

Electrocoagulation with bipolar iron electrodes for trivalent chromium removal from synthetic wastewater

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Abstract

The aim of this study is to investigate the performance of batch electro coagulation (EC) using iron electrodes with bipolar configuration for simultaneous removal of chromium (Cr^{3+}) from synthetic wastewater. The influences of current density (from 2 to 25 mA/cm^2), initial metal concentration (from 100 to 250 mg/L) and supporting electrolyte (0-12 mmol/L Na_2SO_4) on removal efficiency are explored in a batch stirred cell to determine the best experimental conditions.

The results indicate that EC was very efficient to remove Cr^{3+} from the synthetic wastewater having an initial concentration of 250 mg/L of Cr^{3+} under the best experimental conditions. At the current density of 15 mA/cm^2 with a total energy consumption of ~ 18.5 kWh/m^3 , more than 98.7% removal value was achieved for Cr^{3+} after 20 min EC treatment. Time of 20 minutes EC treatment was chosen as optimum time to gain less than 4 $\text{mg Fe}/\text{L}$ in the treated water.

Keywords: electro coagulation; chromium removal; iron electrode; bipolar electrode configuration; synthetic wastewater treatment; supporting electrolyte.

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1. INTRODUCTION:

Large amount of wastewater containing Cr has been discharged directly or indirectly discharged into the environment from various industry processes such as, leather tanning, metallurgical and metal plating, textiles dyeing and ceramics, printing inks, paints and pigment and wood preservatives, photographic sensitizer manufacturing, etc. Huge quantity of this industrial wastewater containing chromium is discharged into the environment in trivalent Cr^{+3} and hexavalent Cr^{+6} forms and threaten natural life and public health for their non-degradable and carcinogenic properties. Cr^{+6} has a significant mobility in water body for its high solubility. The Cr^{+6} is a powerful carcinogenic agent, because of its ability to modify the DNA transcription process causing important chromosomal aberrations. Exposure to Cr^{+6} may cause health problems of epigastria, nausea, vomiting, severe diarrhea, internal hemorrhage, dermatitis, liver and kidney damage. Long time contamination with Cr^{+6} can result in digestive tract and lung cancers [1, 2].

The Cr^{+3} has also been shown to be a potential hazard, especially in the aquatic environment. As an essential trace element form in mammalian metabolism, Cr^{+3} has effective function for reducing blood glucose levels, and is often offered to diabetes sufferers. However, long time exposure to excessive doses of Cr^{+3} may also cause some adverse health effects [3].

Thus environmental regulations usually define limitation values for total chromium (TCr, Cr^{+6} , Cr^{+3} and other forms of chromium) and Cr^{+6} concentrations in waters. Based on the environmental regulations, almost all the wastewater produced by the plants that use chromium during industrial process needs to be treated before being discharged into the environment [4].

Currently, leather tanning by using trivalent chromium is one of the most common and efficient tanning processes; nevertheless, a significant share of the pollution resulting from tannery wastewater comes from this stage, due to the Cr^{+3} that is not fixed to leather (~15%) [5].

This pollutant has sparked much concern to societies and regulation authorities around the world, due to their toxicity. There has been a serious environmental challenge for the produced Cr industries, due to pressures from public opinion and the numerous environmental regulations imposed [6,7].

Various techniques have been employed for recovering or removing Cr from wastewater such as precipitation and sedimentation [8] cementation [9], coagulation/flocculation [10], adsorption by several types of adsorbents such as activated carbon [11], lignin [12], diatomite [13], natural hydrothermal zeolites [14], synthetic zeolites [15], bentonite clay [16], biosolid sorbent from waste-activated sludge [17], biosorption by aquatic weeds [18], ion-exchange resins [19] and membrane technologies [20-22].

Most of these methods suffer from some drawbacks such as high capital and operational costs, large input of chemicals, incomplete removal and their operational problems.

Among the various techniques mentioned above, EC has been found to be quite interesting both for economical and environmental reasons. EC has been successfully applied to remove soluble ionic species from solutions, particularly heavy metals.

EC has the potential to be the distinct economical and environmental choice for treatment of industrial wastewater and other related water management issues. EC is an efficient technique since adsorption of hydroxide on mineral surfaces are a 100 times greater on in situ rather than on precipitated hydroxides when metal hydroxides are used as coagulant. EC needs simple equipments, designable for virtually any size. It is cost-effective, and easily operable. The start-up and operating costs are relatively low. It requires low maintenance cost with no moving parts. Since practically no chemical addition is required in this process, it brings minimum chance of secondary pollution. It needs low current, and it can be run even by green processes, such as, solar, wind-mills and fuel cells. EC process can effectively destabilize small colloidal particles. It produces minimal sludge. Gas bubbles produced during

electrolysis can enhance flotation. It removes the smallest colloidal particles efficiently compared to conventional chemical and biological techniques, because the smallest charged particles have greater probability of being coagulated by the electric field that sets them in motion [23]. In addition to these, the following advantages of EC process can be added: electrochemical-based systems allow controlled and rapid reactions, smaller systems become viable and, instead of using chemicals and microorganisms, the systems employ only electrons to facilitate water treatment.

The advantages of EC have encouraged many studies on the use of this technology for treatment of several industrial effluents such as paper wastes [24], oil wastes [25,26], textile dyes wastes [27], polymeric wastes [28], phenolic waste [29]. Electro coagulation has been found a promising technique in treating urban wastewater [30], restaurant wastewater [31], potato chips wastewater [32], laundry wastewater [33], alcohol distillery wastewater [34], house wastewaters [35], dairy wastewater [36] and biodiesel wastewaters [37].

In recent years, there is much interest in using EC for treatment of water and wastewater containing phosphate [38], fluorine [39], nitrate [40], phenol [29], sulfide, sulphate and sulfite ions [41], suspended particles [42], humic acids [43] and heavy metals including Cr [44-47].

Many systems and reactors (batch or continuous mode) with monopolar or bipolar EC connection were investigated [48-51].

Monopolar electrodes need an external electrical contact to the power supply and their two faces are active with the same polarity (a voltage, U is connected between "n" pairs of anodes and cathodes, connected in parallel via copper bus bars). The current in parallel connections at monopolar electrodes is divided between all the electrodes in relation to the resistance of the individual cells. Hence, a lower potential difference is required in parallel connection when compared with serial connections [49-51]. Monopolar electrodes in serial connections for each pair of electrodes is internally connected with each other, because the cell voltages sum up, a higher potential difference is required for a given current [51].

There is no electrical connection between inner electrodes for bipolar electrodes in serial connections. The outer electrodes are only connected to the power supply. Outer electrodes are monopolar and inner ones are bipolar. The voltage applied between the latter electrodes by the power supply causes the polarization of the intermediate bipolar electrodes, which then present different polarities in the opposite faces. This connection mode has a simple setup and requires less maintenance cost during operation. The costs of higher voltage/lower current transformer rectifiers are lower for the same total power output than the lower voltage/higher current required for monopolar electrode configurations. However, the large terminal voltage between a pair of feeder electrodes also causes a proportion of the current to flow in the solution, by passing the bipolar electrodes [49] and [50].

The target of the present study was to examine the treatability of synthetic wastewater containing Cr^{+3} by batch EC using iron bipolar electrodes and to compare the effects of varying operating parameters such as the applied current density, initial concentration and supporting electrolytes on Cr^{+3} removal.

2. THEORETICAL BACKGROUND ON EC PROCES:

Electrochemical water and wastewater treatment technology –EC delivers the coagulant in situ by anodic dissolution and produces subsequently, iron or aluminum hydroxides having a considerable sorption capacity, while the simultaneous cathodic reaction allows pollutants removal either by deposition on cathode electrode or by flotation (generation of hydrogen at the cathode) [52-53].

The EC process is generally accepted that the EC process involves three successive stages: formation of coagulants by electrolytic oxidation of the electrode, including metal anode dissolution and water electrolysis; destabilization of the contaminants, particulate suspension, and breaking of emulsions; aggregation of the destabilized phases to form flocs [54].

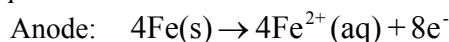
One of the most widely used electrode materials in EC process is iron. When iron electrodes are used, the generated $Fe(aq)^{3+}$ ions will

immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides, and the hydrolysis products may form many monomeric ions $\text{Fe}(\text{OH})_3$ and/or polymeric hydroxyl complexes, such as $\text{Fe}(\text{OH})_4^-$, $\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3^0$, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$, $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})^{2+}$, $\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$ and $\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4^{4+}$ etc., depending on the pH of the aqueous medium and co-precipitate as $[\text{M}, \text{Fe}](\text{OH})_3$ [55]

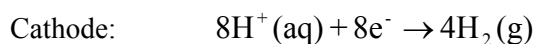
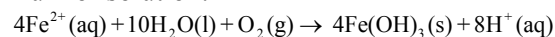
The following mechanisms describe the formation of the iron hydroxides: [55]

• Mechanism 1

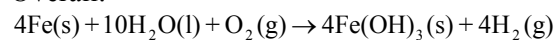
$\text{pH} < 4$



Bulk of solution:

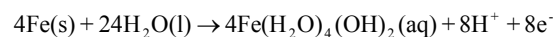


Overall:

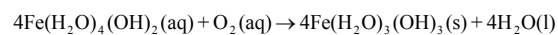


$4 < \text{pH} < 7$

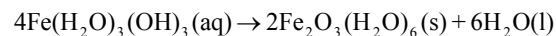
Anode:



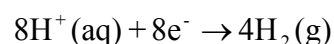
Bulk of solution:



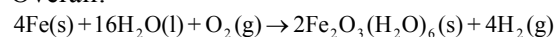
Bulk of solution:



Cathode:



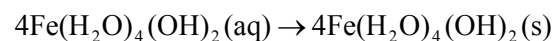
Overall:



$6 < \text{pH} < 9$

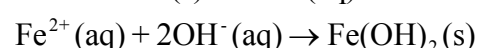
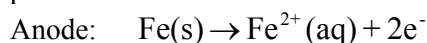
Precipitation of Fe(III) hydroxide continues, and Fe(II) hydroxide precipitation also occurs presenting a dark green floc.

Bulk of solution:

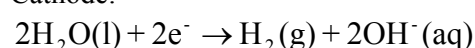


• Mechanism 2

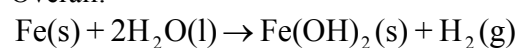
$\text{pH} < 4$



Cathode:



Overall:

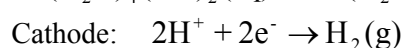
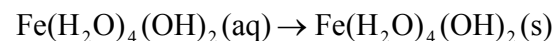


$4 < \text{pH} < 9$

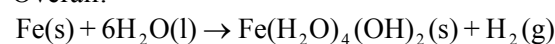
Anode:



Bulk of solution:



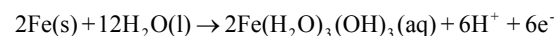
Overall:



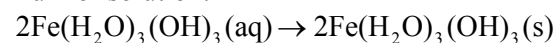
• Mechanism 3

$4 < \text{pH} < 9$

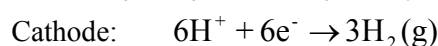
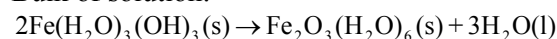
Anode:



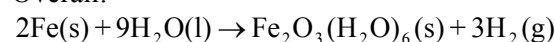
Bulk of solution:



Bulk of solution:



Overall:



The $\text{Fe}(\text{OH})_n(\text{s})$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by electrostatic attraction, followed by coagulation. 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 $\text{Cr}(\text{OH})_3(\text{s})$ [51].

Bigger aggregates/flocs are formed due to sequential interaction of the hydroxides. The settled sludge/floc phase is easily removed from aqueous phase [56].

Coagulation and EC generate sludge, and EC generates scum. As an advantageous of EC, it is relatively a low sludge producing technique. Sludge formed by EC tends to be readily settleable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides. According to (Kushwaha et al., 2010) [57] sludge and scum generated in EC can be dried and used as a fuel in the boilers/incinerators, or can be used for the production of fuel-briquettes. On the other hand, the bottom ash obtained after incineration of scum and sludge may be blended with clay with higher ratio of clay to make fire bricks. Few studies have shown that addition of finely divided materials, such as silica, fly ash, etc. to clays and Portland cement not only increases heat resistance of these materials but also

improves the microstructure and compressive strength of cement pastes [58]. Thus, sludge and scum generated by EC treatment of dairy wastewater can be disposed off through chemical and physical fixation [59]. Besides, some researchers have investigated the use of EC sludge for the treatment of other pollutants. For example, Golder et al., 2007 [56] have searched the removal of phosphate from aqueous solutions using calcined metal hydroxide sludge wastewater generated from EC. According to the study results (Golder et al., 2007) [56], calcined electrocoagulated metal hydroxide sludge has been found as an efficient adsorbent for phosphate removal.

3. MATERIALS AND METHODS:

To demonstrate the effect of varying operating parameters, a stock solution of 1 L containing 1000 mg for Cr^{+3} was prepared with basic chromium sulfate (Merck). A set of experiments were conducted with three different solutions containing Cr^{+3} concentrations of 100, 150 and 250 mg/L by diluting the stock solution.

The effect of initial metal concentrations with different current densities on the system performance was investigated. Experiments were made by using a cylindrical glass cell of 500 mL on a magnetic stirrer (Falc Instruments F60 model, Italy). Six plates of iron electrodes were installed vertically with a spacer to ensure fixed distance and immersed to a 4 cm depth with an effective area of 100 cm^2 each, were used as electrodes in bipolar with serial connections mode in the experiments. The inter-electrode distance was 0.3 cm. The Bench-scale EC reactor with bipolar electrodes in serial connection is shown in Fig. 1.

The electrode surfaces were rinsed with diluted HNO_3 and distilled water and then dried to eliminate the oxides and passivation layers between the experiments. A DC-power supply (Statron type 3262, Germany) characterized by the ranges 0–5 A for current and 0–80 V for voltage was used to apply different current densities i.e. 2, 5, 8, 15 and 25 mA/cm^2 . The polarity of the cell was reversed after each experiment to limit the formation of the passivation layers on the electrodes. To determine the system performance, samples of 5 mL were taken periodically from the reactor at

predetermined time intervals (5 or 10 min), and then filtered using Whatman filter paper (Grade 40) to eliminate sludge formed during electrolysis. The residual Cr^{+3} concentrations were determined by ICP-OES (Varian 720 ES model, Australia).

The pH and conductivity of solutions during the EC were measured by a pH meter (Thermo-Orion 420 A model, USA) and a conductivity meter (WTW Cond 720, Germany). To investigate the effect of current density on the removal yield, a series of experiments were carried out at different supporting electrolytes of 0, 3, 6, 9 and $12 \text{ mmol/L Na}_2\text{SO}_4$, which equal (0, 213, 425, 639, $852 \text{ mg/L Na}_2\text{SO}_4$). Using supporting electrolyte was just for overcoming a high ohmic resistance between the anode and the cathode in bipolar connection when electrical conductivity of the solution is low. All the runs were performed at laboratory temperature and at the stirring speed of 300 rpm.

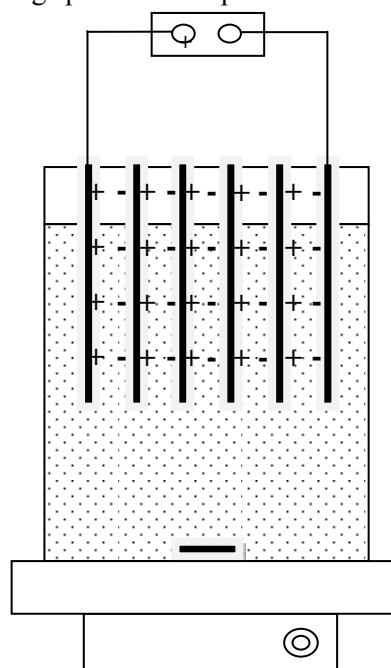


Figure 1. Bench-scale EC reactor with bipolar electrodes in serial connection.

4. RESULTS AND DISCUSSION:

The EC process is affected by several operating parameters, such as initial concentrations, current density, supporting electrolyte and contact time. In this study, all these parameters

were explored in order to evaluate a treatment technology for Cr^{3+} removal from a synthetic wastewater.

4.1. Effect of current density

Current density combines the effect of cell current and effective surface area of electrodes. Current density during EC experiments was varied by changing cell current. Figures 2, 3 and 4 show the effect of current density on EC treatment. Each of these experiments was conducted with same initial concentration of 100, 150 and 250 mg/L of Cr^{3+} . After 20 min of EC, 60.35, 96.3 and 96.9% of Cr^{3+} from the liquid phase was found to be transferred to sludge phase at current densities of 2,5 and 8 mA/cm^2 , respectively for the initial Cr^{3+} concentration of 100 mg/L with different supporting electrolyte (0, 3 and 6 mmol/L Na_2SO_4 respectively) as given in Fig. 2. More or less complete removal (99.35 and 99.7%) of Cr^{3+} was noted at the current densities of 5 and 8 mA/cm^2 , respectively after 30 min of EC treatment.

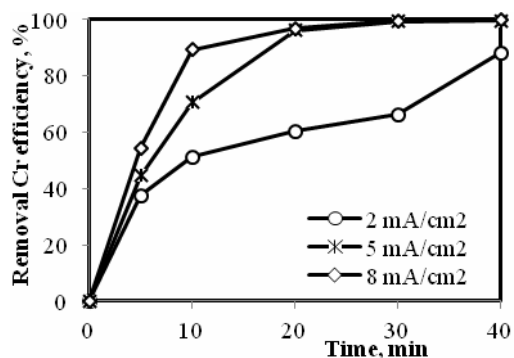


Figure 2.Effect of current densities on the removal efficiency of Cr^{3+} at the initial concentration of 100 mg/L with different supporting electrolyte.

For the initial Cr^{3+} concentration of 150 mg/L, the removal efficiency values were 92.1, 98.57 and 99.37 % at the current densities of 8, 15 and 25 mA/cm^2 , respectively after 10 min EC treatment with different supporting electrolyte (6, 9 and 12 mmol/L Na_2SO_4 respectively) as shown in Fig. 3.

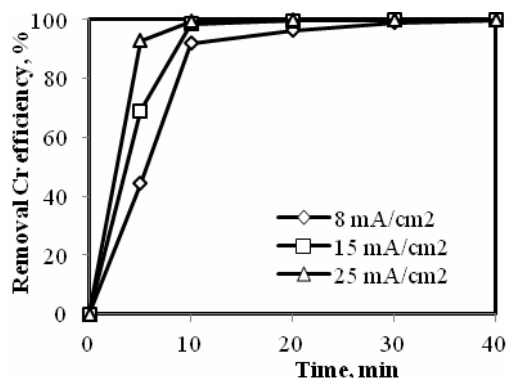


Figure 3.Effect of current densities on the removal efficiency of Cr^{3+} at the initial concentration of 150 mg/L with different supporting electrolyte.

For the initial Cr^{3+} concentration of 250 mg/L, the removal efficiency values were 88.34, 95.22 and 97.10 % at the current densities of 8, 15 and 25 mA/cm^2 , respectively after 10 min EC treatment with the same supporting electrolyte (9 mmol/L Na_2SO_4) as shown in Fig. 4.

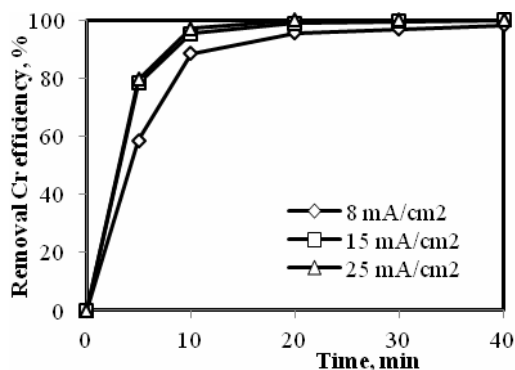


Figure 4.Effect of current densities on the removal efficiency of Cr^{3+} at the initial concentration of 250 mg/L with the same supporting electrolyte.

Therefore, effective removal of Cr^{3+} by electrocoagulation is observed at higher current densities.

At higher current density (Guo et al., 2006) [60]:
 (i) 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 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 $\text{Cr}(\text{OH})_3$ is significantly soluble at this pH (at the initial stage) and $[\text{Cr}, \text{Fe}](\text{OH})_3$ has lower solubility than $\text{Cr}(\text{OH})_{3(\text{s})}$ [26].

(ii) Dissociation of different soluble species of $\text{Fe}^{3+}/\text{Fe}^{2+}$ with generation of OH^- ions at the

cathode surface during EC increase the solution pH. At higher pH, both chromic and iron hydroxides tend to precipitate (chemical precipitation) enhancing chromium removal.

(iii) Due to elevated dissolution rate of anode, more sludge from the metal electrodes is generated. This boosts the Cr^{3+} removal due to sweep coagulation at higher solids loading.

(iv) More bubbles are generated at higher current and this improves the mixing and the removal. The effect may not be appreciable as the system is already agitated.

4.2. Effect of initial concentration

EC treatment for initial concentrations of 100, 150 and 250 mg/L were tested. Initial concentrations did not influence the removal rates, whereas higher initial concentrations caused higher removal rates. Fig. 5, 6 and 7 show the variations of initial Cr^{3+} concentrations as a function of time at different current densities of 8, 15 and 25 mA/cm^2 . All these graphics exhibited a logical trend related with time depending on initial concentrations without direct correlations between Cr^{3+} concentration and removal rates. The EC treatment is more effective at the beginning of the process when the concentration is higher than at the end of the operation when the concentration is relatively lower.

Fig. 5 shows that after 30 min EC treatment the Cr^{3+} residual concentrations at the current density of 8 mA/cm^2 0.3, 1.35 and 7.7 mg/L were achieved for the initial Cr^{3+} concentrations of 100, 150 and 250 mg/L, respectively with different supporting electrolyte (6, 6 and 9 mmol/L Na_2SO_4 respectively).

Fig. 6 shows that after 30 min EC treatment the Cr^{3+} residual concentrations at the current density of 15 mA/cm^2 0.4, and 3.15 mg/L were achieved for the initial Cr^{3+} concentrations of 150 and 250 mg/L, respectively with the same supporting electrolyte (9 mmol/L Na_2SO_4).

Less than the discharge limit for Cr^{3+} (2mg/L) was obtained at the current density of 25 mA/cm^2 after 10 and 20 min EC treatment for the initial Cr^{3+} concentrations of 150 and 250 mg/L, respectively with different supporting electrolyte (12 and 9 mmol/L Na_2SO_4 respectively) as shown in Fig. 7.

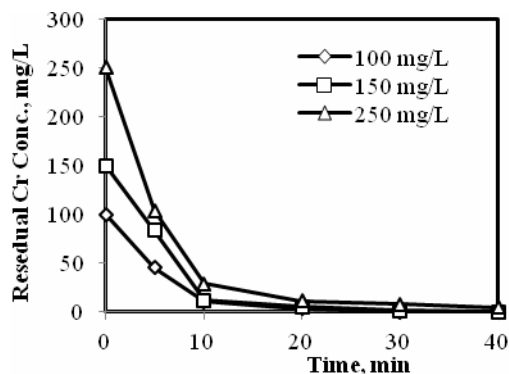


Figure 5. Effect of initial concentration on the residual concentrations of Cr^{3+} at the current density of $i = 8 \text{ mA}/\text{cm}^2$ with different supporting electrolyte.

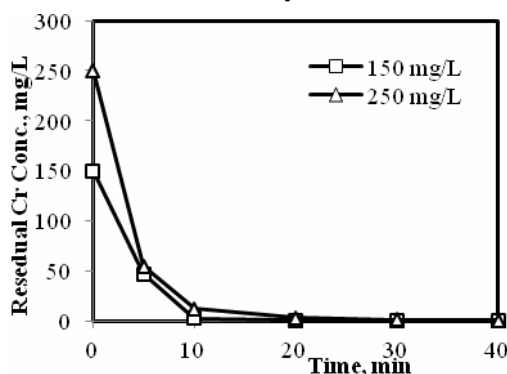


Figure 6. Effect of initial concentration on the residual concentrations of Cr^{3+} at the current density of $i = 15 \text{ mA}/\text{cm}^2$ with the same supporting electrolyte.

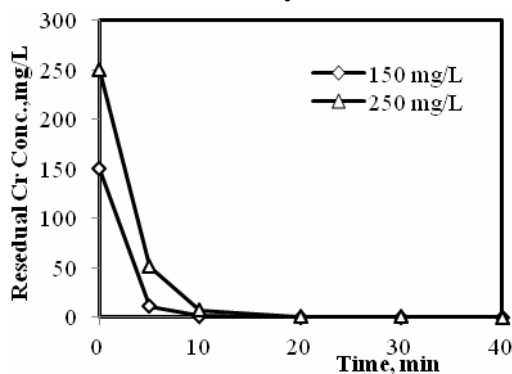


Figure 7. Effect of initial concentration on the residual concentrations of Cr^{3+} at the current density of $i = 25 \text{ mA}/\text{cm}^2$ with different supporting electrolyte.

4.3. Effect of supporting electrolyte on removal efficiency

In electrochemical processes which consist of heterogeneous ion transfer reactions, the

conductivity of the solution to be treated is a significant parameter. Solution conductivity affects the applied current efficiency, voltage, and consumption of electrical energy in electrolytic systems, because the current passing through the circuit is a function of the conductivity under a certain applied voltage. More energy is required for overcoming a high ohmic resistance between the anode and the cathode when electrical conductivity of the solution is low. The most common method used to overcome this problem is to add a small amount of electrolyte, which increases the electric conductivity of the solution and thus reduces the energy consumption during electrocoagulation. Conductivity of the solution increases as the supporting electrolyte concentration increases, so current passing through the circuit increases in potentiostatic mode [36].

In this study, sodium sulfate (Na_2SO_4) was used as the supporting electrolyte for increasing the conductivity of the synthetic wastewater.

The different pollutants which exist in the real industrial wastewater serve as supporting electrolyte.

The concentration of supporting electrolyte was adjusted to the desired levels by adding a suitable amount of Na_2SO_4 to the synthetic wastewater. Fig. 8 illustrates the effect of the supporting electrolyte on the removal efficiency during the electrocoagulation process. It can be seen evidently that increasing the concentration of the supporting electrolyte leads to an increase in Cr^{3+} ion removal efficiency.

When the concentration of the supporting electrolyte increases, the solution ohmic resistance decreases, so the current required to reach the optimum applied voltage diminishes, decreasing the consumed energy.

Fig. 8 shows that, the removal efficiency values of 56.6, 98.57 and 99.13 % were achieved at the current density of 15 mA/cm^2 for the initial Cr^{3+} concentrations of 150 mg/L with different supporting electrolyte (3, 9 and 12 mmol/L Na_2SO_4 respectively) after 10 min EC treatment.

4.4. Evaluation of specific energy consumption
Specific electrical energy consumption during electrocoagulation (SEEC) is a very important

economical parameter in the electrocoagulation process.

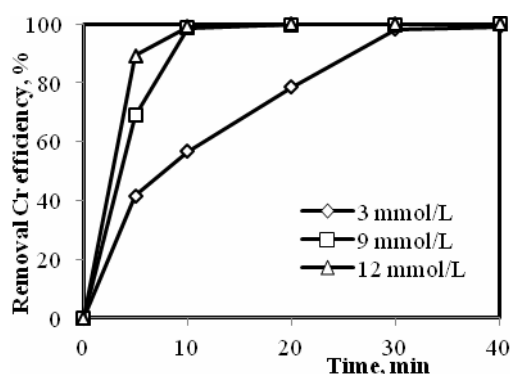


Figure 8. Effect of supporting electrolyte on removal efficiency of Cr^{3+} at the current density of $i = 25 \text{ mA}/\text{cm}^2$ for the initial Cr^{3+} concentrations of 150 mg/L .

Once the required voltages and the corresponding currents were obtained from the electrocoagulation experimental tests, it was possible to estimate the amount of energy consumed. Variation of total energy consumption values with time for Cr^{3+} removal as a function of current density is given in Fig. 9. As also seen in Fig. 9 energy consumption is directly related with the current density.

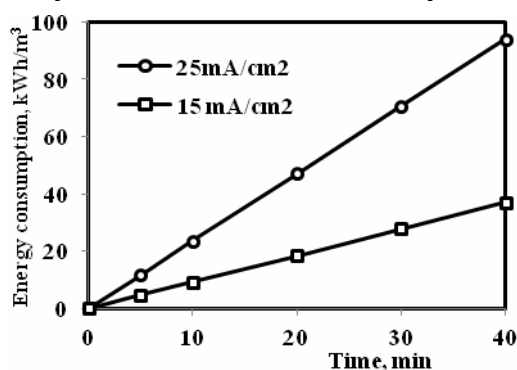


Figure 9. Total energy consumption values as a function of current density at the same supporting electrolyte.

Total energy consumption was $\sim 18.5 \text{ kWh}/\text{m}^3$ to gain more than 98.7% removal value for initial Cr^{3+} concentration of 250 mg/L at the current density of 15 mA/cm^2 after 20 min EC treatment at supporting electrolyte of 9 mmol/L Na_2SO_4 . Using the current average electrical energy price of Syrian Pound 5 for 1 kWh the cost of energy consumed per m^3 of treated water is 92.5 S.P. Time of 20 min EC treatment was chosen for optimum time to gain less than 4 $\text{mg Fe}/\text{L}$ in the

treated water, although this pollution of Fe ions will be useful in real wastewater for its additional coagulation effect.

Other cost items such as steel electrode consumed, maintenance and solid/liquid separation costs were not taken into account. Supporting electrolyte cost was not taken into account too, because the different pollutants which exist in the real industrial wastewater serve as supporting electrolyte.

5. CONCLUSIONS:

Bath electrocoagulation treatment using iron electrodes with bipolar configuration for a synthetic wastewater containing Cr^{3+} was investigated. Removal of Cr^{3+} by EC treatment from aqueous solution is a feasible process. The effects of current density and initial Cr^{3+} concentration on the removal efficiency were examined in a parallel plate electrochemical reactor. Total energy consumption of ~ 18.5 kWh/m³ was determined to gain more than 98.7% removal value for initial Cr^{3+} concentration of 250 mg/L at the current density of 15 mA/cm² after 20 min EC treatment. Using the current average electrical energy price of Syrian Pound 5 for 1kWh the cost of energy consumed per m³ of treated water is 92.5 S.P. Time of 20 min EC treatment was chosen for optimum time to gain less than 4 mg Fe/L in the treated water, although this pollution of Fe ions will be useful in real wastewater for additional coagulation of turbidity and color.

According to all results, EC with iron electrodes is a convenient route for effective removal of Cr^{3+} from a synthetic wastewater.

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