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Removal of Cr(VI) from Aqueous Solution: Electrocoagulation vs Chemical Coagulation

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Abstract: Hydrolyzed products of Al(III) have affinity below pH_{zpc} for oppositely charged mono and bi-nuclear species of hexavalent chromium. This study investigates the comparative performance of electrocoagulation (EC) and chemical coagulation (CC) for the removal of Cr(VI) from aqueous solution. The highest removal of Cr(VI) achieved with EC was about 42% with $4.36\,mA/cm^2$ current density. Cathodic adsorption of chromium boosted up Cr(VI) removal during EC. Simultaneous electro- and chemical-dissolution lead to high current efficiency of about 178%. Both the pH and the coagulant dosage have a significant impact on Cr(VI) removal in the pH ranges from 4.9 to 7.0. CC with alum and aluminum sulfate (AS) removed about 11% and 12% of Cr(VI). Co-adsorption of divalent SO_4^{2-} ions with Cr(VI) is responsible for the lower removal observed with chemical coagulants. About 0.061 and 0.099 mole of SO_4^{2-} was adsorbed per mole Al in the precipitate in the pH range 4.9 to 7.0 with AS and alum. A higher coagulant dosage increases the removal of Cr(VI) but adversely affects the removal efficiency (Cr(VI) removed per unit of Al dosing). Cell current density (CD) has shown little effect on Cr(VI) removal and the pH elevation at the same charge density. Higher initial Cr(VI) concentration improves the removal efficiency as the species of Cr(VI) is acidic in solution and decreases the pH elevation rate.

Keywords: Electrocoagulations, chemical coagulations, adsorption, co-adsorption

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INTRODUCTION

Chromium occurs in stable form with oxidization states of (VI+) and (III+). The hexavalent form of chromium is well-known for its toxicity even at parts per billion levels. The contamination of water bodies by Cr(VI) from anthropogenic sources take place from electroplating and metal finishing industries, tannery operations, chemical and battery manufacturing, acid mine drainage, wood preservation, cooling tower blow-down etc (1, 2). Many technologies including adsorption, chemical reduction-precipitation, coagulation-flocculation, membrane separation (UF, NF, RO), ion exchange, biological reduction, and electrodialysis (ED) have been tried for removal of Cr(VI) from effluents in the last few decades (1–7). Each of the techniques has limitations and advantages in application.

EC is now receiving increasing attention for removal of heavy metals from wastewater. Kongsricharoern and Polprasert (8) investigated electrochemical precipitation (ECP) for removal of Cr(VI) from an electroplating wastewater using steel plate electrodes. The optimum electrical potential, the cell current, teh HRT, and the initial pH were 75 volts, 4.8 amp, 50 min, and above 3.2. Kongsricharoern and Polprasert (9) performed a similar study for removal of Cr(VI) with bipolar electrode configuration. Donald et al. (10) studied the effectiveness of an EC process by removing bacteria (E. coli), Mo concentration from 9.95 to 0.006 mg/l, Fe concentration from 130 to 0.015 mg/l in leachate from a landfill site. Adhoum et al. (11) reported the highest removal efficiency was between the pH range 4.0 to 9.7 for Zn(II) and Cu(II) and 4.0 to 8.0 for Cr(VI) with Al electrodes while treating electroplating effluent streams. Gao et al. (12) worked on the treatment of wastewater containing Cr(VI) by a combined electrocoagulation and electroflotation process. Cr(VI) was first reduced to Cr(III) in the reaction unit, then Cr(III) and Fe(III) were precipitated/coagulated in the coagulation unit by pH adjustment. Coagulated flocs were then removed in two subsequent electroflotation units with a surfactant using the principle of foam flotation. Parga et al. (13) reported above 99% removal of both Cr and As the using Fe electrode.

The hydrolysis of dichromate ion generates various anionic species containing Cr(VI). Among these, dichromate ($Cr_2O_7^{2-}$) and bichromate ($HCrO_4^-$) ions primarily exist in acidic pH (<5.7) and chromate (CrO_4^{2-}) ion is the only significant species in a higher solution pH (>5.7). At higher concentration ($>8.0 \times 10^{-3}$ M), $Cr_2O_7^{2-}$ is the predominant species compared to $HCrO_4^-$ (14). The metal electrocoagulants or chemical coagulants are positively charged below the pH_{zpc}. At the same time, Cr(VI) exists in solution as various oppositely charged species having a strong affinity towards the oppositely charged surfaces. The EC process continuously doses the coagulant generated electrochemically. The present work experimentally investigates the EC process with aluminum electrodes for Cr(VI) removal. The investigation aims at studying the effect of operating parameters/conditions on Cr(VI) removal efficiency. Aluminum sulfate (AS) and alum are commonly

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used aluminum salts used as coagulants in various applications such as paper, textile, tanning, water purification etc. In case of chemical coagulation (CC) with aluminum salts, sulfate ions acts as a powerful "penetrator" and reduce the effective sites replacing the hydroxyl group in the hydrolyzed Al complex species (15). This work also explores the hexavalent chromium removal efficiency of AS and alum, comparing the same with EC using aluminum electrodes.

THEORETICAL BACKGROUND

The anodic material gets dissolved into the solution with a simultaneous formation of hydroxyl ions and hydrogen gas evolution at the cathode during EC using DC source. Dissolved metal ions form various charged hydroxylated species. These charged species adsorbed on $Al(OH)_3(s)$ act as coagulants, and facilitate the removal of Cr(VI). Reactions involved during EC with Al electrode are (16, 17) -

Anodic reaction:

$$Al \longrightarrow Al^{3+} + 3e \tag{1}$$

Cathodic reaction:

$$3H_2O + 3e \longrightarrow 3OH^- + 3/2H_2 \tag{2}$$

Various charged mono and poly-hydroxylated species of Al are formed due to the interaction of Al(III) with water in the bulk depending on the solution pH according to the following reaction:

$$xAl^{3+}yH_2O \longleftrightarrow Al_x(OH)_y^{3x-y} + yH^+ \tag{3}$$

The values of x for the polymeric species at intermediate pH in a concentrated solution of Al(III) have been reported in literature up to 13.0 with an OH/Al ratio close to 2.5 (18). Among these poly-nuclear complexes in concentrated solution (>2.6 mg/l), hydrated bi-nuclear complex, $[Al_2(H_2O)_8(OH)_2]^{4+}$ is present in substantial quantity. At too acidic and alkaline pH, only the monomeric hydroxides (Eq. (4) are the dominant species.

$$Al^{3+}yH_2O \longleftrightarrow Al(OH)_y^{3-y} + yH^+; \quad (y = 0 \text{ to } 4) \tag{4}$$

Similarly, when alum and aluminum sulfate (AS) are used as chemical coagulating agents, the products of hydrolysis of the salts are the charged chemical coagulants.

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EXPERIMENTAL

Electrode Materials

Aluminum sheet purchased from the local market was used as electrode material for the present work. The elemental composition of the electrode material was determined by EDX (Energy Dispersive X-ray) of Oxford, UK (Link: IS-300, Model-6841) equipped with a Scanning Electron Microscope (Model: JSM-5800, Joel, Japan). The Al electrode contains about 95.65% Al, 2.87% Si. Fe content in the sample during "auto scan" was found to be below detectable limits. However on forcing the detections of Fe, 1.48% w/w Fe showed up with comment that this value was unreliable.

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Chemicals

Experiments were carried out with G.R. grade potassium dichromate ($K_2Cr_2O_7$, min assay 99.5%) procured from E. Merck (India) Limited, Mumbai, as the source of Cr(VI). One liter stock solution of Cr(VI) containing 2000 mg/l of the same was prepared by dissolving an appropriate quantity of $K_2Cr_2O_7$ in distilled water. All experiments (both EC and CC) were performed after proper dilution of the stock solution with distilled water. Solution pH was adjusted at the desired value either by addition of 4% HCl (assay: min assay 35%; E. Merck (India) Limited, Mumbai) or 4% NaOH (purified; Sisco Research Laboratories Pvt. Ltd., Mumbai). NaCl was added to the solution to increase the conductivity (extrapure A.R. grade; Research Laboratories Pvt. Ltd., Mumbai). Chloride ions accelerate the dissolution of the electrode materials and it also reduces the passive oxide layer, thinning the same over the electrode surface. Commercial grade alum [$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$] was purchased from a local store. The purity of alum was measured by its aluminum content using an atomic absorption spectrophotometric analysis. It contains about 93% of the stoichiometric Al content of pure alum. AS [$Al_2(SO_4)_3 \cdot 16H_2O$] (min assay 98%) was obtained from M/s E. Merck India. All chemicals were used for the present investigation without any further purification.

Analysis

Cr(VI) Concentration Determination

Concentration of Cr(VI) in the aqueous phase was measured spectrophotometrically using Diphenyl carbazide (G.R. grade; Loba Chemicals, Bombay) (19).

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Al Content in Solution/Sludge

Concentration of Al was analyzed with an atomic absorption spectrophotometer (Perkin Elmer, Model: Analyst-700) after proper pretreatment according to the manufacturer's recommendations.

Measurement of SO_4^{2-}

Sulfate was determined with barium sulfate turbidimetric method and the scanning was performed at 420 nm (19).

pH Measurement

The measurement of pH was performed using a pH meter of make M/s Toshniwal India (Model:CL-46).

Experimental Procedures

Electrocoagulation Experiments

Batch experiments were carried out in a 1 liter borosilicate glass reactor containing 800 ml of solution. Al electrodes having the dimension of 6 cm × 5.1 cm × 0.1 cm, with 30.74 cm^2 effective surface area was used for EC. Two parallel electrodes were placed into the solution using an insulated clamp fixed to a stand. Electrode spacing was kept constant at 22 mm as industrial electrochemical reactors generally use this gap. Electrodes were connected to a regulated D.C. power source (Aplab Regulated DC power supply 7145). The desired cell current was supplied by changing the impressed voltage. Solution was agitated with a magnetic stirrer supplied by M/s Tarson India. The agitation speed of 450 rpm was maintained during the experiments as initial trial runs showed that agitation at 450 rpm was sufficient to reduce the external mass transfer effect. The electrodes were conditioned (used) for several hours prior to the final experiments. During this period the polarity of the electrode pair was reversed a few times. This was done to minimize the effect of the surface quality of the electrodes. Electrodes were cleaned with emery paper between the successive experiments and then washed with dilute H_2SO_4 solution to reduce the effects of the preceding experiments. During the experiments, samples were pipetted out and immediately filtered with Whatman filter paper. The supernatant samples drawn were analyzed for Cr(VI) concentration, Al(III) concentration, pH, and the SO_4^{2-} content. Immediately after measurement of pH, the supernatant was acidified with 4% H_2SO_4 solution to arrest further removal.

Chemical Coagulation (CC) Experiments

Experiments of CC were conducted with similar operating conditions of EC. In each experiment, 800 ml solution was treated in the same container in batch mode. The coagulant dosage was in terms of Al from the coagulating agent added or from the dissolution of the electrode. A predetermined quantity of coagulant was added after every 10 min interval up to the final coagulation time of 60 min. After the addition of each coagulant dose, the pH of the solution/suspension was adjusted to the pH value almost equal (± 0.05) to the pH of EC experiments at the same Al dose (dissolution from electrode) and solution pH. The pH adjustment was by the addition of a 4% aqueous solution of HCl or NaOH. The coagulation experiments were performed at the same agitation level of EC. Just prior to the addition of the coagulant, samples were drawn and analyzed following the procedures as already outlined.

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RESULTS AND DISCUSSIONS

Current Efficiency and Coagulant Dose Determination

The cell current efficiency (η) during EC was calculated using Faraday's law. Aluminum electrodes get dissolved due to the electrochemical process and chemical dissolution due to pH and the action of chloride. High current efficiency is observed due to these effects. Experiments for determining the current efficiency were performed with the same batch cell and electrode specifications and following the procedure already outlined. Runs were conducted for 20, 40, and 60 min. After each run an adequate amount of concentrated HCl was added to the cell liquid and sludge, if any, for bringing all Al in solution. A sample of this liquid was tested for Al concentration and this result was used for calculating the cell current efficiency. A second set of identical experiments for estimating the chemical dissolution effect were carried out by adjusting the solution pH as it varied during EC at every 10 min intervals under identical operating conditions without passing any cell current. The results from these experiments were used to calculate the chemical dissolution of the electrodes under the same conditions. The data are for cell current density (CD) of 4.36 mA/cm^2, initial pH of 4.87 and 50 mg/l initial Cr(VI). The dissolved Al during EC fits a linear function of time with R^2 value of 0.998. Based on this linearity, the current efficiency of the cell (based on electrochemical (total) dissolution of Al) was found to be about 178%. We find that in 60 min about 6.08 mg Al get dissolved due to pH effect/chemical dissolution. The current efficiency, corrected for chemical dissolution is about 164.5%.

The corrected η is well above 100% as the pH in the vicinity of the electrode surfaces is different from the bulk pH. H_2 gas is evolved at the

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cathode surface with simultaneous formation of OH^- ions (Eq. 2). The pH in the vicinity of the cathode is therefore expected to be significantly higher than the bulk pH. At the anode along with the metal ion dissolution reaction, there is a competing reaction of hydroxonium (H_3O^+) ion generation (Eq. 5).

$$3OH^- \longrightarrow O_2 + H_3O^+ + 3e \tag{5}$$

This hydroxonium ion, a proton donor, reduces the pH in the vicinity of the anode surface. This is less significant on anode due to higher standard electrode oxidation potential of Eq. 1 compared to Eq. 5 (16).

Chloride ions catalyze Al dissolution. Aluminum undergoes severe localized attack in the presence of chloride ions by pitting corrosion phenomena. The OH group is located on the surface of the oxide layer of the electrode. At pH below the zero point charge (pH_{zpc}), the surface develops a positive charge by means of a protonation reaction. At, pH above the pH_{zpc}, the surface develops a negative charge by means of deprotonation reaction. Thus adsorption of Cl^- ions is favored below pH_{zpc} i.e., $\sim$8.4 for aluminum oxide. Pits initiation occurs through

i. adsorption of chloride ions on the oxide surface;
ii. migration of Cl^- ions through oxygen vacancies or by oxide film thinning; and
iii. localized dissolution of aluminum atoms at the metal/oxide interface (20, 21).

The effects of low pH close to the anode and high pH close to the cathode surface and also chloride corrosion lead to additional dissolution of Al. This explains higher current efficiency even after correcting for the bulk pH dissolution effect. Higher η in EC is desirable for lower energy requirement. In the present investigation, η was about 78% higher compared to the predicted from Faraday's law. Experiments were also carried out at a higher CD and it was found that η varied only by a small amount.

The amount of Al dissolved during EC were calculated based on 178% current efficiency. The (aluminum) equivalent chemical coagulant (AS/Alum) dose was added after every 10 min and the solution pH was adjusted to bulk pH noted during EC. CC experiments were carried out corresponding to EC experiment conditions with 4.36, 8.72 and 13.08 mA/cm^2 CD.

Influence of pH and Treatment Time on Cr(VI) Removal

Aluminum hydroxide is amphoteric in nature. pH plays an important role for developing the surface charge density around the coagulating particles. At low pH values below the pH_{zpc} aluminum hydroxide species develop positively charged surface while at higher pH values (above pH_{zpc}) the surface charge is negative. Aluminum hydroxide is increasingly soluble at lower and higher pH. The comparative removal of Cr(VI) by EC and CC (with AS and alum) at a different initial solution pH can be seen from Fig. 1. Reproducibility of the experimental results was established to be within 5% with a set of runs.

Concentration of Cr(VI) in solution at initial pH of 2.0 gradually decreases from ~50.0 mg/l to 46.1 mg/l after 60 min i.e., about 8% Cr(VI) was removed (Fig. 1(a)). The figure indicates the elevation of pH during EC. After 60 min of EC solution the pH was about 3.95. The pH elevation was slow during the first 30 min of EC and then the elevation was faster as the solution the pH is a logarithmic function of [H$^+$] ions. Concentration of soluble of Al(III) species are much higher compared to the total (after 60 min) electrochemically dissolved Al(III) in this pH range. Therefore no flocs had appeared. Still about 8% Cr(VI) was removed during EC. This can be explained from a visible accumulation of the chromium layer on cathode. The cathodic layer was dissolved in HCl to determine its Cr(VI)/Cr(III) content. It showed that most of the chromium was Cr(VI). Visible flocs first appeared at the solution pH of about ~4.0. Hence in case of CC with both the salts no removal was noted in this pH range.

Figure 1(b) is the representation of experimental results with the initial pH of 4.87. Cr(VI) concentration in the aqueous medium comes down to 28.9 mg/l in case of EC i.e., about 42.3% was removed. Compared to EC with the initial pH 2, about 34.3% additional Cr(VI) was removed in this

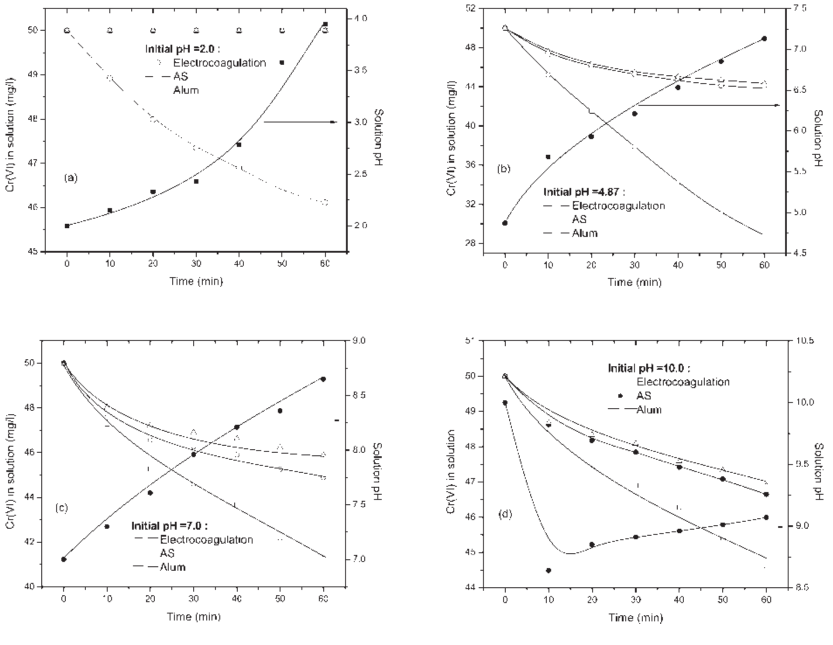

Figure 1. Effect of initial pH on Cr(VI) removal.

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case. Although positively charged monomeric hydroxylated species are formed in the acidic condition, at lower pH, HCl was added to adjust pH dissolves $Al(OH)_3(s)$ species forming soluble aluminum chloride and reduces the available hydroxide for the adsorption. At the range of solution pH from 4.87 to 7.13, along with positively charged mono hydroxylated species, various poly-hydroxylated species (Eqs. 3 and 4) are formed. The concentration of soluble species of Al(III) is also much lower in this pH range. This is the optimum pH range for the formation of $Al(OH)_3(s)$ (22). Due to the combined effect of the surface charge density and the solubility of the Al(III) species, higher removal of Cr(VI) was noted with initial pH of 4.87. A higher chromium layer build up on cathode surface visibly noted at pH 4.87 compared to pH 2 leads to higher Cr(VI) removal.

Both alum and AS show lower Cr(VI) removal efficiencies. About 11.3 and 12.3% Cr(VI) was removed after 60 min of operation. Lower removal of Cr(VI) using chemical coagulants is possibly due to decrease in numbers of effective adsorption sites. Cumulative amounts of about 0.936 g AS and 1.808 g alum were added per 800 ml solution. SO_4^{2-} content of the solution was about 427 and 755 mg in case of AS and alum. After the desired coagulation period, the sulfate content of the solution phase was analyzed. It was found that 18.4 and 24 mg SO_4^{2-} was in the sludge/flocs. Repeat experiments showing results within maximum $\pm 5\%$ deviation confirms simultaneous adsorption of SO_4^{2-} and dichromate/chromate ion containing Cr(VI). Molar ratio of adsorbed SO_4^{2-} and Al in sludge was found to be 0.061 and 0.099. In the pH ranges from 4.87 to 7.13, molar OH/Al ratio in solution varies from 2 to 2.5 or a little higher. Literature (23) also reports that divalent SO_4^{2-} ions present in solution get adsorbed on the oppositely charged sludge matrix. They showed that, 0.110 mole of SO_4^{2-} was adsorbed per mole of Al at molar OH/Al ratio of 3.0 during hydrolysis of AS (5×10^{-2} M Al; 7.5×10^{-2} M SO_4^{2-}).

Influence of SO_4^{2-} on adsorption of Cr(VI) during EC was studied with about 591 mg (average of initial SO_4^{2-} content due to AS and alum addition) of SO_4^{2-}. The cumulative removal of Cr(VI) reduced to 16% from 42.3% in presence of 591 mg of SO_4^{2-}. About 0.132 mole of SO_4^{2-} was adsorbed per mole of Al during EC. Hu et al. (24) showed that the deflouridation efficiency with the Al electrode was reduced to 20–60% from $\sim$100% in presence of 96 to 960 mg/l SO_4^{2-}. They reported that SO_4^{2-} is capable of coordinating with Al(III). Shen et al. (22) observed lower removal of F^- in presence of SO_4^{2-} due to simultaneous adsorption. The lyotropic series of anions is $F^- > SO_4^{2-} \gg Cl^- > NO_3^-$ for Al(III). The lower removal of Cr(VI) in presence of SO_4^{2-} is therefore due to co-adsorption of SO_4^{2-}. Alum shows a slightly lower removal compared to AS possibly due to its higher SO_4^{2-} content. Adsorption of Cr(VI) is not expected to be affected much by Cl^- ions due to its lower affinity for Al(III) species. High concentration of Cl^- ions increases the dissolution of electrode materials and this may improve Cr(VI) removal due to higher coagulant generation during

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EC. However, all experimental results reported in this paper are with Cl^- concentration of 1000 mg/l.

It can be seen from Fig. 1(c) that in case of initial pH 7.0, concentration of Cr(VI) decreases to 41.27, 44.85, and 45.89 from 50 mg/l in case of EC, alum and AS respectively. Much lower removal observed is due to higher pH. The reported value of pH_{zpc} of $Al(OH)_3$ is 8.4 (25). Number of positively charged surface sites decrease with pH getting closer to pH_{zpc} and this result in lower removal.

Concentration of Cr(VI) with initial pH of 10 is presented in Fig. 1(d). The lowest removal of Cr(VI) was noted with this initial pH. At alkaline pH (>8.4, pH_{zpc} of $Al(OH)_3$), monomeric anionic $Al(OH)_4^-$ present in substantial quantity reduces the removal of Cr(VI) present in anions. Additionally at higher solution pH, the solubility of aluminum hydroxide increases and also forms soluble aluminate (AlO_2^-). These also lower Cr(VI) removal. In case of EC at alkaline condition ($pH \approx 10.0$), a quick initial fall of pH was noted and this is followed by a slow rise. Molar ratio of electrochemically generated Al (at anode) and OH (at cathode) is 1:3. Due to formation of $Al(OH)_4^-$ (Al:OH: : 1:4) net OH concentration in solution decreases, and results in the initial fall of pH. A similar observation by other workers has been attributed to the buffering nature of the system (26).

Table 1 summarizes cumulative % Cr(VI) removal with EC and CC. Too high and too low pH reduces the Cr(VI) adsorption. These results are in line with literature (22) that the highest removal is in the pH range from moderate acidic to neutral. Our observation of lower coagulant dose requirement for EC compared to CC is similar to those reported by other workers for different systems (27, 28). Here it is necessary to mention that a direct comparison between EC and EC is not practicable. The systems do not operate on an equivalent basis (29). The chemical coagulants were added in a discrete manner at close intervals of 10 minutes in case of CC but the same was generated continuously in situ during EC.

Table 1. pH and cumulative % removal after 60 min

		Cumulative % removal after 60 min			
		EC			
Initial pH	Final pH	[a]Without SO_4^{2-}	With SO_4^{2-}	AS	Alum
2.0	3.95	8.0		0.0	0.0
4.87	7.13	42.3	16.0	12.3	11.3
7.0	8.65	17.4		10.3	8.2
10.0	9.07	11.0		6.7	6.2

Effect of Al(III) Dissolution/Addition

Coagulant dosing in case of CC can be varied independently and in case of EC the coagulant generated in the system depends on CD and time. CD determines the coagulation generation rate, affects the hydro-dynamics (mixing) of the system, and thereby affects the process efficiency (30). Literature (31) also reports that the different CD for the same charge density does not affect the treatment efficiency of an EC process.

The effect of CD was studied in terms of Cr(VI) removal per unit Al (mg) generation at three different CD (4.36, 8.72, and 13.08 mA/cm^2). These experiments were conducted at the optimum initial pH of 4.87. Progress of EC and corresponding CC experiments are shown in Fig. 2. Increasing the CD from 4.36 to 13.08 mA/cm^2 lead to increase in coagulant dose in 60 minutes from 0.1 to 0.3 kg Al(III)/m^3. The charge density (in 60 min) correspondingly increased from 6.25 to 18.75 F/m^3. At higher CD, cumulative % removal of Cr(VI) increases due to higher coagulant dose. For example, about 24.2, 40.0, and 43.9% Cr(VI) was removed after 30 min of EC at CD of 4.36, 8.72, and 13.08 mA/cm^2. Figure 2 shows the cumulative Cr(VI) removal per unit Al(III) dissolved/dosed with progress of EC/CC for CD 4.36 mA/cm^2. The ratio "Cr(VI) removed (mg)/Al dose (mg)" decreases at a higher Al dose, i.e with time. In case of EC the ratio is much above the CC results, pointing to the fact that EC is more efficient than CC in Cr(VI) removal. The reason for higher efficiency is already discussed earlier. The fall of the ratio in case of EC is close to linear, with a slightly higher fall rate in the initial period. In case of CC, the variation in rate of fall is more pronounced.

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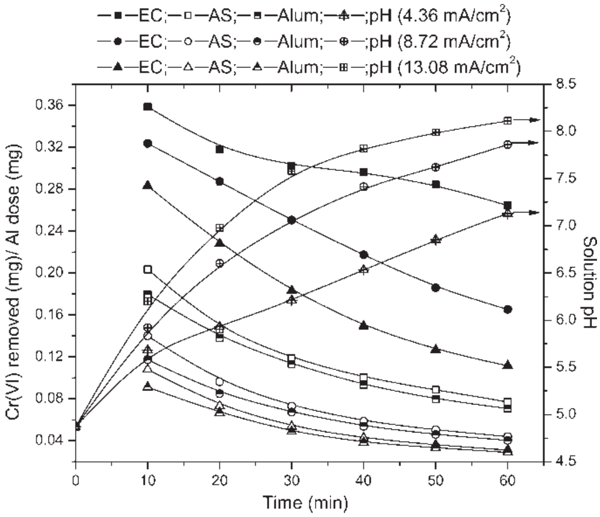

Figure 2. Effect of Al(III) dissolution/coagulant dosing on Cr(VI) removal.

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Table 2. Cr(VI) removal per unit of Al dosed/dissolved in 60 min

Current density, (mA/cm^2)	Cr(VI) removal (%)			Cr(VI) $_{\text{removal}}$/Al, (mg/mg)		
	EC	CC$_{AS}$	CC$_{Alum}$	EC	CC$_{AS}$	CC$_{Alum}$
4.36	42.3	12.3	11.3	0.264	0.077	0.071
8.72	52.9	14.0	12.9	0.165	0.044	0.042
13.08	53.5	14.9	13.8	0.111	0.030	0.029

This fall in the ratio with progress of the process is mainly due to diminishing concentration of Cr(VI) in solution. Similar trends were observed with CD 8.72 and 13.08 mA/cm^2. Table 2 shows Cr(VI) removal per unit of Al dosed/dissolved in 60 min in cases of EC and CC. It can be seen that the process efficiency expressed as the ratio mentioned falls with increasing CD or a higher dosage rate of coagulant.

The variation of pH and Cr(VI) removal % with CD at constant charge density are shown in Fig. 3. It shows the variations for charge density values of 3.125 and 6.25 F/m^3. Practically negligible effect of CD on pH elevation at constant charge density is observed. This corroborates that the current efficiency remains unaltered with CD variation. Increasing CD has a small detrimental effect on the removal % of Cr(VI). Dissolution of electrode material is found to be independent on CD. Formation of various

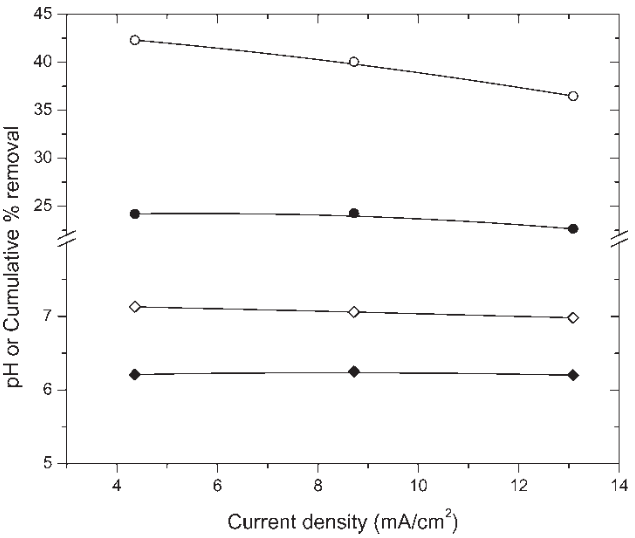

Figure 3. Effect of current density on Cr(VI) removal at constant charge density (Charge density 3.125 F/m^3, Al dosing 0.05 k/m^3: removal (•), pH (◆); Charge density 6.250 F/m^3, Al dosing 0.1 kg/m^3: removal (○), pH (◇).

hydroxide species from electrochemically dissolved Al(III) is a fast reaction and most of Al(III) is converted to hydroxides (32). Adsorption of Cr(VI) on the hydroxides is possibly the rate governing step and slightly lower removal % at higher CD results due to lesser contact time between the Cr(VI) and the hydroxides. These also corroborate the results of Chen et al. (31) showing the removal of pollutants from restaurant wastewater to be practically independent of CD at the same charge density. A higher rate of bubble generation at higher CD may also affect the removal of Cr(VI) by promoting mixing, but in this study the effect may not be appreciable as the reactor is already well-agitated.

Effect of Initial Cr(VI) Concentration

Concentration of Cr(VI) in industrial effluents varies over a wide range. In particular, concentration of Cr(VI) in a conventional electroplating effluent generally varies from 8 to 275 mg/l (2, 33). The effect of different Cr(VI) initial concentration was studied with 25, 50, and 100 mg/l. Experiments were conducted with optimized initial pH of 4.87 and CD of 4.36 mA/cm^2 as removal of Cr(VI) (mg) per mg Al dosing was higher at this CD.

Though the quantity of Cr(VI) removal is significantly higher at higher initial concentration for the same coagulant (Al) dose or EC time, cumulative % removal of Cr(VI) decreases. For example, about 51, 42.3, and 29% Cr(VI) was removed after 60 min of EC with initial Cr(VI) concentration of 25, 50, and 100 mg/l. The corresponding dose of the coagulant was 80 mg (as Al). Figure 4 shows the progress of the efficiency of removal expressed as the ratio of Cr(VI) removal per unit Al dosing for different initial Cr(VI) concentrations. At higher Cr(VI) concentration, the treatment efficiency of the process increases as Cr(VI) removed (mg)/Al dose (mg) increases (Fig. 4). Starting from a higher value, the ratio gradually decreases with progress of treatment. This is attributed to that lower pH elevation (Fig. 4) at higher Cr(VI) concentration because species of Cr(VI) in aqueous solution are acidic in nature. Initially, the rate of the pH elevation was higher and the final pH of 7.28, 7.13, and 6.31 was reached with initial concentration of 25, 50, and 100 mg/l. Compared to initial concentration of 25 and 50 mg/l, the solution was more acidic with 100 mg/l Cr(VI) as more was present Cr(VI) in aqueous phase. The effect of initial concentration of Cr(VI) during CC was studied with 25 and 50 mg/l Cr(VI). It can be seen that like EC, both pH of the solution and Al dosing have an appreciable affect on Cr(VI) removal in this pH range.

Figure 5 shows the effect of Cr(VI) initial concentration at the same pH achieved during EC from initial pH of 4.87. The time required to reach the same solution pH varies linearly with Cr(VI) concentration. This is calculated from Fig. 4. Corresponding Cr(VI) removal was considerably high due to the coagulant dose. At $pH > 7.0$, Cr(VI) removed (mg)/Al dosing (mg) is

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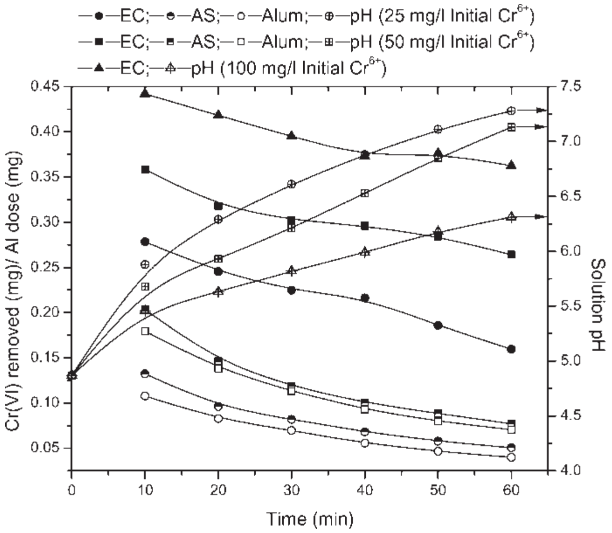

Figure 4. Cr(VI) removed (mg)/Al dosing (mg) at different initial Cr(VI) concentration.

reduced appreciably at higher Al dose due to pH elevation. But at pH < 7.0, increase in the coagulant dose significantly enhance the removal of Cr(VI). About 10 mg Cr(VI) was removed after 10 min of EC (at same coagulant dose) with initial concentration of 38.8 and 72.4 mg/l. Corresponding

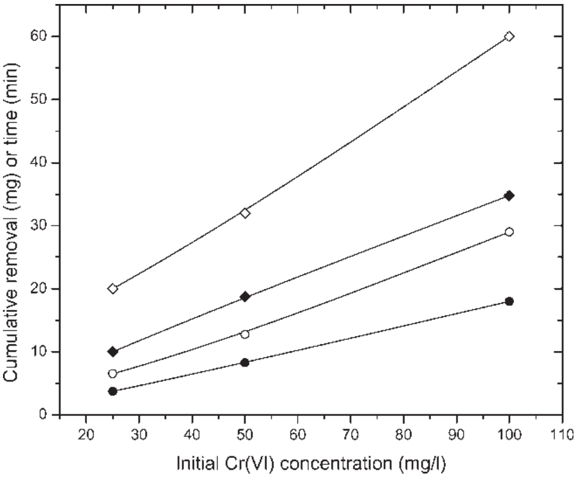

Figure 5. Effect of initial Cr(VI) concentration at constant pH (pH 5.88: removal (•), time (◆); pH 6.29: removal (○), time (◇)).

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solution pH was 5.88 and 6.29 (Fig. 4). This further corroborates that in the pH range ($4.88 < \text{pH} < 7.0$) investigated, both solution pH and coagulant dosing appreciably affects the removal of Cr(VI) from the aqueous solution.

CONCLUSION

Electrocoagulation with the Al electrode in the absence of SO_4^{2-} is more efficient for removal of Cr(VI) from aqueous solution compared to the chemical coagulation with aluminum salts. The removal of Cr(VI) takes place in the order of $EC > CC_{AS} > CC_{alum}$. Al dissolution was significantly high than Faraday's law. This was due to electro-dissolution and acidic and alkaline corrosion of Al from the anode and cathode surface and catalytic action of Cl^-. The electrocoagulation process using Al electrodes do not seem be very attractive for the removal of Cr(VI) from wastewater. Maximum 42% Cr(VI) was removed in the pH ranges from 4.9 to 7.0 with initial concentration of 50 mg/l and CD of 4.36 mA/cm^2. Under the same coagulant dosing (~80 mg Al(III)) and pH range only about ~11.5% Cr(VI) was removed with aluminum salts as chemical coagulants. Competitive adsorption of SO_4^{2-} on the sludge matrix results lower removal of Cr(VI) in case of CC. Higher coagulant dosing leads to higher Cr(VI) removal but it adversely affects the treatment efficiency as more coagulant is required per unit of pollutant removal. Increasing the CD from 4.36 to 13.08 mA/cm^2 increases removal of Cr(VI) from 42.3 to 53.48%. But this will increase the power consumption from 0.67 to 5.02 kWh/m^3 or 23.2 to 216.1 kWh/kgCr(VI).

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