

Simultaneous Removal of Hexavalent Chromium and Nitrate from Wastewater using Electrocoagulation Method

Abbas. Rezaee, Hooshyar Hossini, Hossein Masoumbeigi, and Reza. Darvishi Cheshmeh Soltani

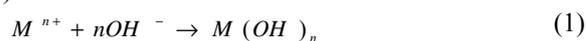
Abstract—The simultaneous removal of hexavalent chromium and nitrate ions from an aqueous solution by electrocoagulation (EC) using aluminum as the anode was investigated. The model wastewater was fabricated in 200 mg L of basic chromium and 500 mg L of nitrate. Different parameters, such as time, applied current and pH, were examined. Moreover, the effects of the EC process on the evolution of pH and ORP and the amount of aluminum released during the EC process were investigated. The removal of both Cr (VI) and nitrate increased with an increase in the current intensity, and the EC process induced a pH increase over a period of 120 min. It is notable that the minimum Cr (VI) removal efficiency was 45% for a current of 0.02 A. In the case of nitrate, it was demonstrated that the nitrate reached zero discharge between 0.5 and 1.0 A. For both ions, the removal efficiency was over 90%. The results showed that, with increasing pH, nitrate and chromium removal increased. The results also show that, with an increase in time and current intensity, the rate of aluminum release also increased. Additionally, the ORP decreased from -257 to -740 mV as the current increased from 0.02 to 1 A, respectively.

Index Terms— Chromium, Electrocoagulation, Nitrate, Wastewater.

I. INTRODUCTION

In recent decades, electrocoagulation (EC) has engrossed much attention as an environmental-friendly and effectiveness process. In addition, the EC process is a potential suitable way for treatment of wastewater with concern to costs and environment [1]. It is very effective in removing contaminants from wastewater. Contaminant removal with electrochemical methods offers several advantages, such as the absence of chemical requirements, no sludge production, the small area occupied by the plant and the ease of operation [2]. In fact, the coagulant is generated by the dissolution of a sacrificial anode for the EC process. This process can be very effective at removing oil from synthetic oily wastes, suspended solids (as well as oil and greases), metal ions and petroleum wastewater [3-8]. Also Vlyssides et al [9] using this technology, attempted to refine

of leachate from a domestic solid waste. Heavy metal ions present in surface and ground waters are dangerous to environmental and human health; therefore, they must be removed to prevent their accumulation [15]. Chromium (VI) is released into the environment from various industries, such as the electroplating, metal finishing, tannery and fertilizer industries. Chromium (VI) is known to be a toxic and carcinogenic ion [7]; therefore, wastewater that contains chromium should be treated before it is released [12]. Additionally, nitrate contamination has become an environmental and health problem because of its harmful effects. Nitrate ions are soluble in water and can move through the soil into the groundwater [13]. Pollution of ground and surface waters by nitrate ions is a serious problem [14]. Moreover, the presence of nitrate in surface water contributes to eutrophication. To protect ecosystems from the adverse effects associated with the presence of nitrate ions in drinking water, standards should be established to reduce its concentration prior to discharge [15]. New methods, based on the reduction of nitrates, are currently under study [3]. According to the above statements, wastewater from plating and tannery industries contains nitrate and chromium (VI) ions; therefore, we selected these industrial pollutants for simultaneous electrochemical treatment because of EC's advantages and suitability for the simultaneous removal of hexavalent chromium and nitrate ions. The EC process involves in situ generation of coagulants by electrically dissolving either aluminum or iron ions from aluminum or iron electrodes. The metal ion generation occurs at the anode, and hydrogen gas is released from the cathode [16]. Chromium removal by the EC process has been reported with electrodes of different materials. However, iron and aluminum electrodes are generally better than other reported materials. With respect to the anodic reaction, most anodic materials are soluble and are the so-called 'sacrificed' electrodes; aluminum and iron anode materials have high efficiency but they produce hydroxy sludge as seen from Eq. (1).



The hydroxyl ions formed at the cathode increase the pH of the solution and result in the precipitation of Cr (III) ions as chromium hydroxide [17].



The connection between electrochemical process intensity and the amount of coagulants dissolved into the solution from the anode is described by Faraday's law, where WA is the amount of dissolved anode material (g); I is the current

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A. Rezaee and H. Hossini are with the Department of Environmental Health, Faculty of Medical Sciences, Tarbiat Modares University, Tehran, Iran (e-mail: rezaee@modares.ac.ir).

H. Masoumbeigi is with the Baqiyatallah University of Medical Sciences, Tehran, Iran.

R. Darvishi Cheshmeh Soltani is with the Department of Environmental Health, Faculty of Medical Sciences, Tarbiat Modares University, Tehran, Iran.

intensity (A); t is the run time (s); m is the specific molecular weight (g/mol); F is Faraday's constant (96485 As/mol); and n is the number of electrons involved [18].

$$W_A = I \cdot t \cdot \frac{m}{n \cdot F} \quad (3)$$

The removal efficiency and aluminum remaining in the solution are calculated by the following equations [19]:

$$\%Al_{\text{remaining}} = \frac{\text{dissolved mass}}{\text{remained mass}} \times 100 \quad (4)$$

$$\% \text{ Removal} = \frac{C_1 - C_2}{C_1} \times 100 \quad (5)$$

In general, the electro-reduction of ions, such as chromium and nitrate, depends on the reaction time, the cathode potential, the current density and the pH of the solution, all of which have been examined in our study. To the best of our searches, the simultaneous removal of Cr (VI) and nitrate by the EC process has not been investigated. The results of this paper can be used to improve industrial wastewater treatment.

II. MATERIALS AND METHODS

A. Model wastewater characteristics

All reagents were of analytical grade (Merck, Germany), and deionized water was used in all preparations. Stock solutions of Cr (VI) and nitrate were made by adding the specific values of potassium dichromate ($K_2Cr_2O_7$) and potassium nitrate (KNO_3) in deionized water. The model wastewater concentration was prepared from the stock solution by suitable dilution. The wastewater model was fabricated in 200 mg/L of basic chromium and 500 mg/L of nitrates. The pH was adjusted to the desired value with 1 M HCl and 1 M NaOH. The NaCl solution was prepared at 100 mg/L. Sodium chloride (100 mg/L) was prepared as a supportive electrolyte.

B. Batch experiments

Electrocoagulation (EC) was carried out in batch reactors with a 1000 mL capacity as shown in Fig.1. The EC reduction was performed with a bipolar mode and with aluminum-aluminum anode-cathode electrodes. The outer electrodes were connected to the DC power supply (TEK-8051, 30 V and 5 A double), and four electrodes with the dimensions 150×60×2 mm, were placed vertically at a fixed distance of 1 cm. The contents of the EC reactor were gently aerated with a magnet rotator (Alfa, HS-860). In this study, both low and high currents were investigated. The currents were fixed at 0.02, 0.25, 0.5 and 1 A. Before starting-up the process, the electrodes were cleaned with 1 M H_2SO_4 and rinsed with deionized water to eliminate impurities from the surface of the electrodes. The effects of the reaction time, the applied current and the pH were investigated. The EC process is independent of the initial concentration; therefore, the initial concentration was not evaluated [12].

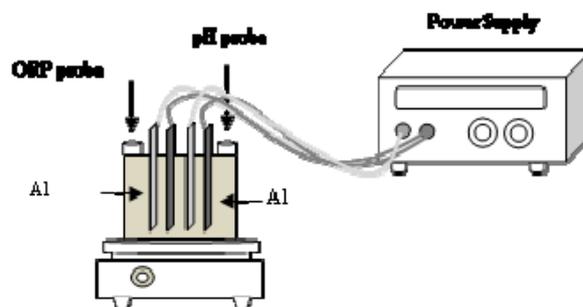


Fig.1. Schematic diagram of electrochemical reactor.

C. Analysis

All experiments were performed according to Standard Methods for the Examination of Water and Wastewater. The pH and ORP were measured with a pH meter (Eutech) and an ORP probe. The samples were collected from the reactor and were filtered to remove solid material. The chromium content was determined by colorimetric methods using a 1, 5 diphenylcarbazide [$CO(NH.NHC_6H_5)_2$] reagent at $\lambda=540$ nm, and nitrate was measured by UV-spectrophotometer with an absorption maximum at $\lambda=220$ nm (Rayleigh UV 9200, China). After taking these measurements, the concentrations of nitrate and Cr (VI) were determined by calibration curves [20].

III. RESULTS AND DISCUSSION

A. Effect of time and applied current

In the EC process, the current and the time are the most important parameters affecting removal efficiency [11]. To evaluate the effect of the applied current, experiments were conducted with a constant initial Cr (VI) concentration (200 mg/L) and applied currents varying from 0.02 to 1.0 A. Figure 2a shows the increase in Cr (VI) removal during the EC reaction due to increasing time. The removal rate of Cr (VI) and nitrate are plotted against the reaction time. The removal of both Cr (VI) and nitrate ions increased with increasing current, and the EC reaction induced a pH increase. In the case of Cr (VI) removal, the concentration of Cr (VI) decreased and attained maximum removal at 120 min for all applied currents (Fig. 2a). The removal rate of Cr (VI) occurred at high currents. After the reaction time, the minimum efficiency was 45% at a current of 0.02 A. According to Faraday's law [Eq. (3)], increasing the current leads to a higher Al^{3+} and OH^- dosage over time. The more current that was applied, the more Al^{3+} and OH^- that were divided into the system and the faster the Cr (VI) concentration decreased; therefore, the EC reaction time was hastened. Moreover, the more current that was introduced into the reactor, the more Cr (VI) that was reduced and precipitated as $Cr(OH)_3$. Ölmez (2009) investigated the treatability of hexavalent chromium by EC having with a high Cr (VI) concentration of 1470 mg/L. The highest Cr (VI) removal (100%) was achieved with an applied current of 7.4 A over 70 min [21]. Mouedhen et al. [17] have shown that an increase in the current density reduces the treatment duration without inducing a strong increase in the charge loading. In the case of nitrate removal, Fig. 2b illustrates the variations in nitrate concentration over time. The removal of nitrate at the

applied current increased with increasing current. Moreover, we found that the pH increased during the reaction time. Increasing the current from 0.25 to 1.0 A did not lead to an increase in the speed of Cr (VI) removal. The nitrate reached zero discharge between 0.5 and 1.0 A.

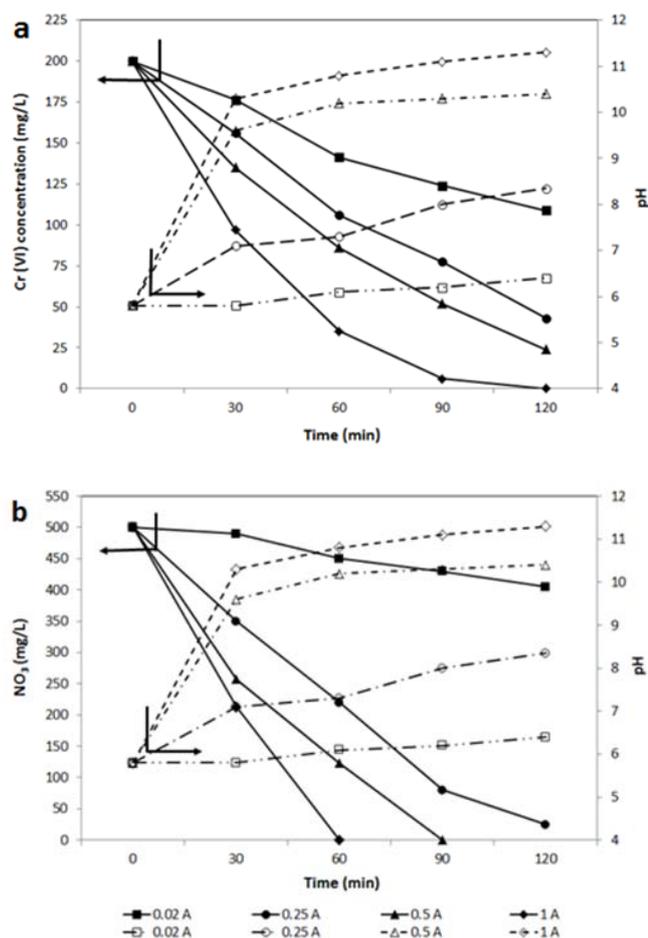
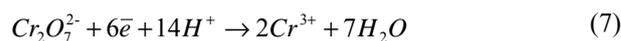


Fig. 2. The trend of Cr (a) and nitrate (b) removal and pH variation at different currents varying 0.02 to 1.0 A.

B. Effect of initial pH

Solubility of metal hydroxide and nitrogen species strongly depends on the pH of the solution because it influences ion speciation in the solution. Both the Cr (VI) and the nitrate removals during EC were affected by the pH of the solution as illustrated in Fig. 3a. To study the effect of the pH on EC with an aluminum electrode, the initial pH was varied from 4.0 to 8.0 at 0.25 A. The results showed an increase in Cr (VI) removal during EC when pH decreased, as shown in Fig. 3a. Adhoum et al. [22] reports that the removal efficiency of chromium is not influenced by pH between 4 and 8, but when the initial pH is increases above 8, a decrease in the removal efficiency of chromium is observed. This variance may be the result of different experimental conditions (pH, electrolyte and electrochemical duration) [17]. The latter result is similar to the result of this study. The corresponding reactions (water reduction and electrochemical metal reduction) are affected by the pH of solution as follows:

Acidic conditions:



Alkaline conditions:

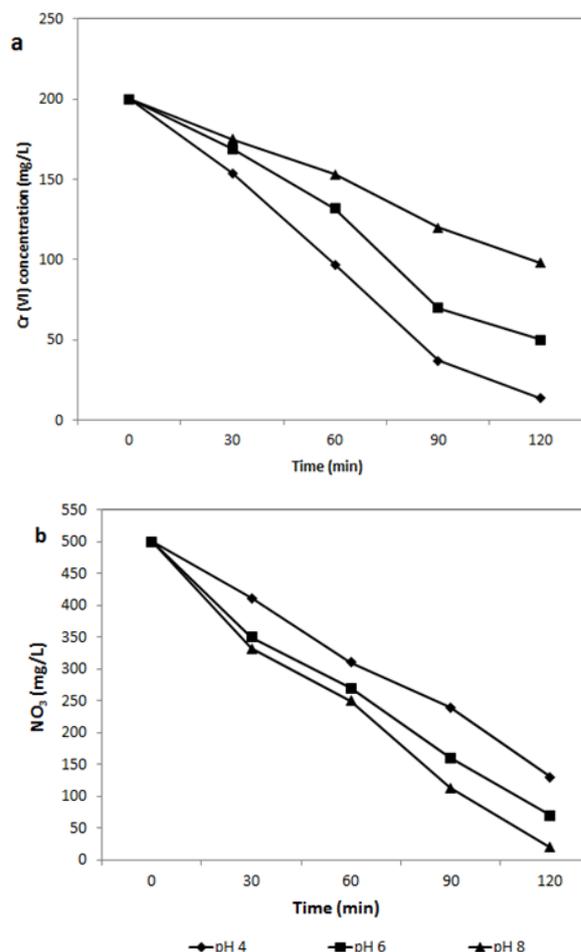
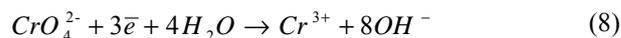
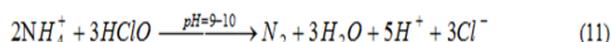


Fig.3. Effect of initial pH (4, 6 and 8) on Chromium and nitrate removal at current intensity of 0.25 A.

In acidic solution, Cr^{+6} ions are reduced to Cr^{+3} ions. Therefore, the removal efficiency of Cr (VI) is considerable [11]. Aber et al. [11] have shown that for pH 5–8, the efficient removal of both Cr (VI) and total chromium can be achieved using the EC process. When the pH was between 4 and 8, the aluminum cations produced at the anode formed polymeric species $Al13O4(OH)247+$ and precipitated $Al(OH)_3$, which lead to effective chromium removal [22]. The pH is considered to be effective at converting nitrate to N_2 gas. According to Fig. 3b, the maximum removal efficiency of nitrate was achieved at high pH values because the transformation of nitrate to other species occurred. Sanjeev Kumar and Goel [23] have shown that the alkaline pH range (9.5) corresponds to the maximum nitrate removal efficiency. Paidar et al. (1999) have shown that the reduction of nitrate to N_2 gas is possible during the EC process, and nitrate removal can occur with precipitation of metal hydroxide [16]. The reduction of chloride occurs close to the anode surface, and the following reactions take place:



Chloride ions increase the solution conductivity and decrease the passivity of electrodes by removing the oxide layer on the electrode surface. Moreover, the ions increase the availability of aluminum hydroxide in the solution. Therefore, in the presence of chloride ions, the removal of Cr^{3+} increases [17, 24]. Chloride is discharged to form chlorine, which is further hydrolyzed to hypochlorous acid. HClO reacts with ammonia in a reaction zone close to the electrode, which results in the formation of N_2 and decreases the local pH, while a small amount of free and combined chlorine diffuses into the bulk solution [25]. Fig. 4 illustrates the electroreduction of chloride on the anode surface and subsequent nitrogen formation.

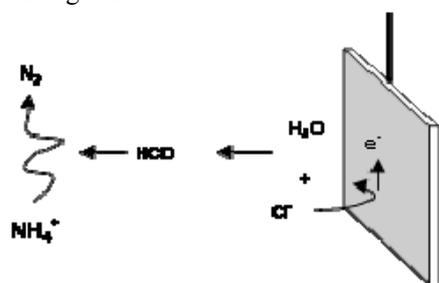


Fig.4. Electroreduction of the chloride on the anode surface.

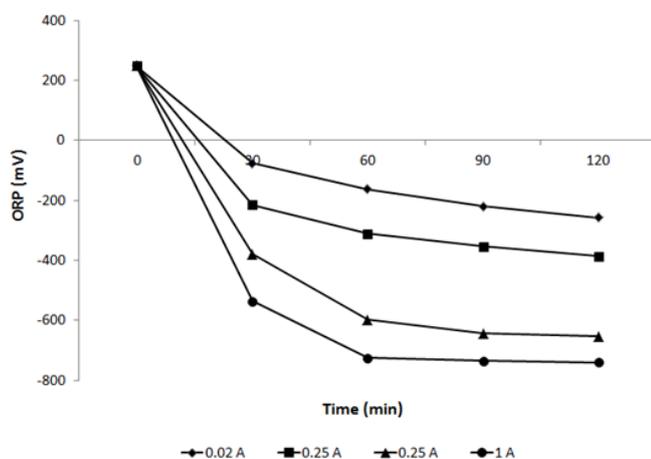


Fig.5. Variations of ORP (mV) during EC versus time (min).

C. ORP variations during the EC process

The oxidation reduction potential (ORP) or redox potential is a main factor in the EC process and is very important to the formation of Cr (chromites and chromate) and nitrogen species (N_2 , NO_3 , NO_2 and NH_3). Cr (VI) usually exists as oxyanions, such as chromate (CrO_4^{2-}) and dichromate ions ($Cr_2O_7^{2-}$) [26], in aqueous solutions. With a low positive and negative ORP, these species transform to trivalent chromium (chromites) and insoluble hydroxide ($Cr(OH)_3$) that separate from the wastewater. The main cathodic reactions in the electrochemical reduction of nitrate ions to nitrogen and ammonia are as follows [27].

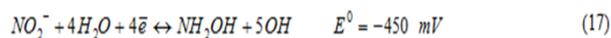
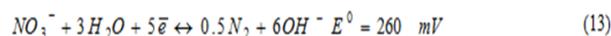


Fig. 5 presents variations in the ORP over time. The ORP decreased from -257 to -540 mV as the current increased from 0.02 to 1 A, respectively. Moreover, with increasing time, the ORP decreased for all of the applied currents. It can be confirmed from Fig. 5 that as the applied current increased, the time to achieve a reductive environment decreased. With a high negative ORP (about -450 mV), nitrate was transformed to ammonia immediately. Air stripping using an aquarium pump was done to exhaust the ammonia air. At the end of the process, the negligible amount of ammonia was determined.

D. Anode release during the EC process

The study of aluminum release during electrochemical reactions has technological merits because the coagulant dosage is a critical parameter for the EC process [17]. The amount of anode released during EC was estimated according to Faraday's law, and the effects of reaction time and current intensity were investigated. Table 1 indicates the theoretical rate of anode release during the EC process. The results illustrate that with an increase in time and current intensity the rate of dissolution of the anode increased as shown in Table 1. Golder et al. [24] have shown that doubling the current density from 16.26 mA cm^2 leads to 18% (w/w) more sludge generation for the same chromium removal. In our study, the dissolution ratio was 1: 2: 4: 50 at currents of 0.02, 0.25, 0.5 and 1.0 A, respectively. It appears that between 0.02 and 0.25 A, a critical value for aluminum release was exceeded. Table 1 shows a sharp increase in the amount released over the current intensity range of 0.25–1.0 A.

TABLE. 1 ANODE RELEASE (MG/MIN) AT DIFFERENT CURRENT INTENSITY ACCORDING TO FARADAY'S LAW.

Time (min)	Rate of dissolved aluminum (mg/min)			
	0.02 A	0.25 A	0.5 A	1 A
5	0.6	7	14	28
15	1.7	21	41.9	83.9
30	3.4	41.9	83.9	167.8
45	5	62.2	125.8	251.7
60	6.7	83.9	167.8	335.6
90	10.1	125.8	251.7	503.3
120	13.4	167.8	335.6	671.1

In the case of reaction time, the variation in the amount of aluminum released seems to be very significant beyond 60 min. Ricordel et al. [28] have shown that the electrocoagulation–electroflotation process leads to great decreases in phosphate and nitrate anions and dissolved organic compounds with an aluminum anode. In fact, the current efficiency of aluminum dissolution reported in the published data ranged between 109 and 215%. It has been suggested that efficiencies exceeding 100% could be explained by “pitting corrosion” of the anode due to chloride ions present in the solution [17]. Table 1 Anode release (mg/min) at different current intensities according to Faraday’s law.

IV. CONCLUSIONS

The electrocoagulation (EC) process was used for the removal of hexavalent chromium and nitrate ions from model wastewater. The experimental results show that Cr (VI) and nitrate removal are enhanced by an increase in the current intensity. In addition, a desirable concentration of nitrate and Cr (VI) was achieved in the pH range between 4 and 8 over 120 min. As pH increased, Cr (VI) removal efficiency decreased, and the removal efficiency of nitrate increased. During the EC process, the Cr (VI) ion was reduced at the cathode and precipitated as Cr (OH)₃, and nitrate removal was complete and accompanied by the precipitation of Al (OH)₃ produced in the solution from the anode release. We conclude that nitrate can be removed completely from model wastewater by using the EC process. Moreover, the oxidation reduction potential decreased as the current intensity increased. This behavior can reduce the nitrate ions to N₂ gas. The results show that, with an increase in time and current intensity, the rate of anode dissolution increased. The results of this study have shown that simultaneous nitrate and Cr (VI) removal can be achieved by coupling the cathodic reduction of the nitrate and Cr (VI) ions with the oxidation of ammonia operated by chlorine and an increase in the pH as a result of the Al (OH)₃ produced in the solution by anode release.

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