

Conference Paper No: PF-04

Current density dependent removal of aqueous Cr(VI) by electrocoagulation

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Abstract

Electrocoagulation (EC) is a proven green technology for the remediation of potentially toxic metalloids and metal ions contaminated water and waste water. The EC performance was carried out on a laboratory scale batch mode reactor using Al as anode and cathode for the removal of 5 ppm of Cr(VI) in synthetic water prepared with 150 ppm of Ca^{2+} , 50 ppm of Mg^{2+} and 5 ppm of F^- ions. The results showed that the removal efficiency of Cr(VI) increases with increasing both electrocoagulation time and the current density. At current densities, 4 mA/cm², 2 mA/cm² and 1 mA/cm², removal efficiencies were 98%, 93% and 48% respectively after 140 minutes at initial pH of 6.0. Energy consumption of EC process was found to be 6.57 kWh/m³, 1.84 kWh/m³, and 0.56 kWh/m³ in the same order of decrease in current densities. The EC process gives promising results towards the removal of Cr(VI) at a low consumption of energy, making the process attainable and possible to scale up.

Keywords: Electrocoagulation, Batch-mode reactor, Al electrodes, Cr(VI) removal, Energy consumption

Introduction

The contamination of ground water by heavy metals has become a world-wide problem due to their harmful effects on human, aquatic and other terrestrial life in the environment. Among the causative hazardous heavy metal, chromium is considered to be of higher priority due to its toxicity. Chromium species could enter the environment from both natural and anthropogenic sources (Gallios, 2007, Deng et al., 1996) and exists in the environment in two main oxidation states as hexavalent chromium, Cr(VI) and trivalent chromium, Cr(III) (Krishnani, et al., 2006). Cr(VI) is well pronounced as carcinogenic and mutagenic agent while Cr(III) at very low levels is an essential element in humans which is less toxic (Hu et al., 2009). Cr(VI) is abundantly used in chemical, refractory and metallurgical industries and discharged from the effluents of chromium smelting and mining, chrome plating, dyeing and leather, etc. (Zhang et al., 2018, Bhatti et al., 2009).

Speciation of Cr in water depends on initial concentration and pH. $\text{Cr}_2\text{O}_7^{2-}$ is the most predominant species of Cr(VI) at pH 6.0 and at high Cr concentration while at pH 2.0 - 4.0, Cr(VI) exist as HCrO_4^- . At pH higher than 6.0, CrO_4^{2-} is the predominant form. Due to toxicity of Cr(VI), maximum allowed total chromium concentration level in drinking water, has been announced as 0.1 mg/L by EPA (Environmental Protection Agency) (Hu et al., 2009). The most common approach for the removal of Cr(VI) is treating under alkaline conditions (Bhatti et al., 2009). Adsorption, ultrafiltration, ion exchange, reverse osmosis, membrane separation, electro dialysis, and electrochemical treatment are the other viable technologies demonstrated for efficient removal of Cr(VI) (Hu et al., 2009,

Zhang et al., 2018, Bhatti et al., 2009, Golder, et al., 2007). All these methods require multi-step process and a post-treatment for promising results (Hernández, et al., 2012).

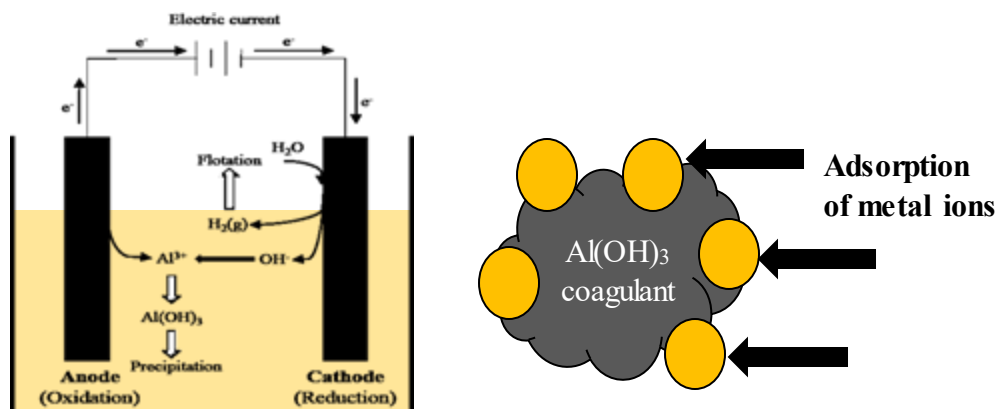


Figure 1. In situ generation of Aluminium hydroxide during electrocoagulation process.

Electrocoagulation (EC) is a proven low cost and an effective technology for the removal of hardness, fluoride and heavy metals in contaminated water at a practically higher efficiency (Radjenovic et al., 2015). EC is based on the generation of coagulant species in situ by electro oxidation of sacrificial anode materials, Al/Fe triggered by electric current applied through the electrodes (Jean, et al., 2017). The metal ions generated by electrochemical dissolution of the anode spontaneously undergo hydrolysis in water. Depending on the pH, various coagulant species including monomeric and polymeric aluminum hydroxides with different compositions are formed and are capable of removing pollutants by adsorption/settling mechanism (Gomesa et al., 2007).

EC process offers many advantages such as easy construction and operation, removes a variety of pollutants, no need for controlling pH, free of hazardous chemicals, low sludge production and the sludge produced is more acid-resistant, more stable and can be separated easily through filtration (Hernández et al., 2012).

Methodology/materials and methods

A batch type reactor was designed and fabricated using 4 mm acrylic sheet with an area of 8 cm×8 cm and a height of 35 cm. Aluminium electrodes were used as sacrificial electrodes, arranged in monopolar configuration. Two electrodes were positioned vertically with spaces of 10 mm. The plates have rectangular geometry with the dimensions 75 mm×200 mm×4 mm. The total effective surface area of an electrode immersed in synthetic water was 150 cm². The electrodes were connected to a direct current power supply providing voltage in the range of 0-30 V (TENMA 72-2930) and electrical current in the range of 0-6 A. During the EC process, contaminant solution was agitated continuously using magnetic stirrer (AREC f20510011) with rotational speed of about 600 rpm.

All chemicals used in the study were analytical grade and procured from Sigma Aldrich and were used as received. For ICP-MS analysis, traceable grade nitric acid was used in sample preparation. Cr(VI) solution was prepared from stock solution of (500 ppm) of K₂Cr₂O₇. Synthetic water was prepared using deionized water, and the composition of the ions present in synthetic water was 150 ppm Ca²⁺ ions, 50 ppm Mg²⁺ ions and 5 ppm F⁻ ions. Electrolysis was carried out using a batch mode reactor containing 1.5 L of the synthetic water spiked with 5 ppm chromium solution. Before each experiment each

electrode surface was mechanically polished with sand paper, soaked in 15% HNO₃ and rinsed with distilled water to ensure the surface reproducibility. Electrocoagulation was carried out for 180 minutes under three current densities 4 mA/cm², 2mA/cm² and 1mA/cm² for the electrochemical removal of hexavalent chromium. Samples were withdrawn in each and every 10 minutes and filtered using syringe filters (0.45 μm pore size) and analyzed by ICP-MS (Perkin-Elmer Nexion 2000). The initial conductivity of the solution was around 900 μs/cm. The change in pH and conductivity was monitored throughout the process using a multiparameter analyzer (HANNA HI5522-02). Analysis was carried out in triplicates to minimize standard errors of the experiments.

Results and Discussion

Current density is the key parameter which determines the rate at which electrocoagulant is injected to the solution and has a significant impact on chromium removal efficiency. To investigate the effect of current density, a series of experiments was carried out at pH 6.0 followed by three current densities 4 mA/cm², 2 mA/cm² and 1mA/cm². The removal efficiencies of chromium were 98%, 93% and 48% respectively after 140 minutes of EC process.

The removal percentage (%) of chromium was calculated by using the following equation:

$$\text{Removal \%} = \frac{C_0 - C_e}{C_0} \times 100\%$$

Where C₀ is the initial concentration of Cr(VI) and C_e is the equilibrium concentration of Cr(VI) in supernatant (Hu et al., 2009).

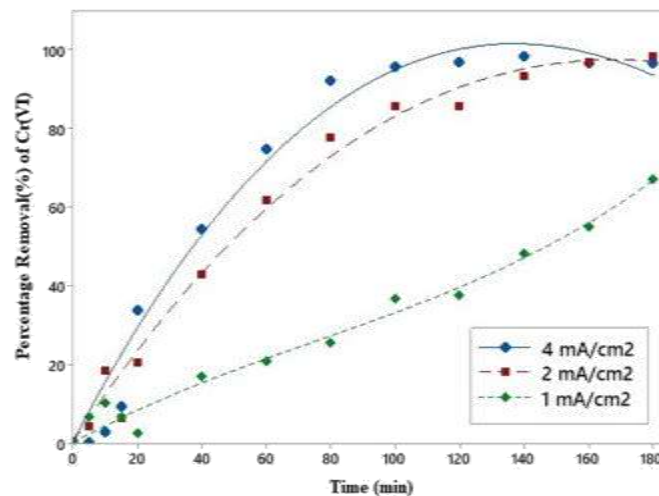


Figure 2. Effect of current density on Cr(VI) removal from its initial concentration of 5 ppm during the electrocoagulation process at pH 6.0

$$W_c = \frac{I \times M \times t}{Z \times F}$$

Where W_c is the weight of Al released from the electrode, I is the current in A, t is the time (s), M is the atomic weight, Z is the charge involved for the generation of Al³⁺ and F is the Faradays constant (96485.3 C/mol) (Vasudevan et al., 2010). The amount of chromium adsorption increases with the increase of adsorbent concentration as

determined, 0.91 kg/m³, 0.45 kg/m³, and 0.23 kg/m³ followed by the current densities 4 mA/cm², 2 mA/cm² and 1mA/cm² respectively, which indicates that the increased amount of colloidal Al(OH)₃ provides more adsorption sites for chromium adsorption.

Table 1. Weight of different Al species generated during the EC process

Current density (mA/cm ²)	Applied current (A)	Weight of Aluminium generated during EC (g)	Weight of adsorbent (Al(OH) ₃) generated during EC (g)	Residual Al in the solution (g/L)	Dry weight of the sludge produced (g)
4	0.60	0.46	1.35	0.014	1.67
2	0.30	0.23	0.67	0.010	0.83
1	0.15	0.11	0.33	0.008	-

Table 1 shows the theoretical yield of Al released and Al(OH)₃ formed during EC process at different current densities. The experimental measured value of residual Al in the solution increases with increase in current density. The dry weight of sludge measured (1.67 g) at the highest current density is higher than the calculated amount of Al(OH)₃ (1.35 g) due to association of additional weights from CaCO₃, Mg(OH)₂, chromium and fluoride.

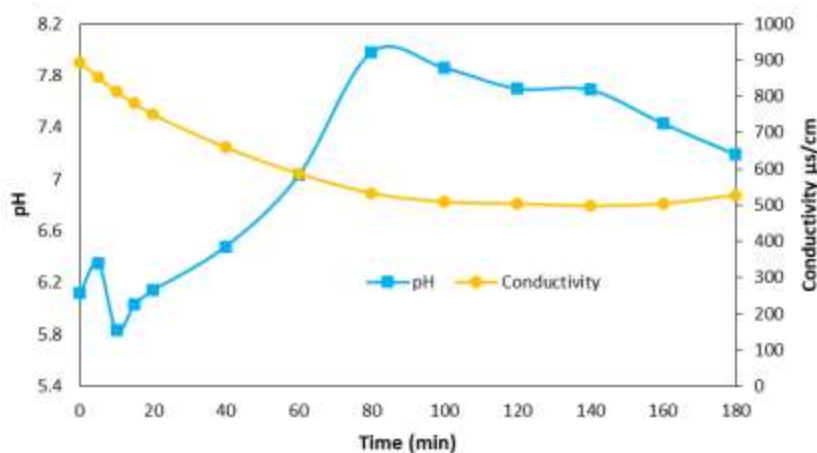


Figure 3. Conductivity and pH variation of Cr(VI) removal from its initial concentration of 5 ppm during the EC process at pH 6.0 at current density 4 mA/cm²

The same trend of slow decrease in conductivity during EC process was noticed at three different current densities (Fig. 3-5). This variation is attributed to removal of Ca²⁺, Mg²⁺ and F⁻ and Cr(VI) ions as insoluble colloidal form of Aluminium hydroxide. A distinct pH variation with time at the lowest current density of 1 mA/cm² compared to that of at two higher current densities (Fig. 3-5) was observed.

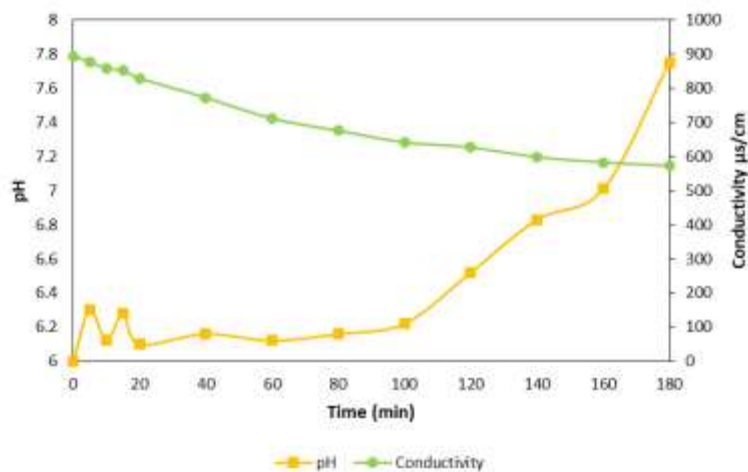


Figure 4. Conductivity and pH variation of Cr(VI) removal from its initial concentration of 5 ppm during the EC process at pH 6.0 at current density 2 mA/cm²

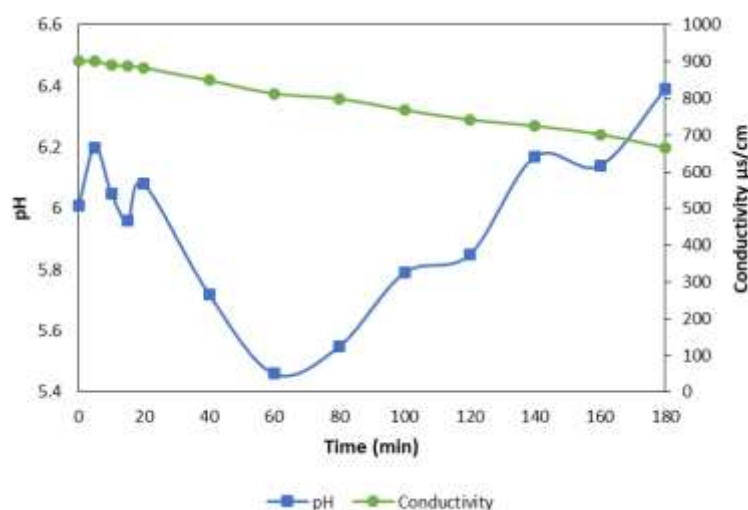


Figure 5. Conductivity and pH variation of Cr(VI) removal from its initial concentration of 5 ppm during the EC process at pH 6.0 at current density 1 mA/cm²

The decrease in pH at the lowest current density (Fig. 5) during the initial stage of the EC process could be attributed to generation of H⁺ ions due to water oxidation at the anode. The subsequent increase in pH with time at high current density during EC process is attributed to higher rate of formation of hydroxyl ions at the cathode but the concentration is regulated as hydroxides are removed as insoluble Mg(OH)₂ and CaCO₃ and Al(OH)₃.

In electrochemical technology energy consumption is one of the most important factor to be considered (Jung, et al., 2015). Energy consumption (E) (Ghosh, et al., 2011; Un et al., 2013, Hashim, et al., 2017) during the EC process was calculated by the following equation 3:

$$E = \frac{I \times V \times t}{\text{Vol.}}$$

Where E is the electrical energy consumption (kW h/m³), I is the current (A), V is the potential (V), t is the electrolysis time (seconds), and Vol. is the volume of solution (m³).

Table 2. Energy consumption of energy on Cr(VI) removal from its initial concentration of 5 ppm during the electrocoagulation process at pH 6.0

Current density (mA/cm ²)	Applied current (A)	Applied potential (V)	Energy Consumption (kW h/m ³)	Energy Consumption ratio
4	0.60	5.47	6.57	3.57
2	0.30	3.07	1.84	3.28
1	0.15	2.37	0.56	1.00

Energy consumption values tabulated in Table 2, depicts that the energy consumption is directly proportional to the applied current and when the applied current was doubled energy consumption increased more than 3 times of the lowest current density.

Conclusion

The results show that Cr(VI) can be removed with 98% efficiency at the current density of 4 mA/cm² after 140 minutes of the EC process. When the applied current density is increased more adsorbent with more binding sites to Cr(VI) is generated causing highest removal of Cr(VI). Low energy consumption makes the electrocoagulation process economically viable for applications in contaminant removal from water.

Acknowledgment

This work was supported by project, “Accelerating Higher Education Expansion and Development Operation (AHEAD), under the research grant DOR No. 79

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