Removal of chromium(III) from tannery wastewater by electrochemical peroxidation process in a bench scale reactor

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ABSTRACT

Chromium(III) used in tanning process is not consumed fully and around 30–40% of Chromium(III) is washed away to the environment causing severe environmental problem especially to the aquatic system. To remove Chromium(III) from wastewater, many different treatment techniques have been developed. This study deals with the ability of electrochemical peroxidation process for the removal of Chromium(III) from tannery wastewater in a batch stirred tank bench scale reactor with hopper bottom of 5 L working volume equipped with two iron electrodes which were investigated. The removal percentage of chromium was determined by varying operating parameters such as pH = 2–8, Fe^{2+} = 2–5 mg/L, H_2O_2 = 5–20 mg/L and current density = 10–40 mA/cm² were studied. The results showed that the Chromium(III) removal efficiency of 87% was achieved under optimum condition such as pH = 2, Fe^{2+} = 2 mg/L H_2O_2 = 15 mg/L, current density = 30 mA/cm² and contact time was 120 min with an electrical energy consumption of 0.073 kWh/L. The operating costs for the removal of Chromium(III) was found to be 0.4 $/m³ for treated tannery wastewater. The electrochemical peroxidation process proved to be an efficient and appropriate technique for the removal of Chromium(III) from tannery wastewater.

Keywords: Electrochemical peroxidation process; Tannery wastewater; Chromium(III); Iron electrodes

1. Introduction

The tannery industry is one of the major contributors to the economy and provides large-scale employment opportunity for economically weaker sections of the society. India is the third largest leather producer in the world, next to China and Italy. The Indian leather industry occupies an important position on the global scale as it is a major source of foreign exchange revenues. In addition, tannery wastes are ranked as the highest pollutants among all the industrial wastes. It is estimated that about 2000–3000 tonnes of chromium are released into the environment annually from tannery industries in India [1].

The process of tanning involves the use of large amounts of fresh water and various chemicals such as lime, sodium bicarbonate, common salt, sodium sulphate, chrome sulphate, fat liquors, vegetable oils and dyes [2]. Although Chromium(III) salts are the most widely used chemicals for tanning processes, only 70% of the total chromium salts react with the hides. The concentration of Chromium(III) in the tannery spent liquor effluent ranges between 2000 to 5000 mg/L which cannot be discharged into the environment without treatment [3]. The two most common valences for chromium in aqueous solutions are 3+ and

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6+. Chromium(III) may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much Chromium(III) can cause health effects as well, for instance skin rashes. In general, toxic effects of chromium are linked with long-term low-level exposures in our environment. It may enter humans through plants grown on contaminated soil or irrigated by contaminated water. It is highly toxic, mutagenic and carcinogenic for the mammals. Its exposure is associated with many chronic diseases; respiratory illnesses, ulcers and perforation of the nasal septum as well as increased lung and nasal cancer, skin irritation diseases, dermatitis, eczema, conjunctivitis, liver and kidney damage [4]. Thus when tanning wastewater is disposed without treatment may cause major pollution problems to environment and people. In order to meet increasingly stringent discharge limit and to protect the environment and economy, the removal and recovery of the chromium content from tannery wastewaters becomes necessary. The Minimal National Standards (MINAS) for safe discharge of wastewater containing chromium in surface water is 2.0 mg/L [5].

Traditionally, physico-chemical processes such as sedimentation, flocculation, precipitation, chemical reduction, adsorption and the usage of biological processes like activated sludge has been used in the leather industry [6]. The treatment of tannery effluent separately has become a common practice and the conventional treatment methods of like ion exchange, membrane separation; ultra filtration, reverse osmosis and adsorption technology are applied. But, these technologies have some disadvantages such as high reagent requirement, annual high operations cost, increased sludge production, costly adsorbent regeneration and clogging filter [7]. The biological treatment methods also do not offer complete solution since many organic substance produced by the industries are inhibitory or resistant to biological treatment. Therefore, it needs an appropriate technology to treat tannery wastewater before discharge to minimize the environmental problems. Advanced oxidation process (AOP) is a promising technique for the treatment of polluted water containing recalcitrant organic compounds. Various studies have been done on advanced oxidation methods like ozonation, ultrasonic techniques, and photocatalysis for the treatment of tannery effluent [8–10]. It is obvious that these processes, help in breaking down the pollutants into harmless final products. But oxidation processes have some limitations in the long run because these processes requires high operation and investment costs, and involves difficulties in installation of process equipment which restrict the application of these process [11].

In the present scenario, electrochemical technologies have outgrown all other technologies in terms of their cost effectiveness and easy availability of materials. These techniques have become an indispensable step in treating wastewater containing refractory pollutants due to their potential higher efficiency. Electrochemical technologies offer various treatment processes such as electrochemical peroxidation process, electrooxidation, electrocoagulation, electrodisinfection, and electrodeposition. An extensive research has been carried out by many researchers for treating various wastewaters by using electrochemical technologies [12].

Hybrid processes like electrochemical peroxidation (ECP) [13], depend on Fenton's and electrocoagulation (EC)

processes can often yield the highest water quality that can be achieved and it is one of the best methods that can be used for the removal of heavy metals [14,15] and similar results are reported in the literatures [16–18]. ECP is a proprietary process that utilizes sacrificial iron electrodes and stoichiometrically balanced applications of hydrogen peroxide to efficiently destroy aqueous phase contaminants. ECP involves the oxidation of organic matter by the action of hydroxyl radical produced from hydrogen peroxide and ferrous iron followed by Coagulation [19]. The applied DC current between them dissolves the anode and provide Fe^{2+} ions that react with the hydrogen peroxide to produce Fe^{3+} ions. The major advantage of ECP process is that the ferric ions can be recycled into ferrous ions, so that they behave like a catalyst [20].

To initiate the reaction given in Eq. (1), before applying voltage, a pre-decided amount of Fe^{2+} and H_2O_2 was added. It can be pointed out that it provides faster ion transport and thus makes the process extremely effective. Therefore in each run, a pre-decided amount of ferrous sulphate heptahydrate and hydrogen peroxide were added into the reactor to activate Fenton's reaction before the electrical current was turned on. The ferrous species is persistently created in the electrochemical cell that is responsible for electrocoagulation of organic matters in Eq. (2). The reactions occurring at the iron electrodes are presented in Eqs. (2) and (3), where the sacrificial iron anode releases Fe^{2+} ions into the solution [Eq. (2)], simultaneously at the cathode; regeneration of Fe^{2+} by continuous reduction of Fe^{3+} happens as per Eq. (3). Then the ECP reactions occurs by manual addition of H_2O_2 and Fe^{2+} as shown in Eq. (1).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \tag{1}$$

$$Fe \rightarrow Fe^{2+} + 2e^- \, (anode) \tag{2}$$

$$Fe^{3+} + 3e^- \leftrightarrow Fe^{2+} \, (cathode) \tag{3}$$

The mechanism of Cr removal in ECP is as follows. The ferrous ion (Fe^{2+}) generated by electrooxidation of the iron anode reduces $Cr^{3+}_{(aq)}$ ion is then precipitated as $Cr(OH)_3$ and it is self-oxidized to ferric(Fe^{3+}) ion according to Eq. (4). Chromium(III) hydroxide [$Cr(OH)_3$] are the only water soluble compounds. The Fe^{2+} ion can also reduce $Cr_2O_7^{2-}$ under acidic conditions according to the following Eq. (4):

$$Cr_2O_7^{2-}{}_{(aq)} + 6Fe^{2+}_{(aq)} + 14H^* \rightarrow 2Cr^{3+}_{(aq)} + 6Fe^{3+}_{(aq)} + 7H_2O_{(l)} \tag{4}$$
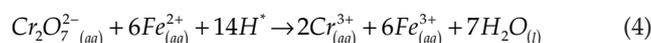
The H_2 produced as a result of the redox reduction may remove dissolved organics or any suspended materials by flotation. Similarly, the Fe^{3+} ions may undergo hydration and depending on the pH of the solution. $Fe(OH)^{3+}$ $Fe(OH)_2^+$ and $Fe(OH)_3$ species may be produced under acidic conditions. The reactions involved are given in Eqs. (5)–(7):

$$Fe^{3+} + H_2O_{(l)} \rightarrow Fe(OH)^+_{2(aq)} + 2H^+_{(aq)} \tag{5}$$

$$Fe^{3+} + 2H_2O_{(l)} \rightarrow Fe(OH)^+_{2(aq)} + 2H^+_{(aq)} \tag{6}$$

$$Fe^{3+} + 3H_2O_{(l)} \rightarrow Fe(OH)^+_{2(aq)} + 3H^+_{(aq)} \tag{7}$$
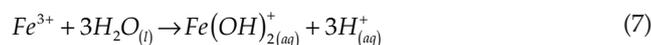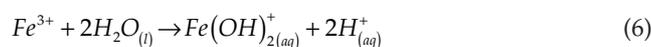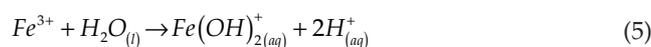
Fe^{3+} and $OH^{\bullet}$ ions generated at electrode surfaces react in the wastewater to form ferric hydroxide as given in Eq. (8):

$$Fe^{3+} + 3OH^{\bullet} \rightarrow Fe(OH)_3 \qquad (8)$$

The suspended iron hydroxides can remove pollutants from the solution by sorption, co-precipitation or electrostatic attraction, followed by coagulation [22]. The dissolved metal ions at an appropriate pH, can form a wide range of coagulated species and metal hydroxides that either destabilize and aggregate the suspended particles or precipitate and adsorb the dissolved contaminants [13,23]. Nevertheless, some of hydroxyl radicals may react with Fe^{2+} and H_2O_2 resulting in $HO_2^{\bullet}$, which is not viable in oxidation process [24]. Eqs. (9) and (10) necessitates quantifying H_2O_2 and Fe^{2+}. The $OH^{\bullet}$ radicals created, oxidize the organic compounds (RH) to deliver H_2O and CO_2 appearing in Eq. (11).

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \qquad (9)$$

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad (10)$$

$$R - H + OH^{\bullet} \rightarrow intermediates \rightarrow H_2O + CO_2 \qquad (11)$$
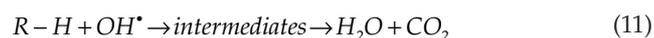
The objectives of this work is to evaluate the extent of removal of Cr(III) from tannery wastewater by ECP process using iron electrodes, and to assess the effects of operational ECP parameters such as pH, current density, H_2O_2 concentration, and Fe^{2+} concentration the removal efficiency and to optimize the operating conditions for tannery wastewater treatment.

2. Materials and methods

2.1. Materials

All chemicals are commercially available as analytical grade reagents and are used as received without further purification. The procurement of Sodium hydroxide, Sodium sulfate, Sulphuric acid, Hydrogen peroxide (30%, w/w), ferrous sulphate heptahydrate and all other reagents were received from Merck. All solutions were diluted with deionized water to the desired concentrations and experiments were carried out at room temperature.

2.2. Collection and characterization of wastewater

The tannery wastewaters were collected from the tannery industry located in Dindigul District, Tamilnadu. The tests were performed with samples collected at the outlet of the plain sedimentation tank with no modifications. The samples were collected in plastic cans that were transferred to the laboratory which were then kept at 4°C. The tannery wastewater was analyzed to determine the physicochemical characteristics as per standard methods [25]. The amount of sludge was measured using the Imhoff cone apparatus [26]. The characteristics of the collected tannery wastewater were pH = 7.5, Chromium(III) (mg/L) = 16, COD (mg/L) = 2370, BOD_5 (mg/L) = 985, total solids (mg/L) = 5250, chloride (mg/L) = 507, electrical conductivity (μ/cm) = 7834.

2.3. ECP reactor and procedures

The electrochemical peroxidation experiments in this study were done by using bench scale reactor which is made of acrylic material and hopper bottom of dimensions of 21.5 cm × 15 cm × 25 cm with a working volume of 5 L. The reactor had an iron plate cathode (218 cm²) and iron plate anode (218 cm²). The arrangement included 6 cm spacing between the two parallel electrodes. To provide desired current, the electrodes were connected to DC power supply (0–30 V, 0–5 A).The photograph of the experimental setup is shown in Fig. 1. Emery paper (No.P320) is used to clean the electrodes between the successive runs and further washed using H_2SO_4 solution (5% v/v) in order to reduce the effects on successive experiments [27].

The wastewater was permitted to settle for 60 min and after sedimentation; the initial pH of the solution was regulated to the desired values using concentrated sulfuric acid or sodium hydroxide. In order to activate Fenton's reaction, a pre-decided quantity of ferrous sulphate heptahydrate and hydrogen peroxide were added into the reactor during each run, before the electrical current was turned on. Samples of 5 ml volume were taken out every 10 min and instantly the pH of the sample was modified for the usage of NaOH and sodium sulphite which quenches the generation of $OH^{\bullet}$ thereby stopping the degradation process and allowing the remaining iron precipitate [28]. The samples were given a 30 min settling time to bring about coagulation and the supernatant was then taken for quality measurements [29]. The removal of Cr(III) was evaluated by atomic absorption spectroscopy (AAS) [30].

3. Results and discussions

3.1. Effect of pH

The initial pH of the solution is one of the most important factor in ECP. In the present study, the effect of pH in ECP on Cr(III) removal was studied in the range 2–8. Fig. 2 shows that the concentration of Cr(III) removal is seriously affected by pH. It can also be observed that the concentration of Cr(III) decreased from 16 to 2.6 mg/L at pH 2 and it was found to be maximum removal compared to the other pH. For pH 3, 4, 6 and 8 the concentration of Cr(III)

Fig. 1. Experimental setup of electro-chemical peroxidation reactor.
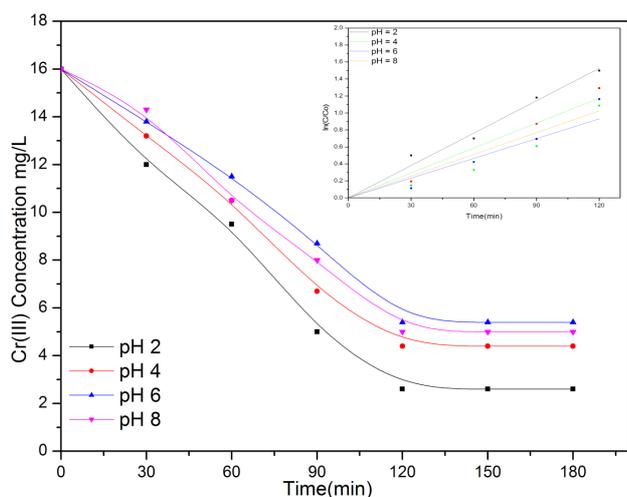
Fig. 2. Effect of pH on Cr(III) removal from Tannery wastewater.

was found to decrease from the initial value of 16 mg/L to 4.4, 5.4 and 5 mg/L respectively. The attained outcome demonstrates that pH value influences the generation of hydroxyl radicals and ferrous ions concentrations [31]. The maximum Cr(III) removal efficiency was obtained as 87% at pH 2 in a reaction time of 120 min. This could be due to the occurrence of Fenton reaction and generation of $OH^•$ with Cr(III) and degrade them [32]. In pH values lower than 2, Fe-containing complexes such as $[Fe(H_2O)_6]^{2+}$ which react much more slowly with hydrogen peroxide than other species. Moreover, in the presence of high H^+ concentrations, hydrogen peroxide would decompose and be converted into the stable species ($[H_3O_2]^+$) which reacts with Fe^{2+} slower than hydrogen peroxide [31]. This finding is consistent with the results of many authors about optimum pH 2–4 in ECP [32,33]. In a literature reported by Pekey [13] employed ECP to remove colour and TOC from co-complex dye and achieved the maximum colour and TOC at optimum pH 3.

In addition the pH values were greater than 3–8, the Cr(III) removal efficiency decreased significantly, while the iron ions are precipitated as colloid particles and as ferric ions. From this results and observations, it seems that in pH values higher than 8, the Cr(III) removal concentration was decreased to 8 mg/L at 90 min and 5 mg/L in 120 min, because ferrous ions are unstable and thus the formed ferric ions [Eqs. (8) and (9)] promote the production of ferric hydroxo complexes. The decrease in removal concentration of Cr(III) may also be due to the formation of $Fe(OH)^+$, which has lesser reaction rate resulting in decreased hydroxyl radical production thereby reducing the oxidation efficiency [30,34]. So it is evident that when the increasing pH > 3, the removal rate of Cr(III) concentration is decreased [17].

3.2. Effect of current density

In Electro Chemical Peroxidation (ECP) processes, current density is one of the most important parameters for controlling the reaction rate within the ECP reactor since its value proves to be decisive in determining operational

cost and process efficiency, and it affects the H_2O_2 production, Fe^{2+} reduction and $OH^•$ production. The applied current act as a driving force to generate oxidized iron (Fe) at an anode and the other side it generates HO at cathode through oxygen reduction. Fe^{2+} produced at anode reacts with H_2O_2 and produces hydroxyl radical which reduces the complex species of the tannery wastewater. In order to get optimum efficiency, the generation of Fe^{2+} at anode has to be proportionate to the H_2O_2 generated. Increasing the current density would lead to an almost linear increase in the Fe^{2+} concentration. Therefore, the behaviour of iron electrodes can evidently be observed at the variable current densities. Based on the results, increasing the current density would increase the efficiency of the system, particularly $OH^•$ generation [35]. It is obvious that the current density determined by the production rate of coagulant (amount of Fe^{2+} ions released by the anode), adjusts also bubble production, its size and distribution, and which in turn affects the growth of flocs coagulate particles in the ECP reactor [13].

The experiment was done in the absence of current density and it was observed that the removal efficiency of Cr(III) concentration was less compared with application of current density. The removal efficiencies of Cr(III) concentration at different current densities are depicted in Fig. 3. This behaviour is due to the applied current density that determines the coagulant dosage rate, the bubble production rate and size of flocs growth resulting in a faster removal of pollutants. According to Faraday's law, when current density is constant, a constant amount of Fe^{2+} is released to the solution. The presence of ferrous ions enhances the reduction and removal of chromium. In other words by increasing the current of the cell the amount of hydrogen bubbles at the cathode increased, resulting in a greater upward flux and a faster removal of the pollutant and sludge flotation [37]. The removal of trivalent chromium from wastewater by electrocoagulation in mechanically stirred cell with Fe anode and found that the rate of Cr^{3+} removal increases with increasing the current [38].

Fig. 3 indicates that the removal rates of Cr(III) increased with increasing current density. For the initial Cr(III) concentration of 16 mg/L, the removal concentration values were 12, 8, 5 and 2 mg/L at the current densities of 10, 20, 30 and 40 mA/cm² at 120 min respectively. It is observed that for a current density of 10 mA/cm² there was a decrease in concentration of the Cr(III) removal from 16 to 5 mg/L in 120 min. When current density increases from 10 to 30 mA/cm², the anode dissolution rate also increases. This leads to an increase in the number of metal hydroxide flocs resulting in the increase in Cr(III) removal efficiency from 40% to 86% [22]. An increase in current density above the 30 mA/cm² does not result in an increase in the Cr(III) removal efficiency, as sufficient numbers of metal hydroxide flocs are available for the sedimentation of the pollutant. It is also advisable to limit the current density to 30 mA/cm², in order to avoid excessive oxygen evolution as well as to eliminate other adverse effects like heat generation. Therefore, the optimum current density for Cr(III) removal was taken as 30 mA/cm² (0.03A/cm²) for a period of 120 min during the treatment process, which resulted in the removal efficiency of 87 %. The reduction in Cr(III) removal from
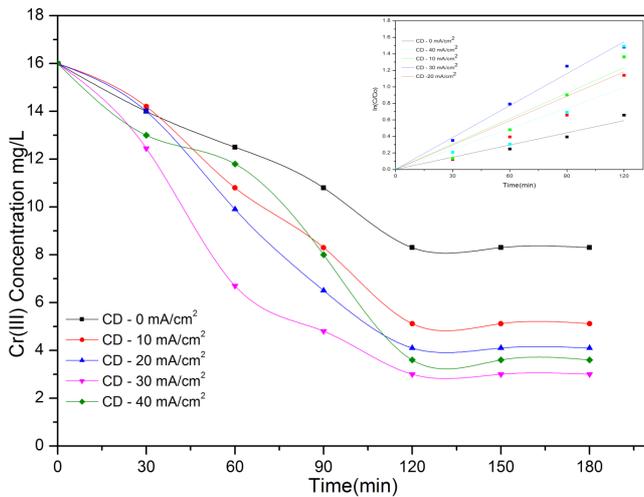
Fig. 3. Effect of current density on Cr(III) removal from Tannery wastewater.

Fig. 4. Effect of hydrogen peroxide on Cr(III) removal from Tannery wastewater.

ECP for a current density > 30 mA/cm² can result in more scarification of anode, generating excess Fe^{2+} which results in the ratio of H_2O_2 to Fe^{2+} below the optimum level of 8. The excess metal species scavenging the available responsive $OH^•$ available Eq. (10), degrade with the organic compounds [36]. In addition, high current density inhibit the main reaction of the process, leading to a decrease in the pollutant removal efficiency in Eq. (12).

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad (12)$$

At higher currents, the supply of metal ions was generated rapidly compared to the peroxidation process at lower currents, resulting in a decrease of removal efficiency. In a literature reported by Moussavi and Aghanejad (2014) [34] studied the performance of ECP for the wastewater from a paper recycling plant and achieved the maximum COD reduction at an optimum current density of 5 mA/cm².

3.3. Effect of hydrogen peroxide

To determine the effect of H_2O_2, the degradation of Cr(III) in tannery wastewater was investigated by varying the H_2O_2 concentration from 0 to 20 mg/L. From Fig. 4, it can be observed that the percentage of Cr(III) removal efficiencies are increased with increasing H_2O_2 dosage up to 15 mg/L, due to the formation of highly reactive hydroxyl radical. This can be related to the increase in the concentration of hydrogen peroxide. The adding of desired amount of hydrogen peroxide in ECP process is to avoid the high accumulation of H_2O_2 and improve the Cr(III) removal efficiency [37]. The maximum removal efficiency of 86% in 120 min is attained when 15 mg/L of hydrogen peroxide is added to ECP. The hydroxyl radical possesses strong affinity to oxidize the organic matter present in the tannery wastewater and that results in higher removal concentration of Cr(III) up to 2.6 mg/L. According to Eq. (1), the presence of hydrogen peroxide in ECP can lead to a faster production of Fe. On the other hand, when a iron anode is used in ECP, it is
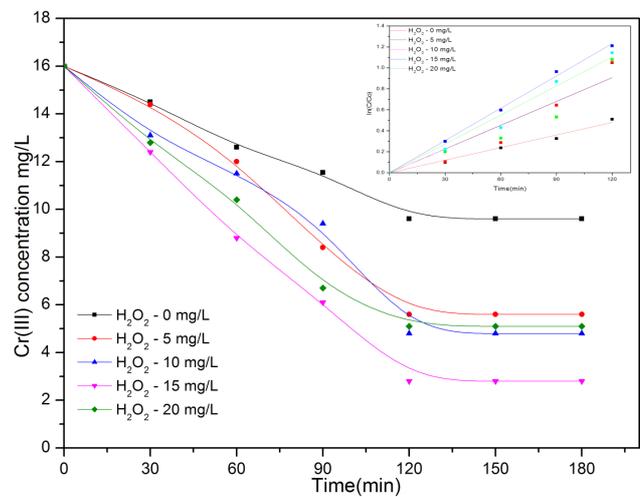
noticed that Fe^{2+} gets dissolved in the reactor from the iron anode where the generation of hydroxide ions and H_2 gas are generated at the cathode according to Eq. (13) [22]. In the presence of O_2, dissolved Fe^{2+} is oxidized to $Fe(OH)_3$ according to Eq. (14) [38].

$$2H_2O_2 + 2e^- \rightarrow 2OH^- + H_2 \qquad (13)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^• + OH^- \qquad (14)$$
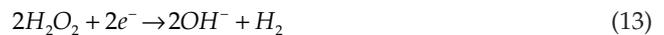
The findings also revealed that the removal efficiency of Cr(III) was less in the absence of H_2O_2 which is depicted in Fig. 4. Fenton process is a combination of coagulation and oxidation process [25,39]. Therefore, when the amount of iron is more than hydrogen peroxide, ferrous ion can be used as a reactant in the Fenton reaction. Therefore, in Cr(III) removal by Fenton, coagulating properties were dominant; and Fenton oxidation properties had no effect on the removal of this pollutant. This process can lead to the consumption of hydroxyl radicals produced by trivalent iron ions (Fe^{3+}), and oxidize them into bivalent iron (Fe^{2+}) leading to the non beneficial degradation of hydrogen peroxide.

On the contrary when H_2O_2 dosage increases from 15 to 20 mg/L, the Cr(III) removal efficiency decreases from 85 to 64%. This may be due to the competition between hydrogen peroxide and Cr(III) for accepting an electron, that leads to the reduction of ferrous ions in the solution. Consecutively, this reaction can also be due to the reversible conversion of Cr(III) [17].The decrease in removal of Cr(III) in acidic pH is due to the increase in the hydroxyls radical scavenging effect which inhibits the reaction between H_2O_2 and Fe^{2+}. The over-dosage of hydrogen peroxide in the reactor, also leads to the faster consumption of hydrogen peroxide. Finally, the hydroperoxyl radical generated from the hydrogen peroxide decomposition [Eq. (14)], a weak oxidant compared with the hydroxyl radical [40] results in slower degradation. Ozyonar et al. [20] reported that for the maximum removal of COD and TOC from pre-treated coke wastewater by ECP was achieved at an optimum H_2O_2 concentration of 10 g/L.

3.4. Effect of Fe^{2+} concentration

In order to examine the effect of Fe^{2+} concentration, experiments were conducted at various Fe^{2+} dosage from 0 to 5 mg/L and the observations are shown in Fig. 5. Suitable Fe^{2+} concentration is an important prerequisite for the initiation of Fenton's reaction to destroy large molecules in real wastewater when compared with synthetic wastewater [23,37]. Ferrous salts added to accomplish coagulation of metals could be sufficient to reduce Cr(III) ions completely as long as the concentration remains low. It was observed from the figure that in the absence of Fe^{2+} dosage, the removal efficiency of Cr(III) concentration was found to be very less. This is because the oxidizing power of hydrogen peroxide was not adequate to destroy large molecules in the absence of ferrous ions. The presence of Fe^{2+} enhances the reduction and removal of chromium by ECP with iron electrode is faster [15]. Increasing the amount of Fe^{2+} concentration from 0 to 2 mg/L, attained an increased removal efficiency of Cr(III) from 40 to 86% and in terms of concentration of Cr (III), a reduction from 16 to 2.8 mg/L was achieved. This is due to that the presence of Fe^{2+} with H_2O_2 that lead to increased production of hydroxyl radicals. This $OH^{\bullet}$ attacked the organic compounds and by accepting a proton became oxidized in the highly reactive organic radicals. Contrarily when $Fe^{2+} > 2$ mg/L had negative impact on Cr(III) removal concentration. The concentration of Cr(III)was found to decrease from the initial value of 16 mg/L to 3.9, 5.2 and 6.4 mg/L for Fe^{2+} dosage of 3,4 and 5 mg/L respectively. The possible reasons may be when iron electrode is utilized as anode and cathode, dissolution of Fe^{2+} in the anode and regeneration of Fe^{2+} in the cathode takes place in the reactor. Fe^{2+} dosage beyond the optimum level of > 2 mg/L leads to scavenging effect of $OH^{\bullet}$ generated in ECP reactions. Moreover utilization of $OH^{\bullet}$ produced by Fe^{3+} oxidize themselves into Fe^{2+} and the suspected solids were trapped by the compounds leading to the precipitation [17] of metal hydroxides formed and it is accumulated iron sludge adsorbs dissolved contaminants [13]. Wang et al. (2014) [49] observed an increase in the rate of TOC decay by E-Fenton process, when initial Fe^{2+} concentrations were increased from 0 to 1 mM. It was reported that the ferrous ions in the electrolyte solution, when present in excess, consume the hydroxyl radicals and affect the extent of degradation.
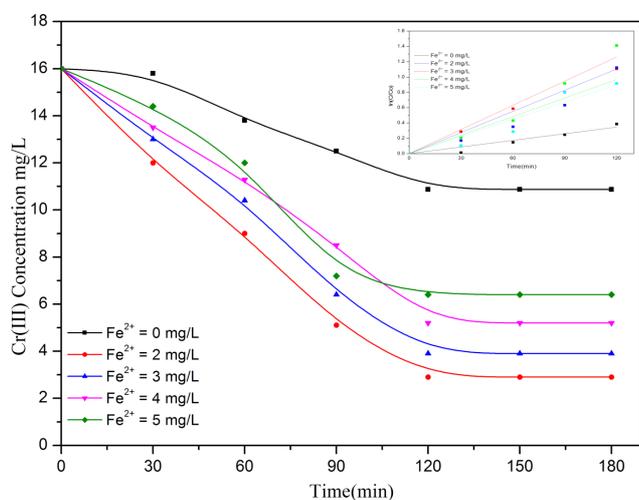
3.5. Effect of interfering ions

In ECP process, iron ions are recovered on the cathode surface [Eq. (3)]. In ECP the production of Fe^{2+} at the anode surface [Eq. (2)] is induced by the usage of iron electrodes and Faraday's law is used to calculate the amount of Fe^{2+} produced at the anode surface. The use of iron electrodes in ECP process induces the production of Fe^{2+} at the anode surface [Eq. (2)] and it can be calculated from Faraday's law [Eq. (15)] [33,41].

$$m = \frac{MIt}{nF} \tag{15}$$

It indicates m is the mass of substance produced at the electrode, M is the molar mass of substance, I is the total electric charge that passes through the solution, t and n represent reaction time and valence number of the substance (as an ion in solution), respectively. F is the Faraday's constant (= 96.485 c/mole). There appears to be an increase in the regeneration and production of iron ions (Fe^{2+}) when iron electrodes are used. To arrive at a desired condition, the iron ions generated were calculated as 217 mg for tannery wastewater [42]. The additional generation of iron ions curtails the external requirements of Fe^{2+}. The mass of evolved hydrogen and formed hydroxyl ions can be calculated correspondingly [27]. The amount of peroxidation dosed into the solution can be increased by increasing the current and the reaction time. But increasing the current density leads to a decreased removal efficiency.

It seems that, a rise in current density causes a rise in removal of Cr(III) in accordance with Faraday law, which is due to acceleration in direct oxidation of sludge on electrode's surface and more production of oxidant agents in the solution oxidizing sludge indirectly. The sludge production was proportional to current density and contact time for ECP process. The sludge produced at optimum condition of reaction was 12.4 mL/L, and it was observed that the sludge was neither corrosive nor reactive, and also did not showed environmental toxicity [43]. It is concluded that this residue is not dangerous for the environment [44].

Fig. 5. Effect of Fe^{2+} concentration on Cr(III) removal from Tannery wastewater.
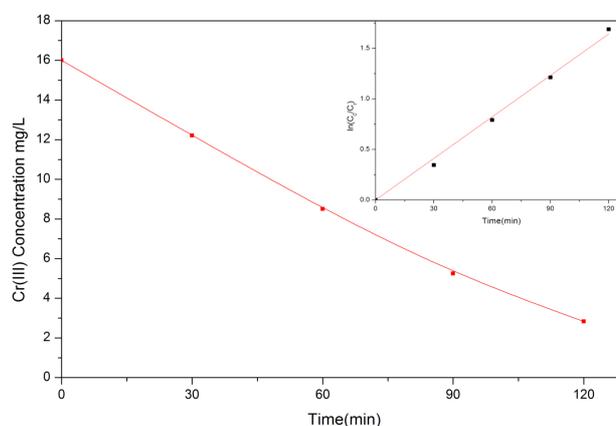
Fig. 6. Kinetics study for ECP process on Cr(III) removal.

3.6. Economic analysis and electrical energy consumption (EEC)

The performance of ECP process is estimated based on the electrical energy consumption. The energy consumption in kWh/L during Cr(III) removal in t time was calculated using the equation [Eq. (16)] [42,45].

$$EEC = \frac{VIt}{V_s} \tag{16}$$

where EEC is electrical energy consumption (kWh/L), V is cell voltage in volt (v), I is current in ampere (A), t is time (h), V_s is the volume of solution (L). Energy consumption for removal of Cr(III) in wastewater at optimum condition is 0.73 kWh/L shown in Fig. 7. The operating cost incorporates the cost of chemicals, electrodes and electrical energy required for ECP [10]. The operational cost of the treatment process under optimum conditions was computed from the following equations:

$$Operating\ Cost\left(\$/m^3\right) = Energy\ cost + product\ cost \tag{17}$$

$$Energy\ cost\left(\$/L\right) = EEC \times Product\ cost \tag{18}$$

$$Product\ cost\left(\$/L\right) = \sum_{i=1}^{k} m_i p_i \tag{19}$$

where m_i is the mass of chemicals needed, electrode, kg/m³ and p_i is price in \$/kg. Utilizing this condition, the electro-chemical peroxidation process operating cost was 0.4\$/m³ at optimum conditions [46]. The outcomes demonstrated that the operational costs of the traditional chemical processes were higher than that of the electro-chemical peroxidation process.

3.7. Effect of contact time

Fig. 6 depicts the effect of contact time on the removal of Chromium(III) in ECP from tannery wastewater. It is clear that increasing contact time increases the removal efficiency
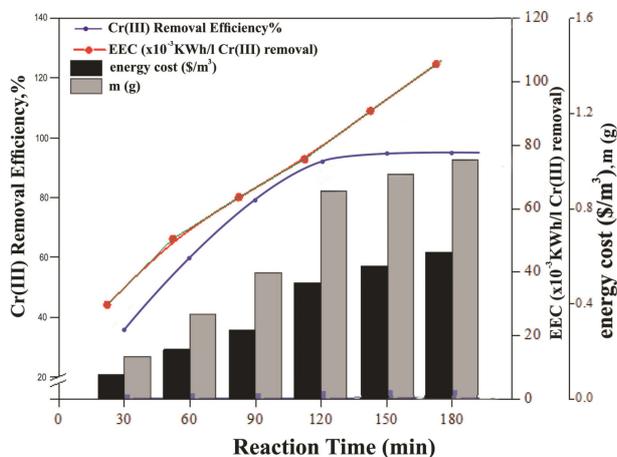
Fig. 7. Performance on electrical energy consumption, energy cost, mass of Fe²⁺ generated in ECP process for tannery wastewater.

but after a certain time the percentage removal becomes almost constant. The maximum removal efficiency of 87% was found be attained in a contact time of 120 min and it was found to be within the discharge limit (2 mg/L). At initial stages the rate of ECP process was high, but after that the rate of peroxidation decreases, and the removal efficiency also becomes constant [47]. The percentage removal of Cr(III) at different time intervals were 24%, 47%, 67%, and 87% at contact times from 30, 60, 90 and 120 min respectively. Therefore the optimum contact time for the removal of Cr(III) from tannery wastewater by ECP process was found to be 120 min. Under optimum conditions, the percentage removal of COD and BOD was found to be 430 mg/L and 210 mg/L for tannery wastewater at 120 min of reaction time.

3.8. Kinetics studies

A kinetic study was performed to describe the Cr(III) removal in ECP process. To achieve on appropriate design of the ECP reactor, it is very important to determine the kinetic coefficients involved in the reaction. For practical applications, the first order kinetic reaction under different operational conditions is given by Eq. (20),

$$\ln\left(\frac{C_o}{C_t}\right) = kt \tag{20}$$

where C_0, C_t, t and k are the initial concentration of Cr(III), final concentration of Cr(III), reaction time and rate constant (min⁻¹) respectively. The degradation rate constant, k has been chosen as the basic kinetic parameter to compare with other studies and it enables to determine the electrochemical peroxidation activity [48] as shown in Figs. 2–5.The experimental data appears to fit the linear kinetic equation, and accordingly the degradation efficiency follows the first order kinetics. The order of rate constant was 0.0173 min⁻¹ and it was found that the first order model is suitable for this study. Therefore, first order kinetic model results showed that the removal of Cr(III) using ECP reaction is very likely to take place on the surface of the electrode [49]. The kinetics of the Cr(III) removal was shown in Fig. 6. This study reveals that the degradation of Cr(III) from tannery wastewater fitted first order kinetics with high correlation coefficients and the same model fit the experimental data well with R^2 values near unity and more suitable to describe the Cr(III) removal process at different operating parameters.

4. Conclusion

In this study, removal of Cr(III) from tannery wastewater using Electro-Chemical Peroxidation process was investigated. The operational parameters, pH, Fe²⁺, H₂O₂ concentration and current density have influenced Cr(III) removal concentration in the ECP processes. The optimum values of these parameters for the ECP process of Cr(III) removal from tannery wastewater were found to be pH = 2, Fe²⁺ = 2 mg/L, H₂O₂ = 15 mg/L and current density = 30 mA/cm². Under these conditions, Cr(III) concentration was reduced from 16 mg/L to 2 mg/L with 0.073 kWh/L of EEC and operating cost of 0.4\$/m³ after the reaction time of 120 min. The dynamic investigation demonstrates that the deg-

radation kinetics of tannery wastewater followed the first order model. As a result, this becomes a supportive tool for the analysis and the acquired outcomes show the possibility of ECP process treated wastewater for internal reuse.

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