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Chromium (VI) Removal from Wastewater by Electrocoagulation Process Using Taguchi Method: Batch Experiments

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Abstract
Electrocoagulation is an electrochemical method for treatment of different types of wastewater whereby sacrificial anodes corrode to release active coagulant (usually aluminium or iron cations) into solution, while simultaneous evolution of hydrogen at the cathode allows for pollutant removal by flotation or settling. The Taguchi method was applied as an experimental design and to determine the best conditions for chromium (VI) removal from wastewater. Various parameters in a batch stirred tank by iron metal electrodes: pH, initial chromium concentration, current density, distance between electrodes and KCl concentration were investigated, and the results have been analyzed using signal-to-noise (S/N) ratio. It was found that the removal efficiency of chromium increased with increasing current density and KCl concentration, and decreases with increasing initial chromium concentration and distance between electrodes, while pH shows peak performance curve. Experimental work have been performed for synthetic solutions and real industrial effluent. The results showed that the removal efficiency of synthetic solution is higher than industrial wastewater, the maximum removal for prepared solution is 91.72 %, while it was 73.54 % for industrial wastewater for the same conditions.

Key words: Electrocoagulation, Chromium (VI) removal, Taguchi method, Iron electrodes.

Introduction
Rivers, channels, and other water resources are always in danger of pollutions as a result of the industrial wastewater discharge and other natural activities [1]. The problem of generating hazardous waste has been increasing recently due to the rapid growth of industrialization activities in the world. Since water is used in large quantities in most of the industrial activities the major part of waste that has been discharged to the environment and cause a serious pollution effects is the wastewater [2]. Heavy metals, including (chromium, copper, cadmium, zinc, and so forth) are the most common pollutants which usually exist in a high concentrations in industrial wastewater and they damage could the aquatic environment and threaten human's health [3].
The two typical oxidative states of chromium in the environment are

hexavalent, Cr (VI), and trivalent, Cr (III). These two oxidation states have widely contrasting toxicity and transport characteristics: hexavalent chromium is more toxic, with high water solubility and mobility, while trivalent chromium is less soluble in water, less mobile and less harmful [4]. Electrocoagulation is a simple and efficient method to remove the flocculating agent generated by electrooxidation of a sacrificial anode and generally made of iron or aluminum. In this process, the treatment is performed without adding any chemical coagulant or flocculants, thus reducing the amount of sludge which must be disposed. On the other hand, electrocoagulation is based on the in situ formation of the coagulant as the sacrificial anode corrodes due to an applied current, while the simultaneous evolution of hydrogen at the cathode allows for pollutant removal by flotation. This technique combines three main interdependent processes, operating synergistically to remove pollutants: electrochemistry, coagulation and hydrodynamics [5, 6]. Contaminant removal with electrochemical method offers several advantages, such as the absence of chemical requirements, lower volume of sludge produced,economic aspects (relatively low investment, maintenance, energy, and treatment costs), simple equipment and compact size of EC systems and the small area occupied by the plant and the ease of operation [7].

Electrolysis is a process in which oxidation and reduction reactions take place when electric current is applied to an electrolytic solution. Electrocoagulation is based on dissolution of the electrode material used as an anode. This so-called "sacrificial anode" produces metal ions which act as coagulant agents in the aqueous solution in situ [8]. At its simplest, an electrocoagulation system consists of an anode and a cathode made of metal plates, both submerged in the aqueous solution being treated [9]. The electrodes are usually made of aluminum or iron (carbon steel or stainless steel), because these metals are cheap, readily available, proven effective, and non-toxic. Thus they have been adopted as the main electrode materials used in EC systems [10, 11].

The mechanisms of EC for water and wastewater treatment are very complex. It is generally believed that there are three other possible mechanisms involved besides EC, i.e. electroflotation, electrochemical oxidation and adsorption. The main electrochemical reactions at the electrodes during EC process [12].

Anodic reactions, sacrificial metal Fe is dissolved [13]:

$$Fe_{(s)} \rightarrow Fe^{2+} + 2e^{-} \qquad E^{\circ} = +0.44\ V \quad \ldots (1)$$

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^{+} + 4e^{-} \qquad E^{\circ} = -1.23\ V \quad \ldots (2)$$

Ferrous iron may be oxidized to Fe^{3+} by atmospheric oxygen or anode oxidation, and may be considered as [14]:

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \qquad E^{\circ} = -0.77\ V \ldots (3)$$

$$Fe^{2+} + \frac{1}{2}O_{2(g)} + H_2O_{(l)} \rightarrow 2Fe^{3+} + 2OH^{-}$$
$$E^{\circ} = -0.37V \quad \ldots (4)$$

At cathodic reactions, H_2 gas is liberated [13]:

$$2H_2O + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-} \qquad E^{\circ} = -0.83\ V \quad \ldots (5)$$

The anodically formed Fe^{3+} combines with the cathodically formed OH^{-} to produce insoluble $Fe(OH)_3$.

$$Fe^{3+}+3OH^{-}\rightarrow Fe(OH)_3 \quad \dots (6)$$

Additionally, when chloride is present and the anode potential is sufficiently high, the following reactions may take place in the EC cell [15]:

$$2Cl^{-}\rightarrow Cl_2 + 2e^{-} \qquad E^{\circ}= -1.36\ V \dots (7)$$

$$Cl_2+H_2O\rightarrow HClO+ H^{+}+Cl^{-} \quad E^{\circ}=-0.93\ V \quad \dots (8)$$

$$HClO\rightarrow H^{+}+OCl^{-} \quad \dots (9)$$

The formation of active chlorine species (Cl_2, HClO, OCl^{-}) enhances the performance of the EC reactor through oxidation reactions.

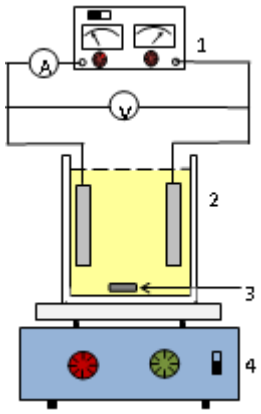
The aim of this work to studying the parameters that are effective on the percentage of chromate removal in a batch stirred tank by iron metal electrodes. Furthermore finding the best conditions for the process , the studied parameter are: pH change, Initial chromium concentration, Current density, Concentration of KCl salt, Distance between the two electrodes (Anode and Cathode) by using iron metal (carbon steel) of electrode.

Material and Methods

The schematic diagram of a batch experimental set up as shown in Figure 1. A stock solution 1000 mg/l of chromate was prepared by dissolving 1.362 gram of potassium dichromate ($K_2Cr_2O_7$) in 1000 ml deionized water . Other concentrations were prepared daily from stock solution by dilution in the range 50, 100, 300, and 500 mg/l, according to equation below:

$$V_1 C_1 = V_2 C_2 \quad \dots (10)$$

The initial pH of the solution was adjusted by using 0.1 N NaOH or 0.1 N H_2SO_4.



(1) DC power supply; (2) EC cell; (3) Teflon bar (4) Magnetic stirrer.

Fig. 1: Schematic diagram of batch electrocoagulation (EC) process unit

UV-visible spectrophotometer (Jenway Model 6800 Double Beam) was employed to determine the remaining concentrations of Cr (VI) in the sample. The filtrate was analysed for the remaining Cr (VI) concentration. A real industrial wastewater containing chromium was supplied by the General Company for Electrical Industries that located in Alwaziriya/Baghdad to compare the removal efficiency with the synthetic solution. Analysis of this wastewater was done in the Corporation of Research and Industrial Development/ Energy and Environment Research Center by using device ICP (Inductive Coupled Plasma), Agilent technologies, model (700 series ICP-OES) and the properties of real samples of industrial wastewater as given in Table 1.

Table 1: Characteristic of industrial wastewater

pH	6.75
Cr (VI)	488.427 ppm
Cd	0.187 ppm
As	0.673 ppm
Mn	0.087 ppm
Zn	53.773 ppm
Ba	0.022 ppm
Cu	0.022 ppm
Ni	0.0799 ppm

The percent removal of chromate was calculated using the Equation 11:

$$\% \text{ Removal} = \left(\frac{C_i - C_t}{C_i}\right) 100\% \quad \ldots (11)$$

Where: C_i is the initial concentration of chromium and C_t is the final concentration of chromium. The batch operation mode was done to study the effect of several parameters: initial pH, initial chromium concentration, current density, distance between electrodes and concentration of KCl. All the variables studied are illustrated in details as given in Table 2.

Table 2: Various parameters tested in batch mode experiments

Parameters tested	Value
pH	3, 5, 7, 9
Initial concentration (mg/l)	50, 100, 300, 500
Current density (mA/cm^2)	2, 6, 10, 14
Distance between the electrode (cm)	1, 2.5, 4, 5.5
concentration of KCl (g/l)	1, 5, 10, 15

Experimental Design

Taguchi method involves reducing the variation in a process through robust design of experiments. The experimental design proposed by Taguchi involves using orthogonal arrays to organize the parameters affecting the process and the levels at which they should be varied; it allows for the collection of the necessary data to determine which factors most affect product quality with a minimum amount of experimentation, thus saving time and resources. Analysis of variance on the collected data from the Taguchi design of experiments can be used to select new parameter values to optimize the performance characteristic [16].

The Taguchi's experimental design results are transformed into a signal-to-noise (S/N) ratio. Table 3 shows the results and corresponding calculated S/N ratio data for chromium removal. S/N calculation was performed and calculated from Equation 12 to maximize % response i.e. the percentage of chromium removal by electrocoagulation (larger is better).

$$SN_L = -10\log_{10}\left[\frac{1}{n}\sum_{i=1}^{n} 1/y_i^2\right] \quad \ldots (12)$$

The effect of each process parameter (Delta = maximum – minimum) was estimated by averaging the S/N ratios and means for all the experiments as given in Table 4 and Table 5.

Table 3: Experimental layout for using the orthogonal array (OA) and experimental result for chromium removal by electrocoagulation

No.	pH	C_i (mg/l)	Current density (mA/cm^2)	Distance (cm)	KCl concentration (g/l)	Removal% After 60 min		S/N ratio	Mean
						First	second		
1	3	50	2	1	1	81.8	81.0	38.21	81.4
2	3	100	6	2.5	5	92.3	88.2	39.10	90.25
3	3	300	10	4	10	71.4	73.6	37.20	72.5
4	3	500	14	5.5	15	54.9	48.7	34.23	51.8
5	5	50	6	4	15	95.6	93.0	39.48	94.3
6	5	100	2	5.5	10	74.92	71.38	37.27	73.15
7	5	300	14	1	5	77.8	92.0	38.48	84.9
8	5	500	10	2.5	1	49.8	49.0	33.87	49.4
9	7	50	10	5.5	5	94.8	87.2	39.15	91.0
10	7	100	14	4	1	100.0	100.0	40.0	100.0
11	7	300	2	2.5	15	64.6	70.8	36.58	67.7
12	7	500	6	1	10	58.5	58.1	35.31	58.3
13	9	50	14	2.5	10	100.0	100.0	40.0	100.0
14	9	100	10	1	15	98.4	100.0	39.92	99.2
15	9	300	6	5.5	1	63.5	59.5	35.76	61.5
16	9	500	2	4	5	36.8	30.0	30.33	33.4

Table 4: Response signal to noise ratios

level	pH	Initial con.	Current density	Distance	Con. of KCl
1	37.19	39.21	35.60	37.99	36.96
2	37.28	39.08	37.42	37.39	36.77
3	37.76	37.01	37.54	36.76	37.45
4	36.51	33.44	38.18	36.61	37.56
Delta	1.26	5.77	2.58	1.38	0.79
Rank	4	1	2	3	5

Table 5: Response for means

level	pH	Initial con.	Current density	Distance	Con. of KCl
1	73.99	91.67	63.91	80.95	73.08
2	75.44	90.65	76.09	76.84	74.89
3	79.25	71.65	78.03	75.05	75.99
4	73.52	48.23	84.17	69.36	78.25
Delta	5.73	43.45	20.26	11.59	5.17
Rank	4	1	2	3	5

Results and Discussions

Effect of Initial pH

It has been established that pH is an important parameter that affected on the efficiency of the electrocoagulation process. A set of experiments was performed by varying the pH as 3, 5, 7 and 9 of the synthetic potassium dichromate solution to study the effect of pH on the hexavalent chromium removal efficiency. The solutions were adjusted to the desired pH for each experiment using sodium hydroxide or sulfuric acid solution 0.1 N. The results after 60 min are shown in Figure 2. It can be noticed that the pH of the solution has a significant effect on the Cr (VI) removal efficiency, also as observed by other investigators, the pH of the solution was changed during the process. This change depends on the type of electrode material and initial pH and alkalinity.

The Cr (VI) removal efficiency was found to increase with increase in the pH of the solution from 3 to 7, is ascribed to the hydrogen evolution and the generation of OH^- ions at the cathode. While the removal efficiency substantially decrease at pH >7. In alkaline medium (pH > 7) the final pH does not change markedly because the generated OH ions at the cathodes are consumed by the generated Fe^{3+} ions at the anode forming the needed $Fe(OH)_3$ flocs. Furthermore, OH^- ions can also partially combine with chromium ions to form the insoluble hydroxide precipitates $Cr(OH)_3$. For this reason, in alkaline medium no pH increase is noticed but a slight pH decrease.

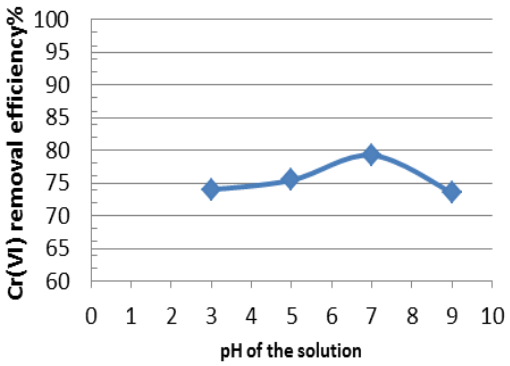


Fig. 2: Effect of initial pH of solution on Cr(VI) removal efficiency

Effect of Initial Concentration

Chromium solutions with different initial concentrations in the range of 50–500 mg/l were treated by electrocoagulation. Figure 3 show the effect of initial concentration on the removal of chromium, it was observed that when increasing the initial

concentration the chromium removal efficiency decreases.

The removal efficiency respectively equaled 91.67, 90.65, 71.65, and 48.23 percent for the initial concentrations of 50, 100, 300 and 500 milligram per liter of chromium during 60 minutes electrolysis. This is due to two factors: (i) under the present experimental conditions, available $Fe(OH)_3$ coagulant is limited and their active surface area can become fully saturated with Cr (VI) and Cr (III) ions with no more active surface left to adsorb further chromium ions. (ii) It is also possible that higher Cr (VI) concentration tends to passivate the anode chemically.

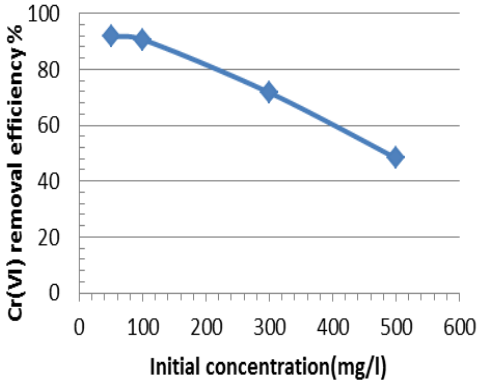


Fig. 3: Effect of initial concentration of solution on Cr(VI) removal efficiency

Effect of Current Density

The current density is one of the important parameters to control the reaction rate in the electrochemical processes. The current density determines the coagulant dosage rate, the bubble production rate and size and the floc growth resulting in a faster removal of pollutants. A large current means a small electrocoagulation unit. However, when too large current is used, there is a high chance of wasting electrical energy. A series of experiments were carried out to evaluate the effect of current density on Cr(VI) removal efficiency. The current density was varied from 2 to 14 mA/cm^2, and the results are shown in Figure 4.

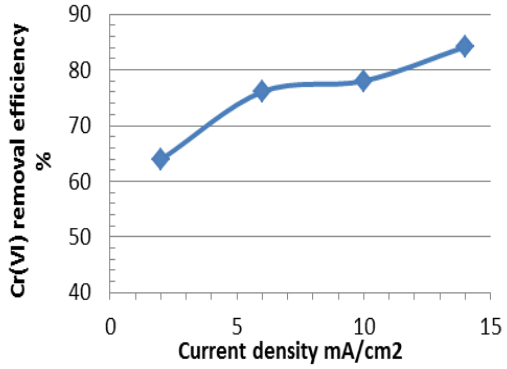


Fig. 4: Effect of current density on Cr (VI) removal efficiency

It can be noticed that there is an increase in the chromium removal efficiency with an increase in the current density. The highest chromium removal efficiency was achieved with an applied current of 14 mA/cm^2 for an electrolysis time after 60 min.

Effect of the Distance between Eectrodes

To examine the effect of electrode distance on the electrocoagulation process, experiments were conducted by varing electrode distances 1, 2.5, 4 and 5.5 cm and the results are shown in Figure 5. It was observed that when the distance between electrodes (D) increased, the Cr (VI) removal efficiency decreased. When D was 1 cm, the Cr(VI) removal efficiency = 80.95, while when D was increase to 5.5 cm, the removal efficiency decreased to 69.36 %.

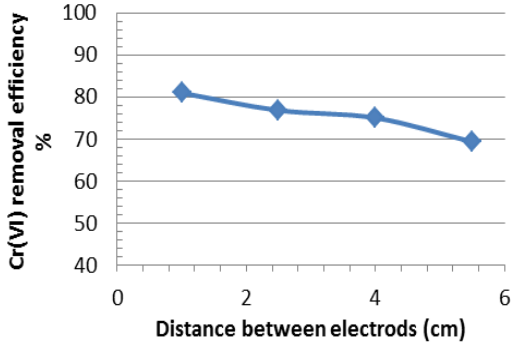


Fig. 5: Effect of distance between the electrodes on Cr (VI) removal efficiency

Effect of Potassium Chloride Concentration

In all experiments, electrolyte solution contains KCl with varying conductivity because it is easily found in water and wastewater. A set of experiments was performed by varying the concentration as 1, 5, 10 and 15 g/l of potassium chloride to study the effect on the hexavalent chromium removal efficiency, the results were shown in Figure 6.

It was observed that when the KCl electrolyte solution concentration increased, the Cr (VI) removal efficiency increased. When the KCl concentration of the feed solution was raised to 15 g/l , the Cr (VI) removal efficiency increases to 78.25% after 60 min of electrocoagulation, because it increased conductivity of the solution and thus reduced the energy consumption.

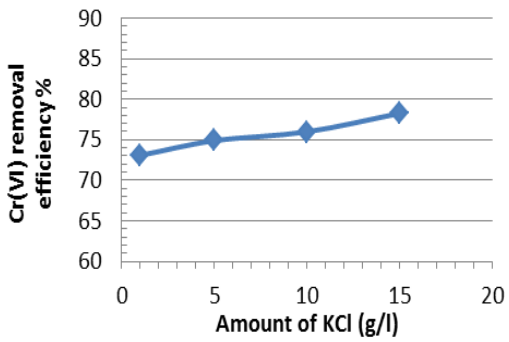


Fig. 6: Effect of KCl concentration on Cr(VI) removal efficiency

Treatment of Real Industrial Wastewater

A comparison between the synthetic and real industrial wastewater supplied from chromium plating unit at the General Company for Electrical Industries in Baghdad is shown in Figure 7. The result shows that the removal efficiency for synthetic solution was higher than industrial solution at the same operating conditions.

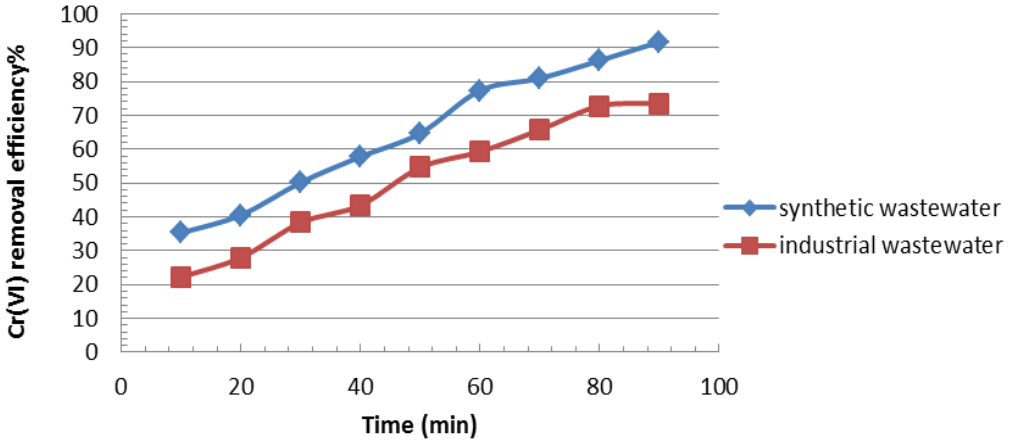


Fig. 7: Comparison between synthetic and industrial wastewater for batch mode experiments (pH=6.7, C_i=488.427 mg/l, i=14 mA/cm^2, d=1cm, C_{KCl}=15g/l)

From Figure 7 for batch mode, it was observed that the percent of chromate removal for synthetic solution is higher than that of industrial solution for pH = 6.7, initial concentration of chromium = 488.427 mg/l, current density = 14 mA/cm^2, distance between electrodes = 1 cm and KCl concentration = 15 g/l. The removal efficiency of synthetic solution after 90 min was 91.72 % while industrial wastewater showed 73.54 %. This may be because the presence of other impurities (such as metal ions) in the real wastewater which may interfere in the electrocoagulation process.

Conclusions

From the present work, it can be conclude that:

1. The electrocoagulation process is successfully applied to remove chromium from aqueous solution. The chromium removal efficiency was found to be dependent on pH of the solution, the initial chromium concentration, applied current density, distance between electrodes and KCl concentration.
2. The optimum pH for chromium removal efficiency is 7.
3. In batch operation mode, the results showed that applied current density, and KCl concentration are directly proportional to chromium removal efficiency, while initial chromium concentration, and distance between electrodes were inversely proportional to chromium removal efficiency, while pH showed a peak performance curve.
4. The best conditions for wastewater treatment in the range of used parameters were initial concentration = 50 mg/l, current density = 14 mA/cm^2, distance between electrodes = 1 cm, KCl concentration = 15 g/l.
5. The removal efficiency of prepared solution was higher than industrial wastewater. In batch system the maximum removal efficiency obtained for synthetic solution was 91.72 %, while for industrial wastewater was approximately 73.54%.

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