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Electrochemical removal of chromium from wastewater by using carbon aerogel electrodes

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Abstract

A study has been carried out to determine the feasibility of electrochemical removal of chromium ions from industrial wastewater using carbon aerogel electrodes. In this work the effect of key variables including pH (2–7), concentration 2–8 (mg/l), and charge 0.3–1.3 (A h) was determined. The metal ion removal was significantly increased at reduced pH and high charge conditions. The metal concentration in the wastewater can be reduced by 98.5% under high charge (0.8 A h) and acidic conditions (pH 2). The effect of the independent parameters—pH, effluent concentration and charge on the percentage removal was depicted by a quadratic equation obtained using Box–Behnken model. The regression analysis gave a R^2 value of 0.9469 shows a close fit between the experimental results and the model predictions. The model was further used to optimise the parameters to maximise the percentage Cr-removal to more than 98%.

Keywords: Chromium; Carbon aerogel; Electrochemical; pH effect; Response surface methodology

1. Introduction

The wide use of heavy metals and its compounds by modern industries has resulted in large quantities of this element being discharged in to environment. These inorganic micro-pollutants are of considerable concern because they are non- biodegradable, highly toxic and have a probable carcinogenic effect. If directly discharged into the sewage system, their presence decrease the efficiency of the biological treatment to which the sewage is subjected and also make the activated sludge generated by the treatment unsuitable for application to agricultural land [1–5].

Among the heavy metals, chromium is one of the most important heavy metals widely used in many of the industrial processes such as tanning, electroplating, printed circuit boards and metal finishing, metal processing, paint, steel fabrication, etc. [6–9]. Nearly 80% of the tanneries in India practice chrome-tanning process [10].

Most of the chromium is discharged into aqueous waste as Cr (III) and Cr (VI). Cr (VI), which is the more toxic of the two, is present as either dichromate ($Cr_2O_7^{2-}$) or as chromate (CrO_4^{-}) [11].

Some of the generating industries treat chromium wastewater by aerobic or anaerobic, precipitation, or ion exchange methods [12]. There are many other methods also used for chromium removal such as adsorption [13] and reverse osmosis [14]. With these methods up to 96% metal ion removal can be achieved. However, all these methods generate lot of sludge and high cost. Electrochemical treatment in contrast is a promising technique offers several advantages over other techniques for remediation, further electrochemical form of remediation offers a terminal process for recovery of metals from contaminated effluents or wastewaters [15,16].

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In the last few years, various researchers have used different materials as electrodes in electrochemical reactors and filters Because of its stability and potential window for specific purpose to meet desired results. Among these, cloths, felts, foams and sponges of conductive materials such as graphite, carbon, nickel and copper [17]. Recently Daniel and Yoram from Nuclear Research Centre, Israel used reticulated vitreous carbon (RVC). The extent of metal removal after 10 passes through a potentiostatically controlled laboratory scale column was 51%, which is not satisfactory for the utilisation of the process at a large scale [18].

In this paper, a study has been carried out to study feasibility of chromium removal from wastewater using carbon aerogel electrodes. The carbon aerogel electrodes were used due to their unique thermal, mechanical and electrical properties, which are directly related to their unusual nano-structure, which is composed of interconnected particles with microscopic interstitial pores. Carbon aerogel is an ideal electrode material because of its low electrical resistivity ($\leqslant 40\,\mathrm{m\Omega\,cm}$), high specific surface area (400–1100 $\mathrm{m^2/g}$) and controllable pore size distribution ($\leqslant 50\,\mathrm{nm}$) [19–22]. The economic viability of the aerogel based separation process depends upon the life of carbon aerogel electrodes [23].

2. Response surface methodology

Response surface experiments identify the response of a system as a function of a linear independent variables [24]. This methodology is particularly applicable in situations where several input variables potentially influence the performance of the process or the response system. The interaction among the possible influencing parameters can be evaluated with limited number of experiments.

Response surface methodology (RSM) has been used to determine the optimal response of chromium removal percentage to various parameters like pH, concentration and charge. The optimisation process involves three major steps:

(i) Performing statistically designed experiments,
(ii) estimating the coefficient in a mathematical model and predicting the response and
(iii) checking the validity of the model.

Before statistical analysis the natural variables were modified to their coded (dimensionless) variables in the following manner. If, X_1, X_2, X_3 are the original variables representing pH, concentration (mg/l) and charge (A h) respectively. Whereas x_1, x_2, x_3 are the coded variables usually defined to be dimensionless with mean zero and the same standard deviation and are calculated by the following formulae:

$$x_{ij} = \frac{X_{ij} - [(\max X_{ij} + \min X_{ij})/2]}{[(\max X_{ij} - \min X_{ij})/2]}, \tag{1}$$

where $i = (1, 2, 3, \ldots, n)$ variables, and $j = (1, 2, 3, \ldots, N)$ number of the experiment.

It results in all the values of x_1, x_2, x_3 falling between -1 and $+1$ [25–27] as shown in the Table 2 the low, middle and high levels of each variable are designated as -1, 0, $+1$. The mathematical relationship of the response Y and these three variables can be approximated by quadratic (second order) polynomial equation. The system was stated by the following equation:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3, \tag{2}$$

where $\beta_{i,j} = 0, 1, 2, 3, \ldots, k$ are called the regression coefficients with k- regressor variables.

Box–Behnken method has been preferentially selected for designing experiments. As relatively lesser combinations of the variables are adequate to estimate a potentially complex response function. In total, 15 experiments were found to be sufficient to calculate the 10 coefficients of the second-order polynomial regression model. This model contains one constant term, three linear terms, three quadratic terms and three interaction terms, and has been applied for the design of experiments for chromium removal.

3. Materials and methods

3.1. Experimental set up

The experiments were carried out by batch process. The schematic diagram of the experimental set up is shown in the Fig. 1. A glass beaker of 1 l capacity was used and proper provisions were made in the lid for fixing the anode, cathode and salt bridge of the reference electrode system. Carbon aerogel was used for both anode and cathode. The electrodes were placed vertically parallel to each other and with a minimum gap between the electrodes. A saturated Calomel electrode (SCE) was used to measure electrode potentials. The solution was stirred constantly with a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution. A DC power supply was used as a current source. The multi meter was used for the measuring the electrode potential and cell voltage. All experiments were performed at room temperature. The samples were drawn at regular intervals from the cell to determine the percentage chromium removal. The chromium

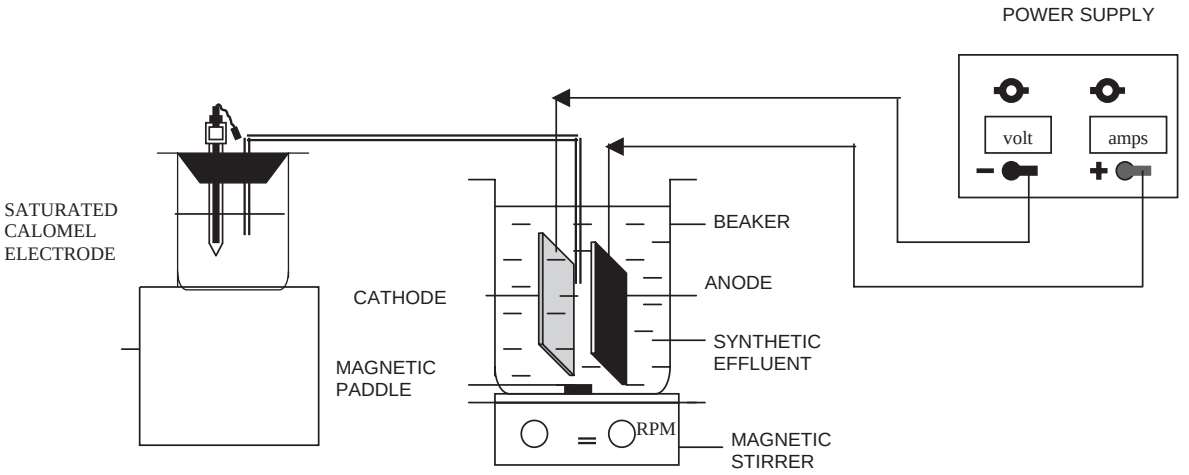

Fig. 1. Schematic diagram of the experimental set up.

Table 1
Characteristics of carbon aerogel

Parameters	Value
Conductivity (mS/Cm)	58
pH	6.06
Cation exchange capacity (Meq/g)	0.8
Moisture (%)	14
Decolorization capacity (mg/g)	4.95
Bulk density (g/ml)	0.71
Specific surface area (m^2/g)	800
Basic surface groups (Meq/g)	0.005
Acidic surface groups	
Carboxylic (Meq/g)	0.015
Lactonic (Meq/g)	0.045
Carbonyl (Meq/g)	nil
Phenolic (Meq/g)	nil

concentration was measured by spectro-photometry using standard methods [25].

3.2. Preparation of electrodes

Prior to the experiments, electrodes are made by gluing a sheet of carbon aerogel to the titanium plate that serves both as a current collector and structural support to carbon aerogel. Conductive carbon epoxy is used for gluing carbon aerogel sheets. A thin film of epoxy with about 5% carbon particles for conductivity was applied to the titanium current collectors and the carbon aerogel electrode was lightly pressed and the epoxy was further cured for 24 h at room temperature. These carbon particles act as a current passage within non-conductive epoxy [23]. Table 1 shows the characteristics of carbon aerogel.

3.3. Adjustments of operating variables

In the experimentation initial pH was adjusted with sulphuric acid in the desired range between 2 and 7. The experiments were conducted at a constant current density of 0.1 A/dm^2 at varying charge from 0.3 to 1.3 A h. The synthetic effluent was prepared using $K_2Cr_2O_7$ with millipore water in the concentration range of 2–8 ppm as chromium content in the wastewater is generally found in this range.

4. Mechanism

In the aqueous streams contaminated with chromium, Cr (VI) exists in the form of ($HCrO_4^-/CrO_4^{2-}/Cr_2O_7^{2-}$) while Cr (III) is in the form of Cr $(OH)^{2+}$, Cr $(OH)_4^-$, CrO_2^- [26]. Transport of anions and cations to the surfaces of their respective electrode is by convection, diffusion and electro-migration, with the relative rates primarily dependent upon the size and charge of ions. Once at the surface of the electrode, the ions undergo complexation and in some cases electrochemical reaction.

Since all Cr (VI) species are anionic, they would be drawn to the anode. Since these anions are already at a high oxidation state, complexation at the anode without any cathodic reduction is expected. In contrast, Cr (III) species could be either cationic or anionic. Since cationic species are already in a low oxidation state, complexation at the cathode without any cathodic reduction is expected, though reduction to metallic Cr is possible in some circumstances. However trivalent anionic species such as Cr $(OH)_4^-$ and CrO_2^- would be forced to the

anode where anodic oxidation to $HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{2-}$ would be possible.

As mentioned above a part of Cr (VI) also get reduced to Cr (III) on the cathode. This cathodically reduced Cr (III) can be electrodeposited on cathode or held in the cathodic layer, while a fraction can also be transported back into the electrolyte.

$$Cr^{6+} \xrightarrow{+e^-} Cr^{3+} \qquad E = +1.33\ V, \tag{3}$$

$$Cr^{3+} \xrightarrow{+e^-} Cr \qquad E = -1.32\ V. \tag{4}$$

Since the initial synthetic sample was prepared from $K_2Cr_2O_7$, total chromium exists in the form of Cr (VI). However, after the experiment, the final sample also consist some amount of Cr (III) validating the above supposition.

5. Results and discussion

The chromium removal was studied under different experimental conditions, viz. pH (2–7), chromium concentration (2–8 mg/l), charge (0.3–1.3 A-h). The experiments were designed based on Box–Behnken method [27].

5.1. Regression model

The application of RSM offers an empirical relationship between the response variable and test variables. These are related by following quadratic expression.

Table 2
The levels of variables chosen for trials

pH	Conc. (mg/l)	Charge (A h)
X_1	X_2	X_3
2 (−1)	2 (−1)	0.3 (−1)
4.5 (0)	5 (0)	0.8 (0)
7 (+1)	8(+1)	1.3 (+1)

Box- behnken design is used to develop the regression model with $k = 3$. A regression model containing three linear (xi), three quadratic (xi^2), three interaction ($xi\ xj$) terms and one block term is used. The result from regression model is represented by Eqs. (5) and (6) for percentage removal (Y_1) and power consumption (Y_2) respectively (Table 2):

$$\begin{aligned} Y_1 = {} & 68 - 15.7875x_1 - 3.25x_2 + 6.2875x_3 + 31.425x_1^2 \\ & - 12.4x_2^2 - 19.875x_3^2 - 0.270x_1x_2 \\ & - 0.15x_1x_3 - 10.075x_2x_3, \end{aligned} \tag{5}$$

$$\begin{aligned} Y_2 = {} & 16.56 + 11.7362x_1 + 5.94x_2 + 23.203x_3 \\ & - 3.4337x_1^2 + 28.1538x_2^2 + 8.2063x_3^2 + 8.04x_1x_2 \\ & + 2.7425x_1x_3 + 10.875x_2x_3. \end{aligned} \tag{6}$$

In the analysis of variance (ANOVA) F- value of 9.902 and R^2 value 0.9469 are obtained. The lack of fit is significant because the probability value (prob > F) is low i.e. 0.0106. A small probability indicates that adding the quadratic terms has improved regression model. Moreover, the standard deviation between the measured and modelled results is only 14.94%, which can be calculated from root mean square error (MSE) and dependent mean tabulated in Table 3.

For each parameter and its interaction, the t-static value and the individual significance probability (prob) of t- value greater than t are shown in Table 4. It can be seen that the main effects and two-way interactions which are significant are x_1, $x_1 \times x_1$, $x_2 \times x_2$, $x_3 \times x_3$, $x_2 \times x_3$. This shows that all the three factors pH, concentration and charge are significant and play an important role.

5.2. Effect of pH

To study the effect of pH on chromium removal the experiments were carried out by varying charge from 0.3 to 1.3 A-h and under different pH from 2 to 7 at fixed concentration. The results were plotted in Fig. 2 and Table 5. This figure shows clearly that at a fixed

Table 3
Regression analysis and response surface model fitting (ANOVA) for degradation chromium removal using carbon aerogel electrodes

Source	Sum of squares	DF	Mean square	F value	Prob > F
Model	9048.359	9	1005.373	9.902	0.0106
Residual	507.638	5	101.527		
Cor total	9555.996	14			
Pure error	0.00	2			
Root MSE[a]	10.07609				
Dep mean[b]	67.460				

C.V. (a/b) = 14.94 %,
$R = 0.9469$.
[a] Root MSE = square root of mean square error,
[b] Dep mean = dependent mean (overall mean of the response).

Table 4
Estimated effects for removal percentage

Variable	Parameter estimate	DF	Standard error	t for H_0 parameter = 0	Prob > t
Intercept	68.00	1	5.81	11.69	
x_1	−15.78	1	3.56	−4.432	0.0068
x_2	−3.41	1	3.56	−0.957	0.3821
x_3	6.12	1	3.56	1.719	0.1462
$x_1 \times x_1$	31.58	1	5.24	6.024	0.0018
$x_2 \times x_2$	−12.56	1	5.24	−2.396	0.0619
$x_3 \times x_3$	−20.03	1	5.24	−3.821	0.0124
$x_1 \times x_2$	−0.27	1	5.03	−5.46E-02	0.9586
$x_1 \times x_3$	−0.15	1	5.03	−2.98E-02	0.9774
$x_2 \times x_3$	−10.40	1	5.03	−2.064	0.0939

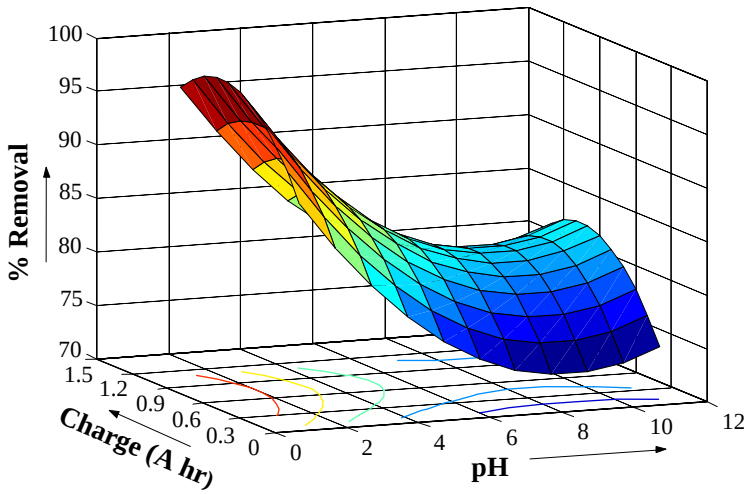

Fig. 2. Electrochemical removal of chromium at constant concentration and varying pH and charge.

Table 5
Experimental design with original variables, X_1, X_2, X_3 representing pH, concentration (mg/l) and charge (A h)

Exp. no.	pH	Cr^{6+} Conc. (mg/l)	Charge (A h)	Response (% Cr removal)	Power consumption (kwh/m^3)
1	2	2	0.8	98.5	35.76
2	7	2	0.8	75	57.84
3	2	8	0.8	99.6	8.64
4	7	8	0.8	75	62.88
5	2	5	0.3	98.8	6.35
6	7	5	0.3	60	9.65
7	2	5	1.3	99.4	27.53
8	7	5	1.3	60	41.8
9	4.5	2	0.3	20	13.32
10	4.5	8	0.3	26.6	26.37
11	4.5	2	1.3	65	57.72
12	4.5	8	1.3	30	114.27
13	4.5	5	0.8	68	16.56
14	4.5	5	0.8	68	16.56
15	4.5	5	0.8	68	16.56

concentration, the maximum chromium removal is achieved under acidic condition rather than neutral.

This may be explained on the basis of the fact that at higher pH values i.e. neutral to alkaline conditions, chromium species occur in chromic form. At higher pH, the following reaction takes place and chromium may also form hydroxide in the form of Cr $(OH)_3$ [28]. Therefore under neutral to alkaline conditions the hydrated Cr^{3+} ion hydrolyses or precipitates as Cr $(OH)_3$ as shown in Fig. 3 [29].

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3. \quad (7)$$

This process takes place rapidly at higher pH and prevents reduction to Cr^{2+}. Therefore, reduction to metallic chromium may not be as effective as that at lower pH. Cr $(OH)_3$, Cr(OH), CrO_4^- species formed are reduced by atomic hydrogen discharged at cationic surfaces. Intermediates in this reaction are chromium hydrides, which decompose with the deposition of metallic chromium and evolution of H_2 at the cathode. From Fig. 4 [6] which gives the pe–pH relationships for dissolved aqueous chromium species it is seen clearly that chromium exists as chromic acid $Cr(OH)_3$ and other hydroxyl forms at conditions beyond pH 4 to alkaline.

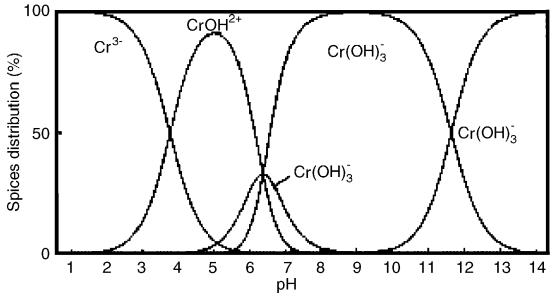

Fig. 3. Distribution of inorganic chromium (III) species as a function of pH [29].

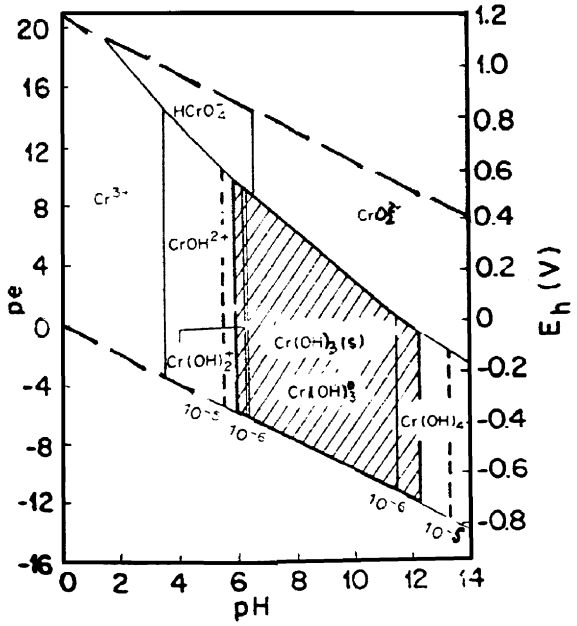

Fig. 4. Pe–pH relationships for dissolved aqueous chromium species [6].

While experimentation at pH 4.5 Cr (III) existed as $Cr(OH)_2^{2+}$, $Cr(OH)_2^+$ form [11]. At pH higher than 6, Cr species further hydrolyse to Cr $(OH)_3$ due to reaction (7). This reaction species reduces to metallic chromium at a very high atomic hydrogen discharge at cathodic surface of electrodes.

At higher current densities, the demanded reduction rate is so high that some Cr (VI) is reduced to Cr (III) along with H_2 evolution. Eventually, a current density is reached where oxide reduction cannot meet the demanded reduction rate and the system shifts through a limiting current to the evolution of hydrogen either from water

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (8)$$

or from H^+ discharge during the electrochemical reactions

$$2H^+ + 2e^- \rightarrow H_2. \quad (9)$$

The evolution of H_2 at cathodic surface reduces chromic to chromous species by the reaction given below

$$Cr(OH)_3 + H^+ + e^- \rightarrow Cr(OH)_2 + H_2O. \quad (10)$$

Hence at slightly acidic conditions of pH 4.5, chromium mostly occurs in chromous state of Cr $(OH)_2^{2+}$, which is more likely to reduce rapidly than $Cr(OH)_3$.

However, in our experiments, we noticed that at pH 7, removal was more significant than at pH 4.5. This is due to the fact that Cr $(OH)_3$ formed at neutral pH along with reduction, also undergo precipitation and the total chromium content in the electrolyte solution become lower than that at pH 4.5 where only reduction of chromium species is taking place.

Under highly acidic conditions i.e., at pH 2, removal of chromium from electrolyte was maximum (more than 95%) for all the concentrations. The maximum electrochemical removal and reduction of Cr (VI) at this pH is based on two theories

(1) Presence of H^+ ions that bring about the cathodic reduction of Cr (VI) to Cr (III) to finally metallic Cr^0.

$$Cr_2O_7^{2-} + 8H^+ + 6e^- \rightarrow Cr_2O_3 + 4H_2O. \quad (11)$$

The reduction of dichromate ion to Cr^{3+} corresponds to a potential of 1330 mV [30].

(2) Addition of sulphuric acid H_2SO_4 for lowering pH.

$$H_2SO_4 \rightarrow SO_4^{2-} + 8H^+. \quad (12)$$

It has been found from H_2O exchange studies that Cr^{3+} ions forms an aquo complex Cr $(H_2O)_6^{3+}$,whose inner coordination sphere is so tightly bounded that Cr cannot be discharged from this complex. Consequently the first requirement for any mechanism put forth to account for the deposition of metallic Cr from Cr (VI) solutions must include the provision for protecting the Cr (III) species from forming this stable aquo complex. This can be prevented by the presence of SO_4^{2-} ions in the electrolyte solution is, which contributes, in the satisfactory deposition of metallic chromium.

It is reported that presence of SO_4^{2-} ions in the electrolyte solution enhances the tendency of chromium to get reduced. The SO_4^{2-} ions present in the electrolyte interacts with water molecule to form HSO_4^- by the reaction

$$SO_4^{2-} + H_2O \rightarrow HSO_4^- + OH^-. \quad (13)$$

In the reduction mechanism HSO_4^- ions exert its influence as a catalyst. In this reduction process there is a formation of complex between CrO and HSO_4^- ions through hydrogen bonding

$$Cr(OH)_2 \rightleftarrows Cr = O + H_2O. \quad (14)$$

Two electrons may be transferred from the cathode to the specifically adsorbed Cr (II) forming successfully Cr (I) and then, metallic Cr with HSO_4^- ion regenerated. Therefore, it is clear that very low pH is required not only for reduction of hexavalent forms to trivalent but also maintains relatively high concentration of HSO_4^- ion for further reduction to metallic chromium.

5.3. Effect of concentration

To study the effect of concentration on chromium removal the experiments were carried out by varying chromium concentration from 2 to 8 mg/l and different pH from 2 to 7 at fixed charge. The results were plotted in Fig. 5.

With an increase in the concentration, the potential also increases [17, 30]. This can be seen clearly at pH 4.5 and 7. The above Fig. 5 shows at the lower concentration removal percentage was higher when compared to higher concentrations. However at pH 2 the removal percentage of the entire concentration range was $\geqslant 98\%$ at very low charge. This is because of (1) low pH condition (2) SO_4^{2-} ions which are highly favourable for Cr ion removal. The effect of concentration is visible in case of pH 4.5 and 7 where at low concentrations higher removal percentage was observed as compared to high concentrations at fixed charge. However, high concentrations can also achieve the same response by increasing the same amount of charge.

5.4. Effect of charge

To study the effect of charge on chromium removal the experiments were carried out under varying charge from 0.3 to 1.3 A-h and under different chromium concentrations from 2 to 8 mg/l at fixed pH. The results were plotted in Fig. 6. This figure shows clearly that the maximum removal is achieved at higher charge. Because, increasing pH, concentration the voltage also increases. Increase in voltage lead to higher charge consumption [17].

All the experiments were carried out at fixed current density of 0.1 A/dm^2. From Fig. 6, it can be seen that

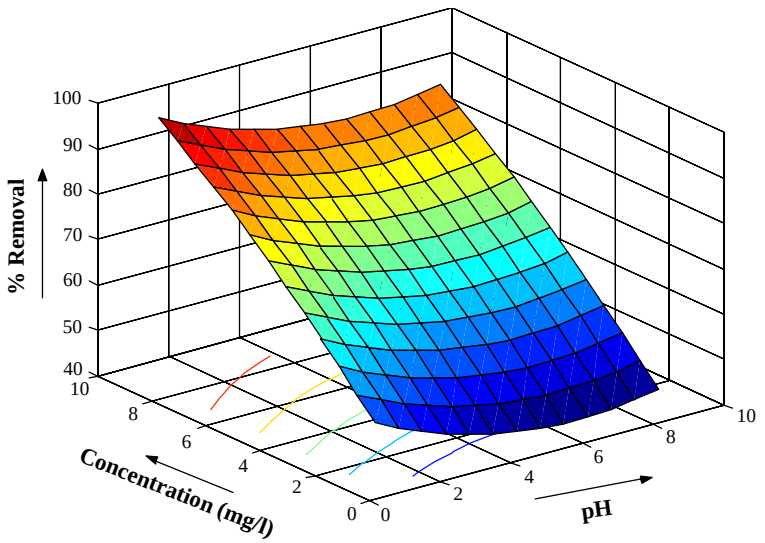

Fig. 5. Electrochemical removal of chromium at constant charge and varying pH and concentration.

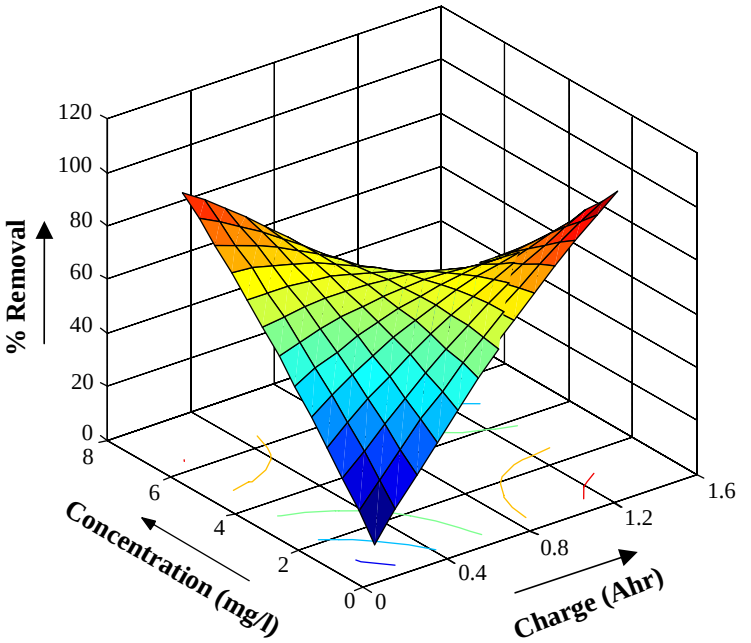

Fig. 6. Electrochemical removal of chromium at constant pH and varying charge and concentration.

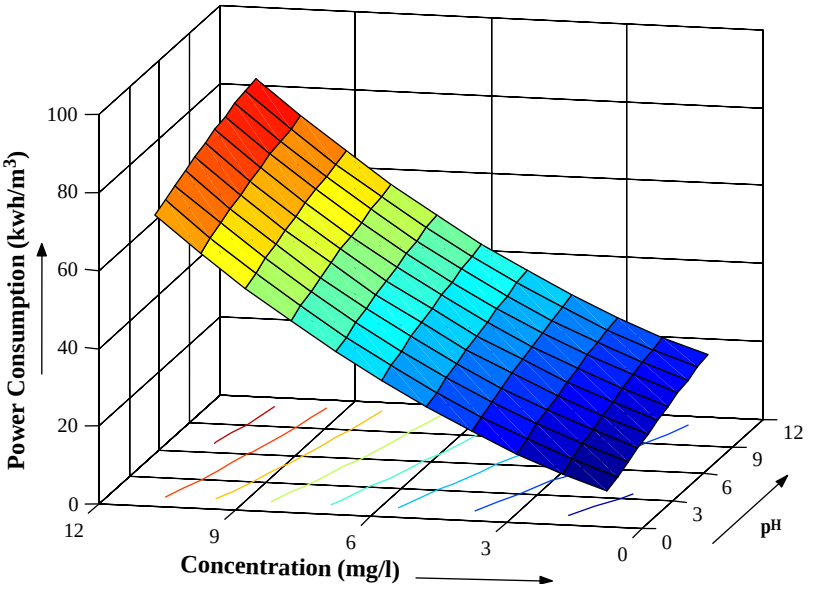

Fig. 7. Power consumption for chromium removal at constant charge and varying pH and concentration.

60–70% removal was achieved at neutral pH, charges above 0.4 A h. However, experiments that were carried out at pH 2, shows maximum removal. The removal was more than 80% in such cases even at the lowest charge of 0.3 A h. The percentage removal of the metal was proportional to the concentration and the charge as well.

5.5. Effect of optimised parameters on energy consumption

Effect of pH, concentration and charge on percentage chromium removal has been discussed above in detail. For the same parameters and experimental conditions

energy consumption was also calculated and the results are shown in Fig. 7.

From Fig. 7 it can be seen clearly that the energy consumption has increases by increasing pH and increasing the concentration. This is because; the potential window gets shifted towards higher potential [17]. However, under acidic conditions, chromium reduction takes place at low potential and hence energy consumption is also low, under the same conditions for concentration 8 mg/l and charge is 0.8 A-h. The energy consumption of the experimental set at pH 2 was 2.88 kwh/m^3 and at pH 7 it was 20.96 kwh/m^3, which is much higher than that under acidic conditions. Similarly energy consumption at 8 mg/l concentration and low charge of 0.3 A h is also more than that at pH 2 and charge 0.8 A h, the energy consumption value for previous condition is 8.77 kwh/m^3 and for later is 2.88 kwh/m^3. At a concentration of 2 mg/l and charge 0.8 A-h also at pH 2 energy - consumption is 11.2 kwh/$m^3$and at pH 7 it is 19.28 kwh/m^3. This clearly shows the influence of pH on energy-consumption. Similarly the energy consumption also increases at higher concentrations. This can be seen from the Fig. 7. At lower concentration the number of ions to be transferred is lower therefore the energy consumption is low, whereas for high concentration energy consumption also higher. The energy consumption is increasing with respect to pH and charge. With an increase in pH, potential also increases and hence energy requirement. Moreover, under acidic conditions the removal takes place at much lower potential leading to low energy consumption.

6. Conclusions

From the present study, it can be concluded that all the three parameters have significant effect on chromium removal, is borne out by our statistical analysis R^2 value of 94.69%. The derived quadratic equation shows the presence of a high correlation between observed and predicted values. Basically, the removal is strongly pH dependent and the carbon aerogel electrode was suitable for the chromium removal because of its unique characteristics.

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