by addition of an alkali, lime or caustic soda. Lime is commonly used, since it is cheaper than caustic soda. The volume of the sludge depends on sulphuric acid concentration in the waste, when the neutralization alkali is lime. The concentration of the metal is another factor, which influences the sludge volume. The step-wise reactions for precipitation of chromium (hexavalent) with ferrous sulphate and lime are:

\[
\begin{align*}
H_2Cr_2O_7 + 6FeSO_4 + 6H_2SO_4 &\rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O \\
Cr_2(SO_4)_3 + 3Ca(OH)_2 &\rightarrow 2Cr(OH)_3 + 3CaSO_4 \\
Fe_2(SO_4)_3 + 3Ca(OH)_2 &\rightarrow 2Fe(OH)_3 + 3CaSO_4
\end{align*}
\]

The sludge generated for 1 kg of chromium removal in this process is 32 kg, of which 90% is metallic sulphates. The conventional methods for electroplating effluents purification include physicochemical treatment, ion exchange resins, vacuum evaporation, solvent extraction and membrane technologies. The physico-chemical treatment is, in many cases, incapable of meeting the legislation requirements (0.1 mg/L), due to the presence of organic and inorganic complexing agents and high salt concentration of these effluents, which allow the concentration of dissolved metal more than that expected, on the basis of the solubility of metal hydroxides. Furthermore, this treatment produces a large amount of sludge, which is difficult to handle. The other conventional methods, although usually effective, but involve some other drawbacks, like the most common ones include-high capital cost with recurring expenses and capability to treat only small effluent volumes and low metal concentrations.

Electrocoagulation is a simple and efficient method, where the flocculating agent is generated by electro-oxidation of a sacrificial anode, generally made of iron or aluminum. In this process, the treatment is done without adding any chemical coagulant or flocculants, thus reducing the amount of sludge, which must be disposed of. This technique is based on the in-situ formation of the coagulant, as the sacrificial anode corrodes due to an applied current, while the simultaneous evolution of hydrogen at the cathode allows for pollutant removal by flotation. This technique combines three main interdependent processes, operating synergistically to remove pollutants: electrochemistry, coagulation, and hydrodynamics. The mechanisms of removal of Cr(VI) by EC will be explained with aluminum and iron.

**Aluminum**

The electrolytic dissolution of the aluminum anode produces the cationic monomeric species such as Al\(^{3+}\) and Al(OH)\(_2^+\) at low pH, later on transformed to Al(OH)\(_3\) and finally polymerized to Al\(_n\)(OH)\(_3n\) according to the following reactions:

\[
\begin{align*}
Al &\rightarrow Al^{3+}_{(aq)} + 3e^- \\
Al^{3+}_{(aq)} + 3H_2O &\rightarrow Al(OH)_3 + 3H^+_{(aq)} \\
nAl(OH)_3 &\rightarrow Al_n(OH)_{3n}
\end{align*}
\]

Under appropriate conditions, various forms of charged multinumeric hydroxo Al\(^{3+}\) species may be formed. Most dominant species are dimeric and polymeric Al\(^{3+}\) hydroxo complexes, which are gelatinous charged species. They are effectively removing Cr(VI) by adsorption on the surface of floc, or by precipitate enmeshment during electrocoagulation process.

**Iron**

Iron upon oxidation in an electrolytic system produces iron hydroxide, Fe(OH)\(_n\) where n=2 or 3. The ferrous ion (Fe\(^{2+}\)) generated by electrooxidation of the iron anode can reduce Cr(VI) to Cr(III) under
In alkaline conditions and is itself oxidized to ferric (Fe$^{3+}$) ion according to the equation,

$$\text{CrO}_4^{2-} (aq) + 3\text{Fe}^{2+} (aq) + 4\text{H}_2\text{O} (l) \rightarrow 3\text{Fe}^{3+} (aq) + \text{Cr}^{3+} (aq) + 8\text{OH}^- (aq)$$

Or

$$\text{CrO}_4^{2-} (aq) + 3\text{Fe}^{2+} (aq) + 4\text{H}_2\text{O} (l) + 4\text{OH}^- (aq) \rightarrow 3\text{Fe(OH)}_3(s) + \text{Cr(OH)}_3(s)$$

The Cr$^{3+}$ (aq) ion is then precipitated as Cr(OH)$_3$(s) by raising the pH of the solution. The Fe$^{2+}$ (aq) ions can also reduce Cr$_2$O$_7^{2-}$ (aq) under acidic conditions according to the following reaction:

$$\text{Cr}_2\text{O}_7^{2-} (aq) + 6\text{Fe}^{2+} (aq) + 14\text{H}^+ (aq) \rightarrow 2\text{Cr}^{3+} (aq) + 6\text{Fe}^{3+} (aq) + 7\text{H}_2\text{O}(l)$$

The H$_2$ produced as a result of the redox reaction may remove dissolved organics or any suspended material by flotation. However, Fe$^{3+}$ ions may undergo hydration and depending on the pH of the solution Fe(OH)$_2^{2+}$, Fe(OH)$_2^+$ and Fe(OH)$_3$ species may be presented under acidic conditions. The reactions involved are

$$\text{Fe}^{3+} (aq) + \text{H}_2\text{O} (l) \rightarrow \text{Fe(OH)}^{2+} (aq) + 2\text{H}^+ (aq)$$

$$\text{Fe}^{3+} (aq) + 2\text{H}_2\text{O} (l) \rightarrow \text{Fe(OH)}_2^+ (aq) + 2\text{H}^+ (aq)$$

$$\text{Fe}^{3+} (aq) + 3\text{H}_2\text{O} (l) \rightarrow \text{Fe(OH)}_3 + 2\text{H}^+ (aq)$$

Under alkaline conditions, Fe(OH)$_2^-$ and Fe(OH)$_3^-$ ions may also be present, it is, therefore, quite apparent that EC of both anionic and cationic species is possibly by using an iron plate as a sacrificial electrode. It should be pointed out that the use of Fe$^{3+}$ as flocculation agent in water treatment has considerable advantage because of its innocuity compared to Al$^{3+}$ ions, which exhibits some toxic effects.

**Experimental Procedure**

All chemicals of analytical grade were used. Stock synthetic solution of 800 mg/L chromium is prepared by dissolving the required amounts of potassium dichromate in water. Solutions of lower concentrations are prepared by suitable dilution. The pH of the solution is adjusted to the required value with $10^{-2}$ M hydrochloric acid or $10^{-2}$ M sodium hydroxide. Aluminum, iron and hybrid Al/Fe plates (100×50×0.5 mm) of 99.9% purity were used as electrodes and laboratory experimental set-up was used for electrocoagulation (Figs 1 & 2). Real sample from a typical electroplating industry in Hyderabad was collected at different unit operations to study electrocoagulation method of treatment. All measurements are carried out at ambient temperature (25ºC) with 200 mL aliquots of synthetic and real industrial wastewater (collected from electroplating unit), added with the same amount of potassium chloride (0.74 g) to avoid excessive ohmic drop and to limit the formation of the passivation layer on aluminum, hybrid Al/Fe and iron electrodes. As has been shown in previous study, the addition of halide salts will decrease the energy consumption and limit the temperature variations, due to the Joule effect.

**Results and Discussion**

As illustrated in Fig. 3, the removal efficiencies ($R$) of chromium after 15 min of electrolysis at 0.8 A,
reached value as high as 99.9%, when pH was just 4, and maintain the same efficiency up to pH 8. In contrast, when the initial pH is increased above 8, a dramatic decrease of the removal efficiency of chromium is observed (96%). Furthermore, it can be seen that the removal efficiency of chromium ions decreased significantly upon decreasing initial pH. The decrease often at a pH less than 4 and higher than 8 was observed and is attributed to an amphoteric behaviour of Al(OH)₃, which leads to soluble Al³⁺ cations, when the initial pH is low and to anions Al(OH)₄⁻, when the initial pH is high⁶. These soluble species are useless for water treatment. When the initial pH is kept in the range 4-8, all aluminum cations produced at the anode, formed polymeric species of Al and precipitated as Al(OH)₃ leading to a more effective treatment. Dichromate ions are converted to soluble chromate (CrO₄²⁻) anions, which go some way towards explaining its less effective removal. As observed by other investigators⁷,⁸, the treatment induced an increase in the pH when the initial pH was low (pH < 4). This might be explained by the excess of hydroxyl ions produced at the cathode in sufficiently acidic conditions and by the liberation of OH⁻ due to the occurrence of a partial exchange of Cl⁻ with OH⁻ in Al(OH)₃. When the initial pH is above 9, the formation of Al(OH)₄⁻ species together with attack of the cathode by hydroxyl ions lead to a slight decrease in the pH. The removal rate increased upon increasing current density (Fig. 4). The removal rate increased upon increasing current density. The highest current (4.8 Adm⁻²) produced the quickest removal rate, with a 99% concentration reduction occurring just after 10 min. This unexpected behaviour is due to the increase of coagulant and bubble generation rate, resulting in a more efficient and faster removal, when the current is increased. Indeed, the amount of aluminium and hydroxide ions generated at a given time, within the electro-coagulation cell are related to the current flow, using Faraday's law. Moreover, it was previously shown that the bubble size decreases with increasing current density⁹,¹⁰, which is beneficial to the separation process. Nevertheless, as the time progresses, the amount of oxidized aluminium and the required charge loading increases. However, this
parameter should be kept at a low level to achieve a low-cost treatment. At high current, the bubble density creates high upwards flux resulting in a faster removal of the coagulant by flotation. Hence, there is a reduction in the probability of collision between the coagulant and pollutants. Regardless of the slight increase (below 20%) of the charge loading observed for Cr(VI), the time required to achieve the treatment can be shortened by a factor of six, when current density is increased from 0.8 to 4.8 A dm$^{-2}$, while the cost of the treatment remain unchanged. Hence, the highest current should be selected to obtain the quickest removal rate (Fig. 5).

It appears that the removal rate of chromium has decreased upon increasing initial concentration of metal. This induced a significant increase of charge loading required to reach residual metal concentrations below the levels permissible for effluents discharge standards (i.e. 2 mg/L). The wastewater has Cr of 25 mg/L and COD content 300 mg/L. By using iron electrodes in electrocoagulation, real electroplating industrial effluents were treated and results are presented in Table 1. This is an indication of presence of some organic compounds, which may be due to addition made to the electroplating bath as brighteners, levelers or wetting agents. It appears from the results shown in Fig. 6, the residual concentration of chromium decreased more slowly and reached 2 mg/L after an electrolysis time of 20 min. The removal rate of Cr(VI) seems to be relatively slow compared to the removal from synthetic wastewater. This type of reduction in

![Fig. 5 — Removal of Cr(VI) at different metal ion concentrations](image)

<table>
<thead>
<tr>
<th>Environmental parameter</th>
<th>Initial concentration</th>
<th>Effluents after primary treatment, treated with EC</th>
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<tr>
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<tr>
<td>$\rho$H</td>
<td>5.2±0.2</td>
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<td>1480±7</td>
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<td>COD, mg/L</td>
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<td>BOD, mg/L</td>
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<tr>
<td>Cr(VI), mg/L</td>
<td>93±9</td>
<td>10.8±0.6</td>
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<thead>
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<th>Environmental parameter</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5 min</td>
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<tr>
<td>$\rho$H</td>
<td>6.8±0.2</td>
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<td>Cr(VI), mg/L</td>
<td>26±0.97</td>
<td>1.89±0.03</td>
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<tr>
<td>$\rho$H</td>
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<td>BOD, mg/L</td>
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<tr>
<td>Cr(VI), mg/L</td>
<td>6±0.91</td>
<td>0.9±0.01</td>
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efficiency is resulted from the presence of organic compounds, which may competitively adsorb on Al(OH)₃ coagulant, leading to a substantial reduction of metal ions removal. The COD decreased from 300 mg/L to less than 10 mg/L after 25 min, which corresponds to a removal efficiency of about 92%. Beyond that time, the residual COD reached a plateau and remained nearly constant. The results of this study have shown the applicability of electrocoagulation as a clean technology for the treatment of wastewaters containing Cr(VI). The most effective removal was achieved in the pH range between 4 and 8. The treatment rate is found to increase upon increasing the current density. Indeed, the optimum current produced the quickest treatment with an effective reduction of Cr(VI) concentrations in the industrial wastewater below permissible level within 20 min. When comparing the electrodes, iron electrodes have been found to be more efficient with regards to chromium removal, in comparison to the aluminum and hybrid Al/Fe electrodes. This may be due to the formation of stable Fe-Cr complex which is much more stable than Al-Cr complexes. The higher charge loading improves electro-coagulation kinetics for effective treatment. Overall, electrocoagulation yields very low quantity of sludge compared to precipitation method. On the other hand, the sediment collected from the electrocoagulation reactor was tested for its leachability. Toxicity characteristics Leaching Procedure (TCLP) results showed that Cr(VI) concentration in leachate is very much below the stipulated standard (0.1 ppm). The conventional chemical coagulation using iron sulphate, requires $250 to bring down the Cr(VI) concentration below 1 mg/L in 1 L of electroplating effluents whereas in electrocoagulation, the estimated cost is $3.5. The rate of removal is faster compared to adsorption on activated carbon and the resultant sludge is quite low. Hence, this way of Cr(VI) decontamination from wastewaters is a cleaner and cheaper method.

Fig. 6 — Removal of Cr(VI) from electroplating effluents

References