

Removal of Hexavalent Chromium from Groundwater by Continuous Electrocoagulation

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Abstract. Continuous electrocoagulation was evaluated for the removal of hexavalent chromium from groundwater. Different operating parameters were examined for their effects on chromium removal, including inlet flow rate, electrode type, applied current density, initial pH, initial chromium concentration, conductivity and temperature. The experimental results indicated that chromium removal was affected by electrode arrangements (iron and/or aluminum); thus the highest removal efficiency (100% chromium removal) was obtained when using Fe-Fe electrode pair at an electrocoagulation time of 5 minutes, an inlet flow rate of 90 ml/min and a current density of 7.94 mA/cm². The results show that electrocoagulation could be considered as an effective solution for the treatment of groundwater with an estimated energy consumption of 0.8 kWh/m³

Keywords: Electrocoagulation, continuous process, hexavalent chromium, groundwater, brackish water

1. Introduction

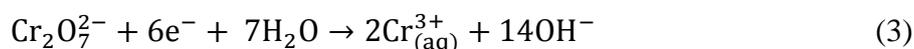
Chromium compounds that have harmful effects on all living forms are extensively used in chrome plating, leather tanning, and manufacturing of cement [1]-[3]. Chromium occurs primarily in two states: hexavalent Cr(VI) and trivalent Cr(III), that are characterized by different chemical behaviours and toxicity. Hexavalent chromium Cr(VI) is certainly more harmful to humans and animals. It has severe risks in terms of toxicity, including skin irritation, and kidney failure, in addition to the carcinogenic effect [4]. To meet environmental regulation, effluent of wastewater contaminated with chromium compounds must be treated before discharge. One of the most underexploited treatment technologies is the electrocoagulation (EC).

Electrocoagulation (EC) is a wastewater treatment technique that works through destabilizing suspended or dissolved contaminants in an aqueous medium by introducing a current into the medium and generating coagulant in-situ by electrolytic oxidation of an appropriate anode material (Aluminium or Iron). The reactions taking place in an electrochemical cell when iron metal (Fe) used as sacrificial electrode can be described by the following equations [2]:

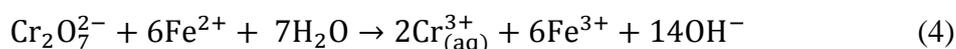
Anodic reaction:



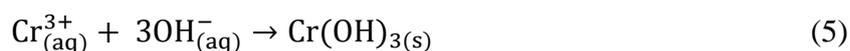
Cathodic reaction:



Bulk reactions:



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Electrocoagulation process has established itself as a convenient, efficient, economical and compact alternative to conventional chemical and other traditional methods. A major advantage of EC is the low occurrence of secondary pollution by in-situ generation of coagulants [5]. Also, EC is characterized by high separation efficiency due to the generation of oxygen and hydrogen bubbles in a compact frame [6]. Such features make this technology especially attractive for use in facilities where purifications in limited space are desired. The performance of continuous electrocoagulation reactors for the treatment of wastewater was rarely investigated, with the exception of limited studies on the reduction of COD [7]-[10], removal of petroleum contaminants [11], and removal of arsenic from synthetic wastewater [12]. The prime objective of this study was to assess the performance of electrocoagulation in a continuous stirred mode (CSTR) for the removal of hexavalent chromium from brackish groundwater.

2. Materials and Methods

2.1. Characterization of Groundwater

Groundwater samples were collected from farm wells located in Al-Ain, UAE. Characterization of the groundwater samples and detailed description of the analytical techniques have been reported in a previous publication [13].

2.2. Continuous Electrocoagulation Procedure

An electrocoagulation reactor with similar configuration to that used for the batch process [13] was utilized for the continuous stirred tank reactor (CSTR) experiments. At the beginning of each continuous experiment, EC reactor was filled with an effective volume of 1000 mL of groundwater, achieving complete metal electrode coverage with surface area of 63 cm². Both electrodes were connected to the middle of the Plexiglas cover at the top of the reactor. This design was retained to decrease the passivation of anode by enhanced mixing between the inter surface of the cover and the anode [14]. The contaminated inlet flow rate was controlled by a peristaltic pump (MasterFlex7553-79). Thus, the treated groundwater leaves the EC reactor by continuous spilling and gently entering a settling container. A continuous stirring at 300 rpm was applied to homogenize the liquid at the feed container and the EC reactor. Treated groundwater samples were collected from the settling container at constant time intervals.

3. Results and Discussion

3.1. Effect of Electrode Material

The effect of electrodes type on chromium removal was experimentally examined using: iron (Fe) and aluminium (Al) at different arrangements. The results, shown in Fig. 1, prove that the chromium removal efficiency of the continuous EC reactor is significantly affected by the material of the sacrificial anode. Generally, it was observed that complete removal of chromium could be achieved when iron is used as an anode material. Thus 100% removal was achieved after 5 minutes of electrolysis time when both electrodes are iron. This may be attributed to the chromium reduction mechanisms that take a place in the EC reactor. According to Eq. 1-5, hexavalent chromium Cr(VI) is reduced to trivalent chromium Cr(III) once the current passes through the cathode surface, followed by in-situ reaction of Cr(III) with hydroxide ions forming chromium hydroxide Cr(OH)₃ solid. In the case of iron as a sacrificial anode, one more additional reduction reaction of chromium occurs in the bulk media (Eq.4) due to the reaction of the dissociated iron ions (Fe²⁺) and the chromium ions Cr(VI), forming insoluble products, Cr(OH)₃ and Fe(OH)₃, in-situ [15], [16]. Therefore the contribution of the two mechanisms to Cr(VI) reduction by iron as a sacrificial anode facilitate chromium removal at short operation time (electrolysis time = 5 min).

On the other hand, for aluminium sacrificial anode, limitation on chromium removal was observed, with only 40 % of the chromium could be removed (electrolysis time = 30 minutes) when both electrodes were made of aluminium. In this case, both electrochemical reduction of Cr(VI) at the cathode surface (Eq. 3) and adsorption of chromium on Al(OH)₃floc [17] take place.

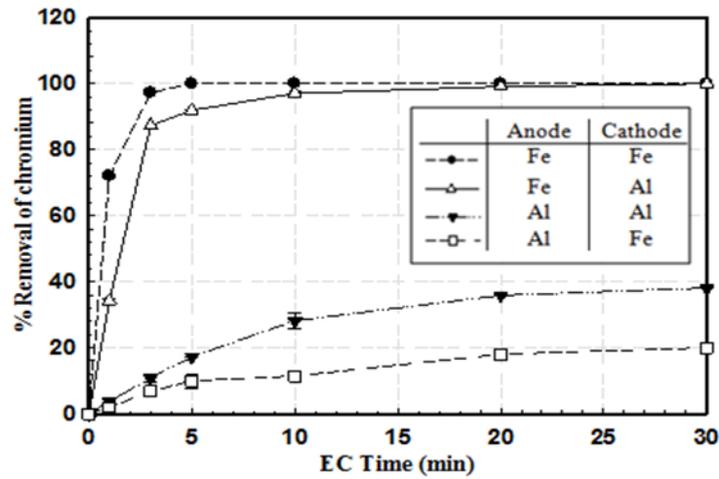


Fig. 1: Influence of electrode material on continuous stirred EC at $Q_L = 90$ ml/min, and $Cr_0 = 5$ mg/L

Whereas, replacing the cathode with iron electrode, seem to have more detrimental effect on the removal efficiency as shown in Fig. 1. In the case of this electrodes pair (Al as an anode and Fe as a cathode) can be attributed to the fact that less aluminium hydroxide is generated thus decreased chromium removal rate [18].

3.2. Effect of Inlet Flow Rate

The effect of inlet flow rate on the performance of EC CSTR with iron electrodes was evaluated using three different flow rates: 30, 90 and 150 mL/min, at an initial chromium concentration of 5 mg/L. Both current density and initial pH were kept constant at 7.94 mA/cm² and 8, respectively. The experimental results are shown in Fig. 2. After three minutes of electrolysis reaction, chromium removal efficiency is decreased from 99% at 90 mL/min to 72% at 150 mL/min. At the same electrolysis time, EC performance is slightly reduced (removal efficiency = 90%) at the lowest inlet flow rate of 30 mL/min.

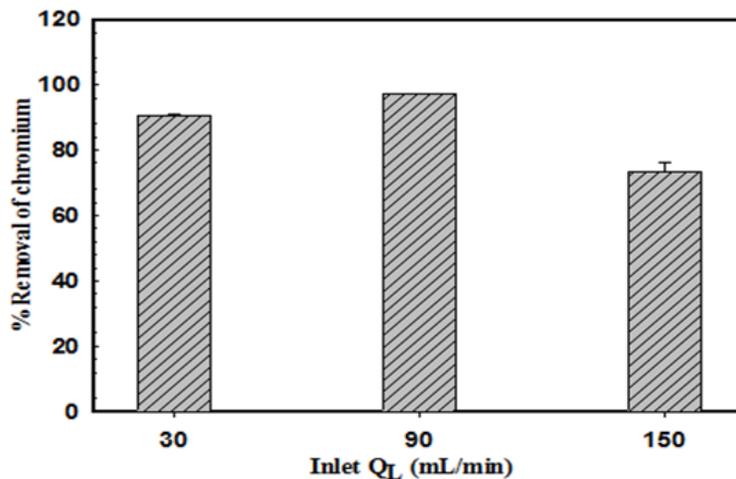


Fig. 2: Influence of inlet flow rate on the removal efficiency of chromium in continuous stirred EC process using iron electrodes

The inverse relation between the inlet flow rate and the removal efficiency can be related to the residence time inside the reactor; low inlet flow rate provides longer reaction time between the pollutant ions present in the groundwater and the iron ions released from anode surface [19], thus giving more time to destabilize chromium compounds and thereby improve the removal rate [20]. However, the decline in chromium removal efficiency at lower flow rate ($Q_L = 30$ mL/min) can be attributed to the generation of large amount of gas bubbles that is observed at the surface of the cathode. These bubbles can cause a small drop in the destabilization rate and therefore the reduction rate of pollutants [21].

3.3. Effect of Applied Current Density

Applied current density (ACD) directly affects coagulant dosage and hydrogen evolution rate, as well as mass transfer near the electrodes. The ACD was varied from 1.50 mA/cm² to 15.87 mA/cm² to assess its effect on the performance efficiency of the EC CSTR. The experimental work was conducted at fixed inlet concentration ($C_0 = 5$ mg/L), inlet flow rate ($Q_L = 90$ mL/min) and constant initial pH of 8, using iron electrodes. The results indicated that the operation time required to achieve a steady-state condition was inversely proportional to the current density as shown in Fig. 3. As the applied current density increases from 1.59 to 7.94 mA/cm², chromium removal efficiency increases from 37% to 99%, after five minutes of electrolysis reaction. High current density accelerates the dissolution rate of Fe²⁺ ions provided by the anode material and therefore raises the destabilizing rate of the pollutants, thus forms larger amount of coagulant and improves the performance of EC process [22]. However, increasing the ACD above 7.94 mA/cm² is not justified as most of the energy supplied would be dissipated into heating the reactor content and hence raising the temperature.

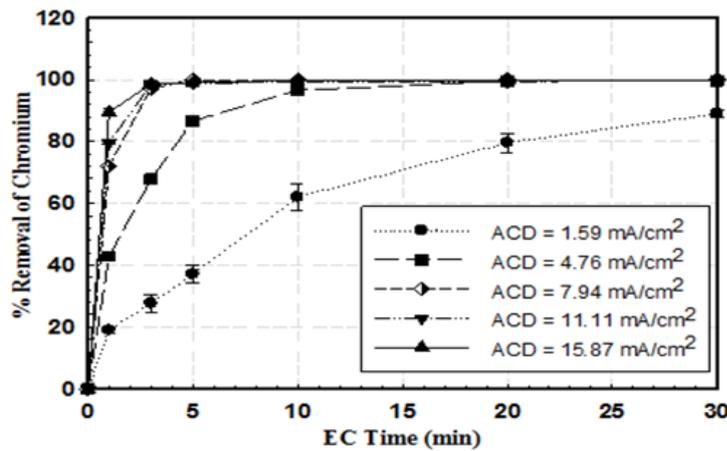


Fig. 3: Influence of Applied Current Density on the performance of continuous stirred EC at $Q_L = 90$ ml/min

3.4. Effect of Initial Concentration

Initial pollutant concentration plays a significant role in the performance of continuous electrocoagulation process. Experiments were conducted at initial chromium concentration ranging between 0.225 and 100 mg/L, using the optimum operating conditions obtained earlier: ACD of 7.94 mA/cm², inlet flow rate of 90 mL/min, initial pH of 8 and iron electrode material. Fig. 4 shows the removal efficiency of chromium from groundwater samples using CSTR electrocoagulation. It can be seen that removal efficiency of chromium reached 91%, 98% and 97% at initial chromium concentration of 0.2 mg/L, 1 mg/L and 5 mg/L, respectively (within an electrolysis time equal to 5 min). At these initial concentrations, steady state could be reached within 10 minute of electrolysis reaction. Higher initial chromium concentration slowed the performance of the CSTR process and decreased the removal efficiency, reaching only 90% and 67% chromium removal for 20 and 100 mg/L, respectively (electrolysis time of 30 min).

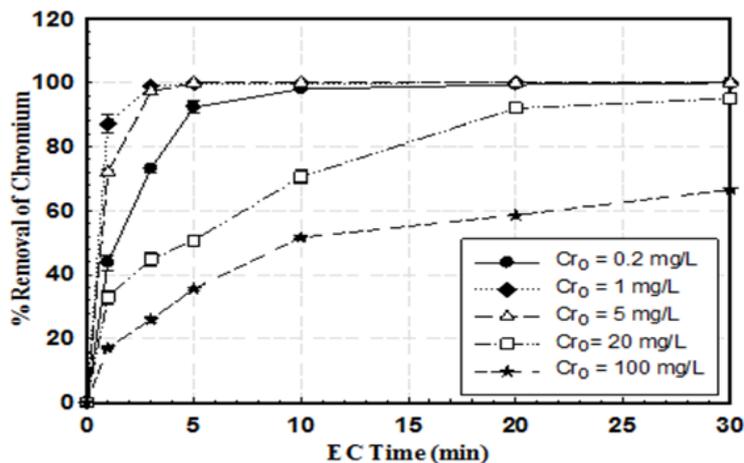


Fig. 4: Influence of initial chromium concentration at $Q_L = 90$ mL/min, pH 8 and ACD equal to 7.94 mA/cm²

4. Conclusions

The performance of continuous EC stirred reactor (CSTR) for the removal of chromium was experimentally examined. Chromium removal efficiency was found to be affected by the inlet flow rate, current density, initial pH, electrode material and initial chromium concentration. The experimental results indicated that the highest removal of chromium (100%) was achieved at inlet flow rate of $Q_L = 90$ ml/min, initial pH = 8, ACD of 7.94 mA/cm² using pairs of iron electrode, at room temperature ($T = 25$ °C). This work emphasizes the opportunities for utilizing continuous EC process for the efficient removal of other pollutants from groundwater at acceptable energy consumption (EEC) of 0.80 kWh/m³.

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