

Adsorptive Removal of Chromium (III) from Aqueous Solution Using Cation-Exchange Resin: Development of an Empirical Model

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Abstract. The capacity of a strong cation-exchange resin for removal of chromium (III) ions from aqueous solutions was investigated under different conditions such as contact time, initial chromium ion concentration, pH of solution, and resin weight. Beyond Quadratic Interpolation with three independent variables was applied to develop an empirical model. The three independent variables chosen were initial chromium concentration (mg/L), adsorbent weight (g), and shaking time (X, Y, Z). Coefficients of empirical model were calculated using the Matlab software which were then used to evaluate the predicted percentage removal (Y_1) and predicted adsorption capacity (Y_2) of chromium (III) ions. The predicted values from the model fitted well with the experimental data for both the percentage removal and adsorption capacity of Cr (III) ions. High values of Regression coefficient R^2 were found to be 0.9912 and 0.9666 for percentage removal and for adsorption capacity of Cr (III) ions respectively.

Keywords: Ion exchange, Chromium (III), Modeling, Quadratic Interpolation, Beyond Quadratic Interpolation.

List of symbols

Symbol	Description	Unit
C_o	initial chromium concentration	mg/L
C_e	Equilibrium chromium concentration	mg/L
m	Mass of adsorbent	g
q	Amount of chromium adsorbed at time t	mg/g
q_e	Amount of chromium adsorbed at equilibrium	mg/g
t	Time	min
V	Volume of solution	L

1. Introduction

The environmental contamination with heavy metals may create acute or chronic toxicity problems due to its accumulation throughout the food chain and hence in the human body which should be avoided whenever possible. Heavy metal is discharged into streams from various industries, such as metal extraction, metal fabrication, and textile, leather tanning facilities, electroplating, surface finishing, paints, pigments and manufacture of batteries [1].

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Chromium (III) is considered as an essential micronutrient for human, plant and animal metabolism. However, the increasing accumulation of Cr (III) in the environment from industrial outputs caused great concern. The maximum permissible levels for Cr³⁺ ions in wastewater are 5 mg /L [2] .The uptake of higher weights of Cr (III) may cause harmful health effects and long-term exposure to Cr (III) can cause allergic skin reactions and cancer [3]. Many separation techniques have been proposed for the removal of chromium (III) from aqueous solutions, which include solvent extraction, ion exchange [4]-[7], co- precipitation, membrane processes, reverse osmosis, and adsorption. Among various techniques, adsorption is the most promising technique to remove and eliminate Cr (III) from waste water. Ion exchange has been recognized as a promising alternative technique to the traditional methods [8]-[15].The main advantages of ion-exchange over chemical precipitation are recovery of metal value, selectivity and less sludge volume produced. The performance of ion exchange process is influenced by the pH, metal concentration and temperature. [16]-[19]. Nowadays, chelating resins are increasingly used in the removal of metal ions due to their high adsorption capacities, selectivity and durability [20]-[23].The purpose of the present study is to develop an empirical model using Beyond Quadratic Interpolation with three independent variables. The three independent variables studied were: initial chromium ions concentration, adsorbent weight, and time. The model established describes the adsorptive removal of Cr (III) by a strong cation-exchange resin from aqueous solution by predicting the percentage removal and adsorption capacity of chromium ions. The predicted values of the model were tested by the actual ones obtained from experimental data.

2. Materials and Methods

2.1. Materials

2.1.1. Standard solutions

Stock solution of chromium (1000 mg/L) was prepared with appropriate weighed quantity of chromium nitrate. Standard solutions of the desired concentrations (150–450 mg/L) were obtained by successive dilutions of this stock solution. All the chemicals used throughout this study were of analytical-grade reagents. Double- distilled water was used for preparing all of the solutions and reagents. The initial pH is adjusted with 0.1 M HCl or 0.1 M NaOH. All the sorption experiments were carried out at room temperature (25±2 °C). All the experiments are duplicated and only the mean values are reported.

2.1.2. Cation exchange Resin

The resin used in the present work is a cation exchange resin named as IR120 H. This resin is a strong acid ion exchanger which is durable, insoluble and compatible obtained from Morgan chemical industries company in Egypt.

2.2. Methods

The concentrations of chromium in the solutions before and after equilibrium were determined by atomic absorption spectrometer.

2.3. Batch Experiments

Batch series experiments for the adsorptive removal of Cr (III) were performed in stoppered conical flasks (250 mL) at room temperature. Known amounts of resin (2- 6 g) were added to the flasks containing 100 mL of chromium nitrate aqueous solution. The solution was stirred till equilibrium time was reached. The solutions were periodically sampled, filtered immediately and the filtrate was analyzed by atomic absorption spectrophotometry. The effects of pH, initial Cr (III) concentration, stirring time, and resin dose on Cr (III) removal were evaluated. The initial Cr (III) concentrations were in the range of (50-450 mg/L). The pH of the solution was adjusted using 0.1N hydrochloric acid or 0.1N sodium hydroxide solutions. Adsorption isotherm and kinetic studies were carried out with different initial concentrations of chromium.

The percentage removal of chromium from the aqueous solution was calculated according to the following equation:

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} * 100 \quad (1)$$

The amount of chromium adsorbed at equilibrium, q_e (mg/g), was calculated by the following mass balance relationship:

$$q_e = (C_0 - C_e) \frac{V}{m} \quad (2)$$

Where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of chromium respectively (mg/l), V the volume of the solution (l), and m is the weight of the adsorbent used (g).

2.4. Development of an Empirical Model using Beyond Quadratic Interpolation with Three Independent Variables

Beyond Quadratic Interpolation, a statistical method based on the multivariate nonlinear model that has been widely used for the optimization of process variables of adsorption and also used to determine the regression model equations and operating conditions from the appropriate experiments. It is also useful in studying the interactions of the various parameters affecting the process [24]-[27]. This model was applied in this present study to develop an empirical model that correlates the response to the adsorption of Cr (III) ions from aqueous solution using matlab software as follows [28]-[33]:

$$F(X,Y,Z) = C_1 + \frac{C_2}{x} + \frac{C_3 Y}{Z} + \frac{C_4 \ln(X)}{Z} \quad (3)$$

The Vandermonde-Shammas matrix is:

$$A = \begin{array}{|c|c|c|c|} \hline 1 & 1/X_1 & Y_1/Z_1 & \ln(X_1)/Z_1 \\ \hline 1 & 1/X_2 & Y_2/Z_2 & \ln(X_2)/Z_2 \\ \hline 1 & 1/X_3 & Y_3/Z_3 & \ln(X_3)/Z_3 \\ \hline 1 & 1/X_4 & Y_4/Z_4 & \ln(X_4)/Z_4 \\ \hline \end{array} \quad (4)$$

$$B = \begin{array}{|c|} \hline F(X_1, Y_1, Z_1) \\ \hline F(X_2, Y_2, Z_2) \\ \hline F(X_3, Y_3, Z_3) \\ \hline F(X_4, Y_4, Z_4) \\ \hline \end{array} \quad (5)$$

The equation that calculates the coefficients of the above equation is:

$$C = A^{-1} * B \quad (6)$$

3. Results and Discussions

3.1. Effect of pH

A set of experiments were conducted to determine the optimum pH for Cr (III) removal. The adsorption of chromium was studied over a pH range of 1.0-10.0 and the results are shown in Fig. 1. The maximum percentage removal of Cr (III) was 93% at pH 5. It is observed that the removal of Cr (III) increases as the initial pH is increased and attains a maximum value at pH 5. After that, it decreases very slowly up to the pH of 10.0. The decrease of the adsorption at higher pH may be attributed to the hydrolysis of Cr (III) in the solution, and therefore the separation may not be due to adsorption.

3.2. Effect of Initial Concentration

The initial concentration of metal ion provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases [34]. The sorption of Cr (III) ions onto cation resin was carried out at different initial Cr (III) ion concentrations ranging from 50 to 450 mg/l. Fig. 2 clearly shows that by increasing the concentration gradually there is a decrease in the percentage removal. As the ratio of sportive surface to ion concentration decreased with increasing metal ion concentration and so metal ion removal was reduced. At low initial concentration of metal ions, more binding sites are available. But as the concentration increases, the number of ions competing for available binding sites in the biomass increased [35].

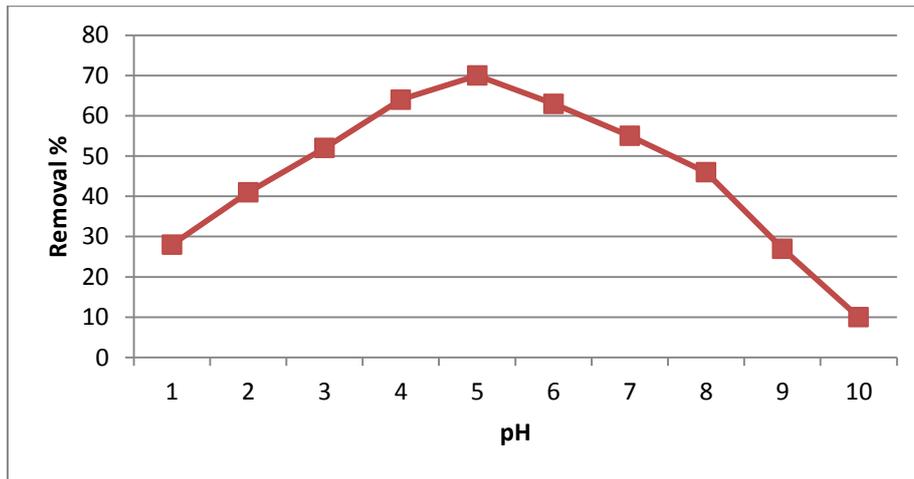


Fig. 1: Effect of pH on Chromium adsorption onto cation exchange.

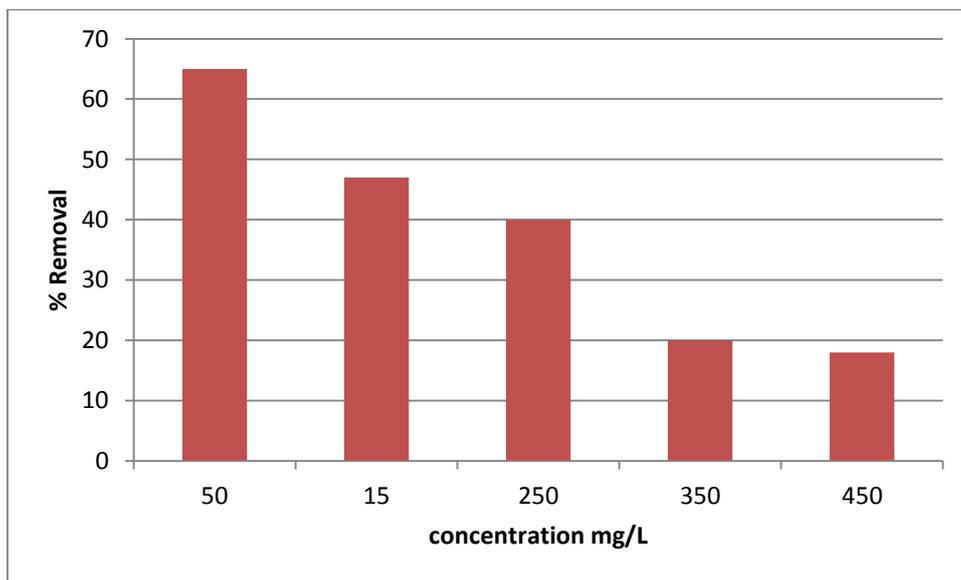


Fig. 2: Effect of the changing concentrations at constant stirring time 1hr of chromium nitrate with 2 gm. zeolite.

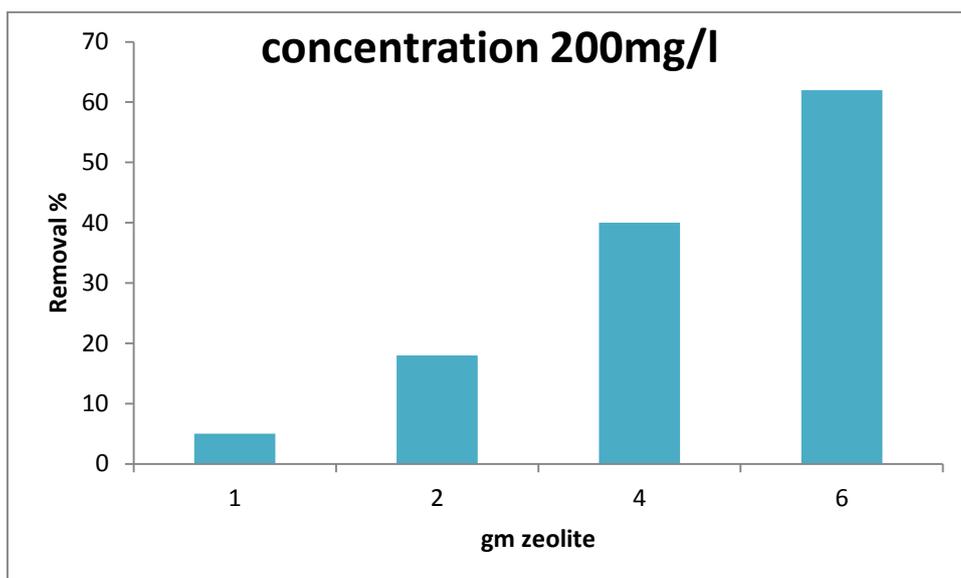


Fig. 3: Effect of the changing dosage (1gm, 2gm, 4gm, and 6gm zeolite) at constant stirring time 1hr and constant concentration 200mg/l of chromium nitrate.

3.3. Effect of Adsorbent Dose

It is obvious from Fig. 3 that an increase in the removal percentage is noted as the amount of adsorbent used increases. That is expected because at a fixed initial concentration of sorbate the increase in the adsorbent amount provides a larger surface area or adsorptive sites [36].

3.4. Development of the Empirical Model

In this present investigation, three independent variables such as initial chromium concentration (mg/L), adsorbent dose (g), and shaking time were chosen as independent variables (X, Y, Z). Experimental data were necessary to estimate the coefficients of the model using Beyond Quadratic Interpolation model with three independent variables. Coefficients of empirical model were calculated using the Matlab software which were then used to evaluate the predicted percentage removal (Y_1) and predicted adsorption capacity (Y_2) of chromium (III) ions.

The model obtained from Matlab software for the percentage removal of Cr (III) ions (Y_1) was reported as follows:

$$Y_1 = 34.1 + \frac{2861}{x} - \frac{2080}{Z} + \frac{685.5 \ln(X)}{Z} \quad (7)$$

The model obtained from Matlab software for the adsorption capacity of Cr (III) ions (Y_2) was reported as follows:

$$Y_2 = 1.7 + \frac{994.7}{x} - \frac{1000.2}{Z} + \frac{353.8 \ln(X)}{Z} \quad (8)$$

3.5. Validation of the Empirical Model

3.5.1. Validation of the model for percentage removal of chromium (III) ions (Y_1):

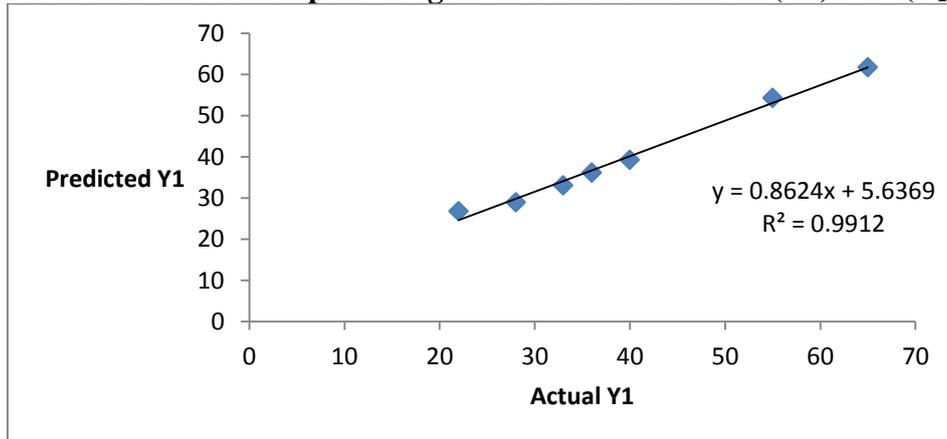


Fig. 4: Actual and predicted plots for percentage removal of Cr (III) ions.

Table 1: Predicted and actual values of percentage removal of Cr (III) ions

X Initial concentration of Cr (III) mg/L	Y adsorbent weight (g)	Z Shaking time (min)	Predicted Percentage removal (Y_1)	Actual Percentage removal (Y_1)
50	2	40	54.3	55
50	2	50	61.7	65
150	2	30	28.95	28
150	2	60	41.04	47
250	2	40	36.125	36
250	2	30	33	33
250	2	60	39.25	40

The actual and predicted plots for percentage removal of Cr (III) ions using Matlab Software are shown in Fig. 4 and their values are shown in Table 1. The value of Regression coefficient R^2 was found to be 0.9912.

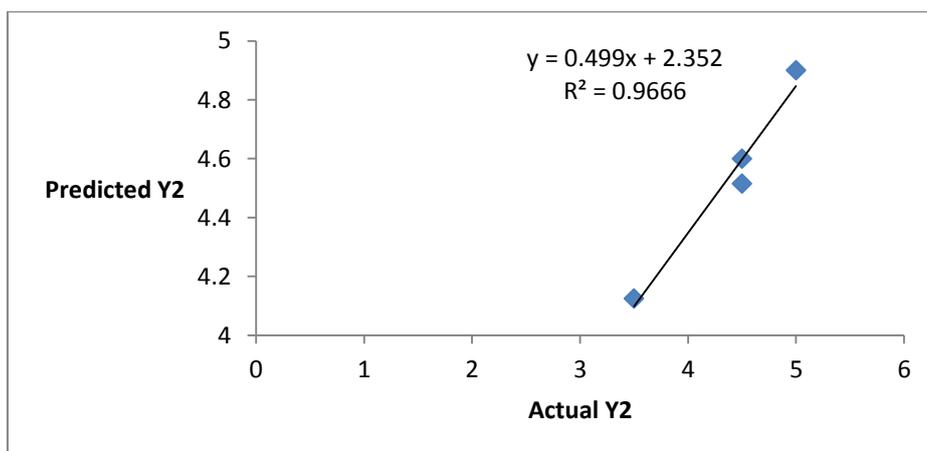


Fig. 5: Actual and predicted plots for adsorption capacity of Cr (III) ions.

3.5.2. Validation of the model for adsorption capacity (Y_2) of chromium (III) ions removal (Y_2):

Fig. 5 presents the actual and predicted plots for adsorption capacity (Y_2) of chromium (III) ions removal. As shown in the Figure, the value of Regression coefficient R^2 was 0.9666. The actual and predicted values of adsorption capacity (Y_2) are shown in Table 2.

Table 2: Predicted and actual values of adsorption capacity of Cr (III) ions

X Initial concentration of Cr (III) mg/L	Y adsorbent weight (g)	Z Shaking time (min)	Predicted Adsorption Capacity (Y_2) mg/g	Actual Adsorption Capacity (Y_2) mg/g
150	2	60	4.6	4.5
250	2	30	4.125	3.5
250	2	40	4.5156	4.5
250	2	60	4.9	5

4. Conclusions

A strong cation exchange resin (IR 120 H) was successfully utilized for the removal of chromium (III) ions from aqueous solution by batch adsorption. The adsorption process was found to be dependent on many factors such as the initial concentration of metal ion, contact time, adsorbent weight, and pH. Beyond Quadratic Interpolation with three independent variables, a statistical method based on the multivariate nonlinear model that has been widely used for the optimization of process variables of adsorption has been used in the present work. The three independent variables (X, Y, Z) were initial chromium concentration (mg/L), adsorbent weight (g), and shaking time (min). The predicted values from the model fitted well with the experimental data for both the percentage removal and adsorption capacity of Cr (III) ions. High values of Regression coefficient R^2 were found to be 0.9912 and 0.9666 for percentage removal and for adsorption capacity of Cr (III) ions respectively using Matlab software.

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