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Scientific paper
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Cr (VI) removal from electroplating industrial effluents: A greener and cheaper method

Electrocoagulation is a greener and cheaper method to remove Cr(VI) form the effluents of electroplating industry. This paper is emphasizing on the removal efficiency of electrocoagulation method. The removal efficiencies (R) of chromium after 15 min of electrolysis at 0.8 A, reached value as high as 99.9%, when pH just 4, and maintain the same efficiency up to pH 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 more efficient to remove chromium comparing the aluminum and hybrid Al/Fe electrodes.

***Key words**: Electrodes, Electrocoagulation, chromium (VI), current density*

INTRODUCTION

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 discolouration, resistance to corrosive environments, easily applicable and low cost, makes chromium platting is 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. On environmental point of view, it is also a worker and environment non-friendly procedure.

From the process, 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 pH of the rinse waters is generally in the neutral range and rarely goes below 5.5. The overall effluent is typically extremely variable (1 liter to 500 liters per m^2 of surface plated) but usually high in chromium, heavy metals and fluorides, cyanides, and oil and grease.

The hexavalent chromium ions in these wastes are highly toxic even in very low concentrations and need to be attain stipulated standards before they discharged into a stream, sewer or on 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 sulfate along with sulfuric acid is commonly used for this purpose. This reduction takes about one hour. Other reducing agents are sulfur dioxide and sodium bisulfite. Maximum reduction occurs in the pH range 2.0 to 2.5. Sodium metabisulfite is equivalent to 66 per cent sulfur dioxide by mass and is more expensive than sulfur dioxide. In small installations the convenience and the safety of handling sodium salts in powder from make them preferable to sulfur 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 the 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 the sulfuric 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 sulfate and lime are:

$$H_2Cr_2O_7 + 6FeSO_4 + 6H_2SO_4 \rightarrow Cr_2(SO)_4 + $$
$$+3Fe_2(SO_4)_3 + 7H_2O$$

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

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Fe(OH)_3 + 3CaSO_4$$

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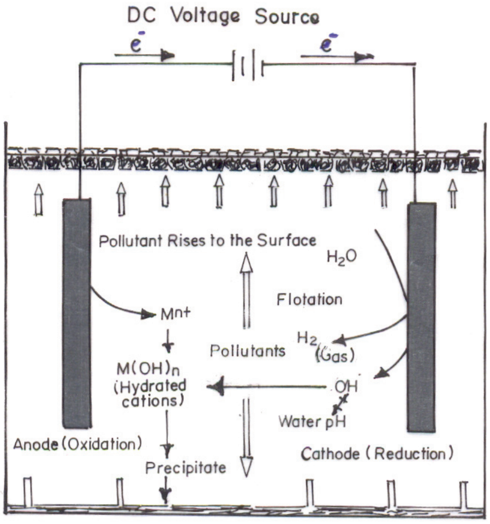
The sludge generated for 1 kg of chromium removal in this process is 32 kg of which 90% is metallic sulfates. The conventional methods for electroplating effluents purification include physiccochemical treatment, ion exchange resins, vacuum evaporation, solvent extraction and membrane technologies [1,2].

While disposal of untreated effluents from electroplating industries into municipal sewers has in many cases prevented direct contamination of a watercourse, it has, on the other hand, posed 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[3] that if the existing number of existing 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 chromium/kg of sludge respecttively, and be totally unfit for use as manure on agricultural land.

The physico-chemical treatment is, in many cases, in capable of meeting the legislation requirements (0.1 mg/l, due to the presence of organic and inorganic complexing agents and to the high salt concentration of these effluents which allow dissolved metal concentrations above those expected according to the solubility production of metal hydroxides. Furthermore, this treatment produces a large amount of sludge, which is difficult to handle. The other conventionnal methods, although usually effective, are not free of drawbacks, high capital cost with recurring expenses and capability to treat only small effluent volumes and low metal concentrations, are the most common.

Electrocoagulation – A promising greener and cheaper method



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[4,5]. 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:

$$Al \rightarrow Al^{3+}_{(aq)} + 3e^-$$

$$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_3 + 3H^+_{(aq)}$$

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n}$$

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 to produced charge neutralization, or by enmeshment in a precipitation.

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 alkaline conditions and is itself oxidized to ferric (Fe^{2+}) ion according to

$$CrO_4^{2-}{}_{(aq)} + 3Fe^{2+}{}_{(aq)} + 4H_2O_{(l)} \rightarrow 3Fe^{3+}{}_{(aq)} + Cr^{3+}{}_{(aq)} + 8OH^-{}_{(aq)}$$

Or

$$CrO_4^{2-}{}_{(aq)} + 3Fe^{2+}{}_{(aq)} + 4H_2O_{(l)} + 4OH^-{}_{(aq)} \rightarrow 3Fe(OH)_3\downarrow + Cr(OH)_3\downarrow$$

The $Cr^{3+}{}_{(aq)}$ ion is then precipitated as $Cr(OH)_{3(s)}$ by raising the pH of the solution by raising the pH of the solution. The $Fe^{2+}{}_{(aq)}$ ions can also reduce $Cr_2O_7^{2-}$

$_{(aq)}$ under acidic conditions according to the following reaction:

$$Cr_2O_7^{2-}{}_{(aq)} + 6Fe^{2+}{}_{(aq)} + 14H^+{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + +6Fe^{3+}{}_{(aq)} + 2H_2O_{(l)}$$

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 $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $Fe(OH)_3$ species may be presented under acidic conditions. The reactions involved are

$$Fe^{3+}{}_{(aq)} + H_2O_{(l)} \rightarrow Fe(OH)^{2+}{}_{(aq)} + 2H^+{}_{(aq)}$$

$$Fe^{3+}{}_{(aq)} + 2H_2O_{(l)} \rightarrow Fe(OH)_2^+{}_{(aq)} + 2H^+{}_{(aq)}$$

$$Fe^{3+}{}_{(aq)} + 3H_2O_{(l)} \rightarrow Fe(OH)_3 + 2H^+{}_{(aq)}$$

Under alkaline conditions, $Fe(OH)_6^-$ and $Fe(OH)_4^-$ 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, however, 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.

MATERIALS & METHODS

All chemicals are of analytical grade was used. Stock synthetic solution of 800 mgl^{-1}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 (100mm x 50mm x 0.5mm) of 99.9% purity were used as electrodes and laboratory experimental setup was started for electrocoagulation (Figure 1).

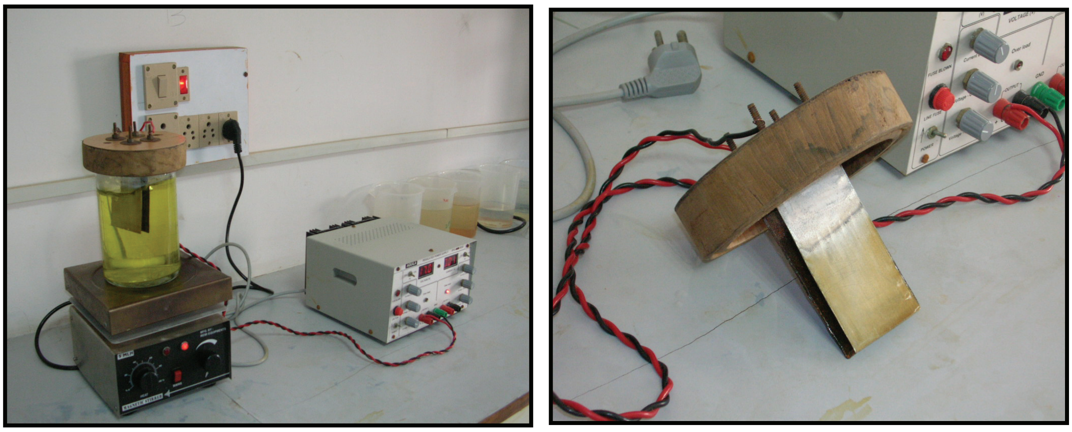


Figure 1 - Laboratory bench-scale Electro coagulation set-up

All measurements are carried out at ambient temperature (25ºC) on 200ml 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, hybride Al/Fe and iron electrodes. As has been shown in previous study [7], 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 Figure 2, the removal efficiencies *(R)* of chromium after 15 min of electrolysis at 0.8 A, reached value as high as 99.9%, when pH 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 is attributed to an amphoteric behavior of $Al(OH)_3$ which lead to soluble Al $^{+3}$ cations, when the initial pH is low and to anions $Al(OH)_4$, when the initial pH is high (Holt et al. 2002). These soluble species are useless for water treatment. When the initial pH is kept in the range 4 - 8, all aluminium captions produced at the anode formed polymeric species Al and precipitated as $Al(OH)_3$ leading to a more effective treatment. Dichromate ions are converted to soluble chromate (CrO_4^{2-}) anions, which go some way towards explaining its less effective removal.

As observed by other investigators [6,7] the treatment induced an increase in the pH when the initial pH was low (between 2 and 9). 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^{-1} with OH^- in $A1(OH)_3$. 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.

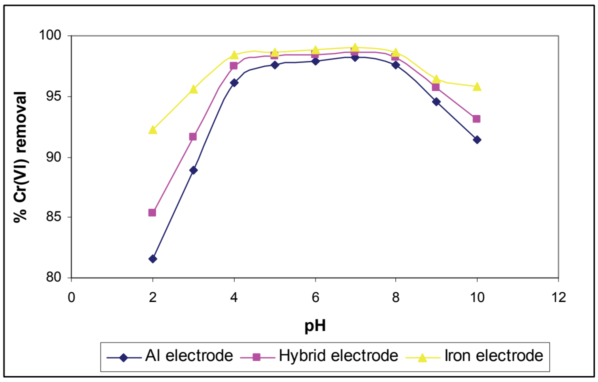


Figure 2 - Removal of Cr (VI) at different pH conditions

A semi-logarithmic plot, showing the normalized concentrations profiles of Cr (VI) for typical electro coagulation runs, where the initial pH was fixed at 6. The removal rate increased upon increasing current density. The highest current (4.8Adm^{-2}) produced the quickest removal rate, with a 99% concentration reduction occurring just after 10 min. This expected behavior is due to the increase of coagulant and bubbles generation rate, resulting in a more efficient and faster removal, when the current is increased. Indeed, the amounts 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 density[8] which is beneficial to the separation process. Nevertheless, as the time progresses, the amount of oxidized aluminum and the required charge loading increase. However, this parameter should be kept at low level to achieve a low-cost treatment.

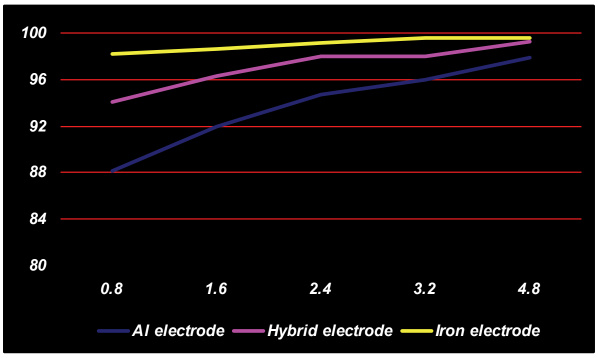


Figure 3 - Removal of Cr (VI) at different current density conditions

At high current, the bubble density crates 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 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 remained unchanged. Hence, the highest current should be selected to obtain the quickest removal rate.

It appears that the removal rate has decreased upon increasing initial concentration of metal ion concentration. 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^{-1}). The effect of initial concentration on the charge loadings required for an effective removal of Cr (VI) current density = 4.8 A dm"^{2}, anode surface = 50cm^2.

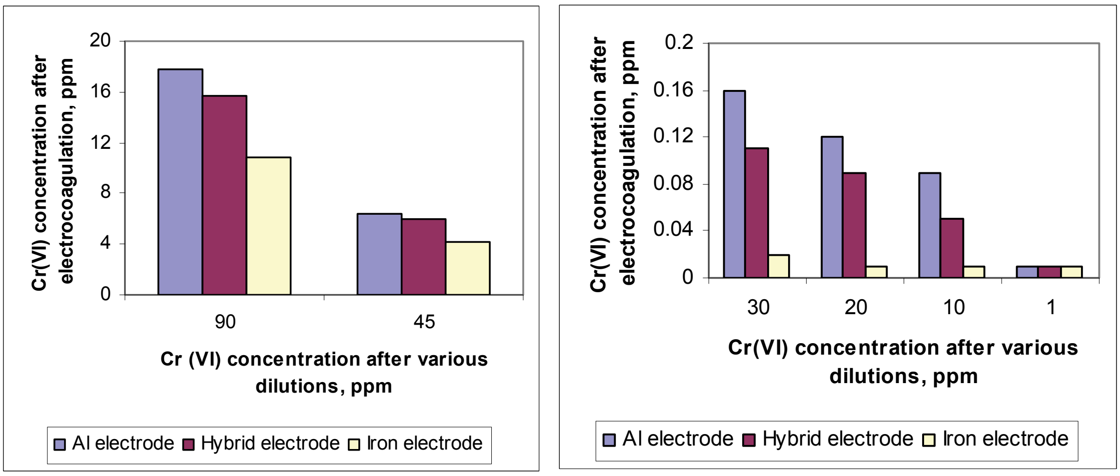


Figure 4 - Removal of Cr (VI) at different metal ion concentrations

The wastewater has Cr of 25mg l^{-1} and COD content is 302 mg l^{-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 Figure 5, the residual concentration of chromium decreased more slowly and reached 2mgl^{-1} after an electrolysis time of 20 min.

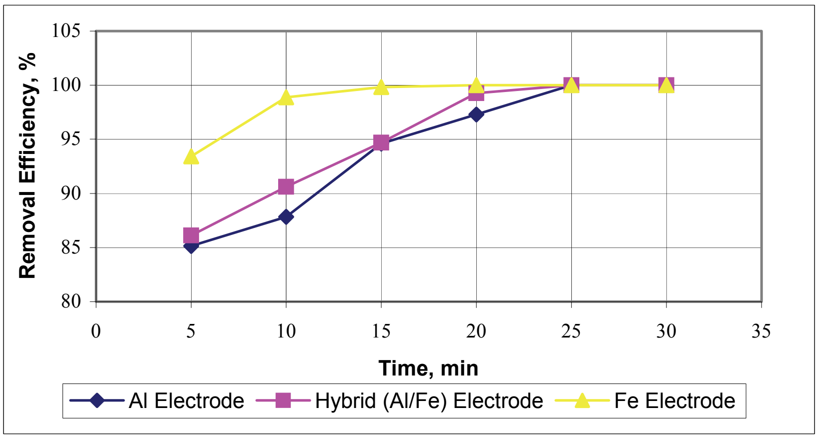


Figure 5 - Removal of Cr (VI) from Industrial Effluent.

The removal rate of Cr (VI) seems to be relatively slow compared to the removal from synthetic wastewater. This type of reduction in efficiency is resulted from the presence of organic compounds, which may competitively adsorb on A1 $(OH)_3$ coagulant, leading to a substantial reduction of metal ions removal.

Table 1 - Efficiency of electrocoagulation for treatment of electroplating effluents

Environmental Parameter	Initial concentration	Effluents before primary treatment treated with EC		
		5 min.	20 min	30 min
PH	6.8±0.2	7.2±0.1	7.3±3.56	7.2±0.1
TDS, mg/l	1270±12.6	286±8.3	61±4.29	25±1.67
COD, mg/l	300±4.8	42±2.1	30±1.2	7±0.83
BOD, mg/l	30±1.4	14±0.94	8±0.81	5±0.58
Cr(VI), mg/l	26±0.97	1.89±0.03	0.09±0.01	0.01±0.006
Environmental Parameter	Initial concentration	Effluents before primary treatment treated with EC		
		5 min.	20 min	30 min
PH	5.2±0.2	7.0±0.1	7.3±0.1	7.2±0.1
TDS, mg/l	8200±42	1480±7	1160±6.1	1085±3.8
COD, mg/l	2520±9	380±4	315±2.6	291±1.2
BOD, mg/l	120±6	63±2.8	46±1.1	30±0.9
Cr(VI), mg/l	93±9	10.8±0.6	5.73±0.2	4.12±0.11
Environmental Parameter	Initial concentration	Effluents before primary treatment treated with EC		
		5 min	20 min	30 min
PH	6.9±0.2	7.3±0.1	7.2±0.1	7.5±0.2
TDS, mg/l	90±2.68	60±1.26	30±0.92	24±0.81
COD, mg/l	80±2.43	48±1.08	10±0.84	8±0.61
BOD, mg/l	30±1.23	13±0.93	5±0.09	ND
Cr(VI), mg/l	6±0.91	0.9±0.01	0.01±0.001	0.006±0.001

The measured COD decreased from 300 mgl^{-1} to less than 10 mgl^{-1} after 25min, whi ch 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 electro coagulation 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 more efficient to remove chromium comparing 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 required achieving an effective treatment. Overall, electro coagulation yields very low quantity of sludge compared to precipitation method. On the other hand, the sediment collected form the electro coagulation reactor was tested for its leachability using Toxicity Characteristics Leaching Procedure (TCLP) results showed leaching is very much below the stipulated standard (0.1 ppm). The rate of removal is faster compared to adsorption on activated carbon is one of the most needed requirement in treatment methods. Hence, this way of Cr (VI) decontamination from wastewaters is a cleaner and cheaper method.

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