

Optimizing Parameters for the Remediation of Chromium(VI) Contaminated Groundwater on Tamil Nadu Chromates and Chemicals Limited (TCCL) Site of Ranipet, Tamilnadu using Electrocoagulation Process

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This paper presents the effects of variables such as electrode material, electrode distance, pH, initial concentration of Cr(VI), applied current, electrolyte and time duration in the treatment of contaminated groundwater for the removal of Cr(VI) at two different concentrations of 200 and 800 mg/L of Cr(VI) using batch electrocoagulation process. Initially, the conditions were optimized from synthetic contaminated water, which was in congruence with chloride and sulphate ions as present in the contaminated groundwater. The optimum conditions obtained on removal of Cr(VI) from synthetic contaminated water were applied in real Cr(VI) contaminated groundwater collected from a bore well at chromate ore processing residue (COPR) dumpsite. The results of the treated contaminated groundwater were found that all the parameters were within the limits of Pollution Control Board discharge standards. The efficiency and energy consumption on the removal of Cr(VI) from real contaminated groundwater were compared with and without addition of NaCl. The results suggest that the optimum conditions for a 99.99% removal efficiency were initial concentration 200 mg/L of Cr(VI), pH 6.0, applied current 2 A, electrolyte 2 g/L of NaCl, time duration 35 min and energy consumption 2.625 Whr/m³.

Keywords: Chromate ore processing residue, Cr(VI) contaminated groundwater, Electrocoagulation.

INTRODUCTION

Industrialization is the basic need for sustained economic growth in developing countries and the pollution caused due to industrial activities is a major threat to the environment. In the naturally contaminated groundwater, the solubility of Cr(VI) is highly dependent on pH, concentration of pollutant and the presence of ligands in the matrices [1]. Various industrial activities such as tanneries [2], steel industries [3], electroplating units [4], paint manufacturing units [5] and textile units [6] are generating a larger quantity of wastewater from the unit operation. Before the enactment of water (prevention and control of pollution) Act 1974 in India, a huge volume of hazardous chromium wastewater generated by these industries were disposed of on land leading to groundwater contamination.

Similarly, the unscientific disposal of chromate ore processing residue (COPR) on land is another major contributor of Cr(VI) in the biota [7]. Due to weathering of COPR, the dissolution of Cr(VI) bearing minerals leach into the groundwater

[8]. The concern of COPR is not only a domestic issue, but also exists in many parts of the world like USA, China and Japan [9]. A study conducted at Scottish island showed the presence of about 91 mg/L of Cr(VI) in the groundwater and 6.7 mg/L was found in the tributary stream. Whereas, in New Jersey, USA it has been reported at about 30 mg/L [10]. However, the permissible level of Cr(VI) prescribed by the regulatory authority for drinking water is 0.05 mg/L and inland surface water is 0.1 mg/L [11].

A variety of technologies have been developed for the removal of Cr(VI) from the wastewater and few among them are listed as adsorption [12], photocatalytic reduction [13,14], electro-chemical treatment [15-17], reverse osmosis [18] and bioremediation [19]. Nevertheless, none of the above technologies has been found to be economically flexible for the treatment of wastewater containing higher concentration. No kinds of literature have been published so far to refer to in selecting the appropriate technology for remediation of Cr(VI) depending on the site-specific conditions. Earlier studies on COPR

site of Ranipet, Tamilnadu state, India have addressed the distribution of Cr(VI) and the problems associated with the contamination of Cr(VI) in the surface and subsurface water sources [20,21]. Therefore, the objective of this study is to evaluate the potential of utilizing the electrocoagulation process for the removal of Cr(VI) from the contaminated groundwater of TCCL site and to optimize the operating conditions to achieve the disposal standard of Cr(VI) prescribed by the regulatory authorities.

EXPERIMENTAL

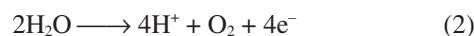
The electrocoagulation process was carried out in a cell capacity of 2500 mL rectangular reactor with a working volume of 2000 mL at room temperature (27 °C). Five numbers of mild steel electrodes each of dimension 150 mm length, 75 mm breadth and 1 mm thick were employed in this work. The effective reactive surface area was fixed at 270 cm². The electrodes were vertically installed on a perforated Plexiglas plate placed at 2 cm from the bottom of the cell. The anodes and cathodes were connected to the positive and negative terminals of a DC power supply with 10 A/15 V capacity. The reactor was placed over a magnetic stirrer with 240 rpm. Sodium chloride salt (99.9% purity) was used to adjust the conductivity. A rectifier equipped with a maximum of 15 volts and an 8 amperage was used for power supply.

Synthetic contaminated water (SCW) was prepared by dissolving the required quantity of dried K₂Cr₂O₄ in distilled water and makeup to 1 L [22], which are in congruence with contaminated groundwater (CGW) with respect to chloride and sulphate ions. The desired concentrations required for this study were obtained by successive dilutions with distilled water. The operation was carried out at different amperages and samples were collected from the reactor at every 10 min intervals. The collected samples were filtered and analyzed for the residual concentration of Cr(VI). Before each run, the electrodes were dipped in H₂SO₄ solution and washed with distilled water, dried and reused. The pH of the SCW was adjusted using 1 N NaOH solution. The pH meter 240 (Model Elico L1614) was used to measure the pH of the solutions. The residual concentration of chromium(VI) was analyzed photometrically with 1.5 mL of diphenylcarbazide at 540 nm, UV-visible spectra photometer (UV-3200, Lab India) and heavy metals were analyzed on an atomic absorption spectrometer (Shimadzu 6800). The Cr(VI) contaminated groundwater collected from a monitoring well of 7 cm diameter and 25 m deep in the TCCL site was taken for this study.

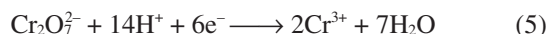
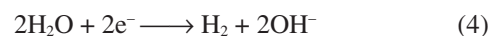
Electrochemical cell: The reactions involved in the electrocoagulation process are oxidation at the anode, reduction at the cathode, dissolution of ions from the electrodes, the formation of coagulants, destabilization of the contaminants present in the wastewater and formation of flocks due to aggregation of the destabilized particles [23]. In this study, mild steel electrodes are used as anode and cathode. When the potential difference is applied to the electrodes, electrochemical oxidation takes place at the anode, which results in the generation of ferrous ions as a primary reaction.



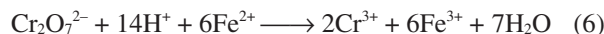
On the application of high potential, the chloride ions exist in the solution due to addition of electrolyte in the form of NaCl are oxidized and emerged as a secondary reaction. The reaction at the anode in the electrochemical cell are depicted below:



Due to simultaneous reaction at the anode and the cathode, the Cr(VI) present in the wastewater is reduced to Cr(III) at the cathode and the reactions are shown below:



The overall reactions at the anode and cathode, to reduce the hazardous Cr(VI) present in the wastewater to Cr(III) is taking place according to the following equations:



In this study, the SCW was made in congruence with that of contaminated groundwater (CGW) in terms of pH, chloride and sulphate concentrations. All other parameters of CGW are listed in Table-1. The effect of various parameters on the removal of Cr(VI) were investigated by using synthetic contaminated water as well as to the real Cr(VI) contaminated groundwater.

TABLE-1
CHARACTERISTICS OF CONTAMINATED GROUNDWATER

Variables	Value
pH	6.1
Hexavalent chromium	1617 mg/L
Conductivity	5,659 μs/cm
Chloride	528.8 mg/L
Sulphate	2344 mg/L
Total dissolved solids (TDS)	4085 mg/L

RESULTS AND DISCUSSION

Effect of electrode material and inter-electrode distances: The effect of electrode materials on the removal of Cr(VI) from SCW was investigated using electrode made from ferrous, aluminium and stainless steel materials. Each experiment was conducted at 2 A applied current with three different monopolar electrode arrangements having an effective electrode area of 270 cm². All the anodes and cathodes were the same kind of materials. The maximum removal efficiency of Cr(VI) from these electrodes in the order of Fe-Fe, SS-SS and Al-Al were recorded at 97.35, 59 and 37%, respectively in the time duration of 30 min. On comparing the efficiency of the electrodes, a maximum and instantaneous reduction was noticed when the Fe-Fe combination was used. Also, the surface roughness of the stainless steels were not easily changed and more resistant than the other two electrodes [24]. Hence, Fe-Fe electrodes were used in this study.

The effects of inter-electrode distances were investigated using Fe-Fe electrodes for the removal of Cr(VI) by varying

the distances at 1, 2, 3 and 4 cm for a time interval of 30 min and the efficiencies were recorded at 90.20, 89.50, 88.40 and 85.69%, respectively. The decreasing efficiency on increasing the electrode distance may be due to the fact that the electrostatic attraction between the electrodes is less at longer distance, which results in lesser formation of flocs needed to coagulate the pollutant [25]. The above results suggest that the inter electrode distance at 2 cm is optimum to conduct all the experimental studies.

Effect of pH: Earlier study has established that while using iron electrodes the initial pH needs to be maintained between 4 and 7 [26]. To investigate the effect of pH, a series of experiments were conducted at various pH levels in the order of 5, 6, 7 and 8 and the maximum removal of efficiencies obtained were 99.85, 99.21, 98.27 and 97.64%, respectively. The difference in the efficiencies at various pH levels proved that the reduction of Cr(VI), solubility of Cr(OH)₃ and Fe(OH)₃ are mainly depend on the pH of the wastewater. The results have indicated that the removal of Cr(VI) is significant in an acid medium, whereas an alkaline medium requires addition of chemicals to precipitate the particle for settling (Fig. 1) [27].

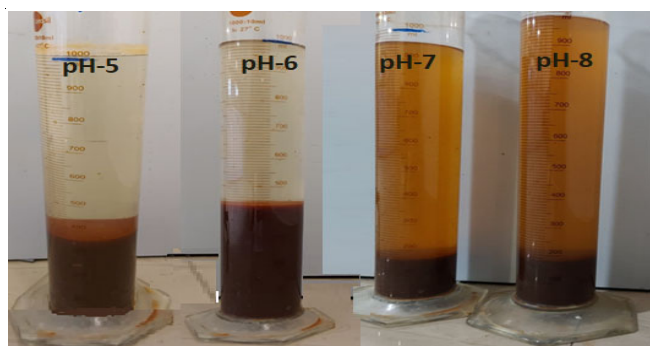


Fig. 1. Suspended solid concentrations at different pH after 30 min of settling

The solubility of metal species is important for the determination of optimum pH for precipitation and coagulation [28]. In the electrocoagulation process at alkaline pH the OH⁻ ions released at the cathode are partially reacted with ferrous ions forming ferrous hydroxide flocs and the remaining OH⁻ ions are combined with chromium(III) ions to form insoluble Cr(OH)₃ precipitate. The precipitation has reported that Fe(III) and Cr(III) can also coprecipitate as an amorphous solid solution of Cr_xFe_{1-x}(OH)₃, between the pH range of 2-6. When the pH of the solution is between 4 and 6, more dissolution of ferrous ions is taking place at the anode, leading to higher removal of Cr(VI) [29]. A maximum 99% removal of chromium is achieved at pH 6 in SCW, it was decided not to adjust the original pH of the CGW as the initial pH of the CGW was found to be 6.

Effect of initial concentration: It has been established that the change in concentration of wastewater is measured as a function of electric charge applied to the cell and the coagulant dosage has a considerable influence in the electrocoagulation process. To investigate these effects, a two different initial concentrations of Cr(VI) at 200 and 800 mg/L were treated in SCW using electrodes Fe-Fe, applied current 2 A and pH of 6 ± 0.1 without adding electrolyte.

As shown in Fig. 2, the maximum removal of 99% of Cr(VI) has reached in 30 min at the initial concentration of 200 mg/L. For higher initial concentration of 800 mg/L, the removal efficiency of Cr(VI) was 55.12% in 60 min. As per the Faraday's Law, at constant applied current the same amount of ferrous ion dosage generated in site increases with increasing the electrolysis time. Present results imply that there is no direct correlation exist between metal ion concentration and removal efficiency which is in accordance with the earlier report [30].

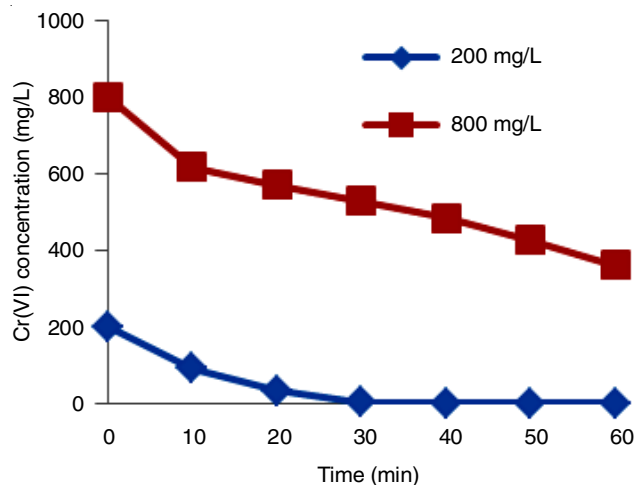


Fig. 2. Effect of initial concentration on the removal of Cr(VI)

Effect of applied current: The applied current determines the economy of the electrocoagulation process as it directly affects the process performance and operating cost. To investigate the effect of applied current on the removal of Cr(VI) experiments were conducted in SCW having two different concentrations of 200 and 800 mg/L without addition of electrolyte and only by varying the applied current from 1 to 3 A.

When the applied current was at 1 A, it required 55 min for a complete removal of Cr(VI) from the concentration of 200 mg/L. For the same concentration, when the applied current was increased from 1 A to 2 A, the removal efficiency has also increased from 64 to 99.1% within the first 30 min and reached 100% in the next 3 min of operation (Fig. 3). Similarly, for the higher concentration of Cr(VI) at 800 mg/L when the applied current was increased from 1 to 2 A, the residual Cr(VI) decreased from 359 to 177.5 mg/L in the time duration of 60 min. Further increasing the applied current is not beneficial, since most of the added energy would be transferred to heating the reactor content. Furthermore, to obtain an optimum yield this process need more conductivity to decrease the IR drop and energy consumption [31]. For lower concentration of Cr(VI) at 200 mg/L, complete removal has occurred at 35 min on 2 A of applied current without addition of electrolyte with energy consumption of 7.0 Whr/m³. Hence, the study was continued to find out the optimum conditions for low energy consumption.

Effect of electrolyte concentration: Generally, electrolyte in the form of common salt is used to obtain the conductivity in the electrocoagulation process. Electrolyte supplies ions to the electrolytic cell, which in turn affects the current efficiency, cell voltage and consumption of electrical energy. To investi-

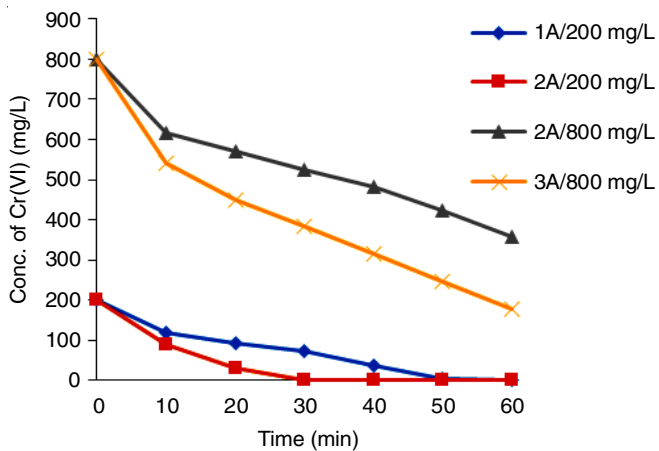


Fig. 3. Effect of applied current on the removal of Cr(VI)

gate the effect of electrolyte, two sets of experiments were conducted at two different concentrations. First experiment was conducted in SCW by varying the current from 1 A to 2 A, at initial pH of original solution (6.0 ± 0.1) with an initial concentration of 200 mg/L of Cr(VI).

It can be seen from Fig. 4, when the concentration of electrolyte increased from 1 to 2 g/L on constant application of 1 A electric current, the removal efficiency also increased marginally from 97.01 to 98.8% in 50 min and further addition of NaCl has not much influenced the oxidation of Fe(II) ions to Fe(III) ions. However, for the dosage of 2 g/L when the applied current was increased from 1 A to 2 A the removal efficiency increased to a maximum of 99.99% in 33 min. According to Faraday's law, this behaviour is due to the fact that the applied current is directly proportional to the amount of sacrificial anode dissolved. The hydroxide ions formed in the cell enhances the reduction of Cr(VI) to Cr(III) and escalates coagulant dosage by forming insoluble hydroxides of $\text{Cr}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ [32].

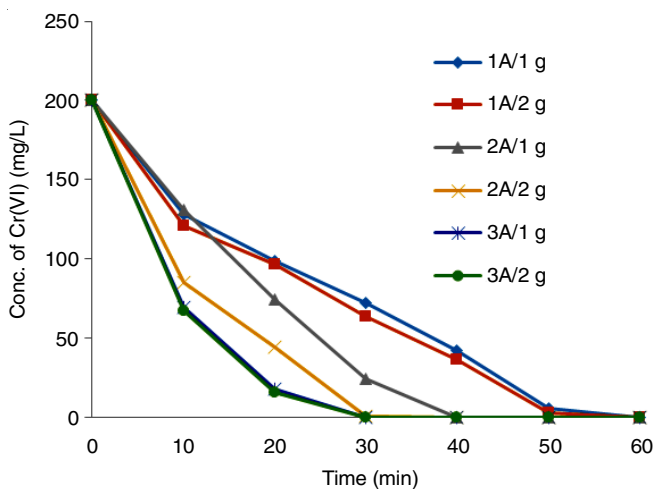


Fig. 4. Effect of electrolyte on the removal of Cr(VI) from SCW (200 mg/L)

Similar experiments were carried out for a higher initial concentration of 800 mg/L by varying the NaCl dosage from 4 to 8 g/L and applied current from 4 to 8 A. From Fig. 5, it is observed that on constant application of 4 A electric current

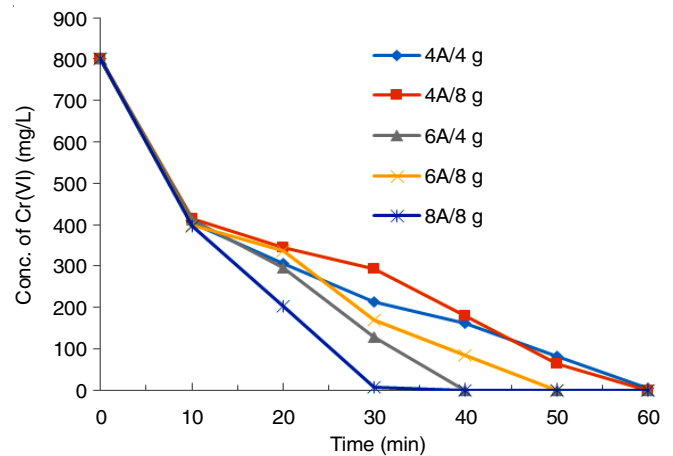


Fig. 5. Effect of electrolyte on the removal of Cr(VI) from SCW (800 mg/L)

the removal of Cr(VI) on the addition of 4 and 8 g/L of NaCl account to 89.88 and 91.18% in a time duration of 50 min with the energy consumption of 12.55 and 8.3 Whr/m³, respectively. When the applied current was increased from 4 to 6 A on addition of 4 and 8 g/L of NaCl, the removal efficiencies have attained in 40 min at the maximum removal efficiency of 99.99% and 89.4% with the energy consumption of 10 and 15 Whr/m³, respectively. Further increasing the applied current to 8 A and addition of 8 g/L of NaCl accounts for 99.08% of Cr(VI) removal in 31 min with energy consumption of 19.63 Whr/m³. Considering the economy of operation, present work suggests the optimum conditions are: applied current 6 A; electrolyte 4 g; time duration 40 min with energy consumption of 10 Whr/m³.

Comparing the results obtained for the SCW from two different concentrations, it is observed that electrocoagulation process is an effective treatment for the removal of Cr(VI) and the removal efficiency is higher for a lower concentration of Cr(VI) with lesser energy consumption.

Applications: The CGW used in this research was collected from a bore well located in a COPR dumpsite at Ranipet, Tamilnadu state, India. The initial pH of the CGW was recorded at 6. During the course of electrocoagulation process, the pH of the CGW in the cell was recorded and noticed that the pH has increased in first 30 to 40 min due to the generation of hydroxyl ions which shifts the solution of pH to an alkaline medium at 10.4. This is due to the fact that the system becomes saturated with ferrous ions, which combines with the hydroxyl ions forms ferrous hydroxide and partially combine with Cr(VI) to form the insoluble hydroxide precipitate as $\text{Cr}(\text{OH})_3$ [33]. The conditions adopted for the treatment of SCW corresponding to the concentrations were applied for the treatment of CGW.

It is observed (Fig. 6) that the optimum conditions for the 100% removal of Cr(VI) from the CGW are initial concentration 200 mg/L; pH 6.0; electrolyte 2 g/L (NaCl); inter electrode distance 2 cm; effective surface area 270 cm²; applied current 2A; time duration 35 min and energy consumption 0.257 Whr/m³. After treating the CGW by electrocoagulation process, the treated water was analyzed and found that the parameters such as pH, TDS and chlorides were within the discharge standards prescribed by the regulatory authorities.

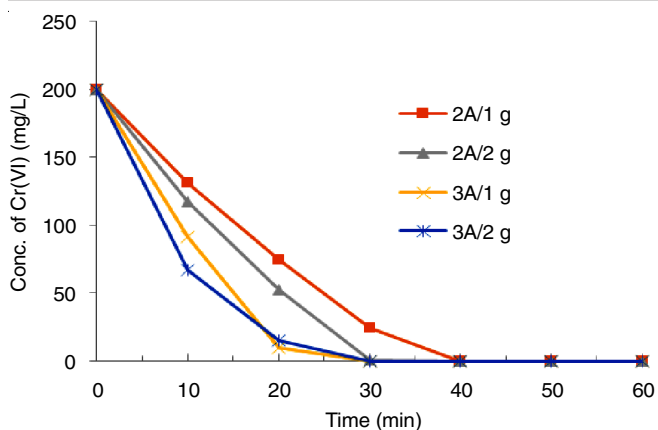


Fig. 6. Effect of removal of Cr(VI) from CGW (200 mg/L)

For a higher concentration of Cr(VI), the optimum conditions were: initial concentration 800 mg/L; pH 6.0; electrolyte 4 g/L (NaCl); inter electrode distance 2 cm; effective surface area 270 cm²; applied current 6 A; time duration 35 min and energy consumption 0.6 Whr/m³. However, upon analyzing the treated water the characteristics such as TDS and chlorides were exceeding the discharge standards as prescribed by the regulatory authorities.

Conclusion

Electrocoagulation proved to be a promising treatment method for the removal of chromium(IV) from contaminated groundwater. Water samples, collected from a bore well located in TCCL site of Ranipet, India were treated in a batch electrocoagulation system using Fe-Fe electrodes. The experimental results proved that the performance of electrocoagulation in the removal of chromium is largely affected by the electrode type, initial pH, inter electrode distance, conductivity, applied current, time duration of treatment and initial chromium(IV) concentration. The experimental results indicated that electrocoagulation can reach 100% removal of Cr(VI) from contaminated groundwater under the optimum conditions. This work shows the opportunities for utilizing a continuous electrocoagulation treatment for 100% removal of Cr(VI) from the contaminated groundwater at the contaminated site.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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