Available online at www.elixirpublishers.com (Elixir International Journal)

Applied Chemistry

Elixir Appl. Chem. 106 (2017) 46786-46790

Awakening to Reality

Elixir ISSN: 2229-712X

# Statistical Optimization of Process Parameters for Chromium (vi) Removal from Waste Water

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**ARTICLE INFO**

**Article history:**

Received: 31 March 2017;

Received in revised form: 12 May 2017;

Accepted: 23 May 2017;

**Keywords**

Central composite face centered design (CCD),
Custard apple peel powder,
Chromium (VI) and adsorption.

**ABSTRACT**

Interaction of various process parameters like initial chromium concentration (VI) (5-30 mg/l), pH (1-10), and adsorbent dosage (6-10 g/l) for chromium adsorption using custard apple powder were evaluated using central composite design (CCD) in response surface methodology. The CCD design in response surface methodology has been applied for designing the experiments as well as for full response surface estimation and 19 experimental data as per the model were used. The optimum conditions for better percentage removal of chromium from waste water with the concentration of 20 mg/l were as adsorbent dosage (9.9966 g/l), pH (2.7877) and initial chromium concentration (15.18693 mg/l). The high correlation coefficient ($R^2$ =0.98929) between the model and the experimental data showed that the model was able to predict the better percentage removal of chromium (VI) from waste water using custard apple peel powder efficiently.



## 1. Introduction

Effluent released from process industries such as petroleum refining, steel industries, paint industries, leather tanning, electroplating, textile industries, etc, causes water contamination with heavy metals in all over world [1, 2, 3]. Several millions of tons of chromites ore are produced in a year, all over world. Direct reduction of the chromite ore is the source for production of ferrochromite. The chemical reduction (the aluminothermic process) or by electrolysis of either $CrO_3$ or chrome alum solutions is the source for production of chromium metal. The chromium prevails in aqueous phase in two oxidation states, i.e. trivalent chromium ($Cr^{+3}$ and $Cr(OH)^{2+}$) and hexavalent chromium ($HCrO_4^-$, $CrO_4^{2-}$ or $Cr_2O_7^{2-}$, etc). Most of the hexavalent compounds are toxic, carcinogenic and mutagenic to humans. For example, it was reported that $Cr_2O_7^{2-}$ can cause lung cancer [4, 5].

Cr (VI) has 100 times more toxicity than Cr (III) because of it has the nature of water solubility, mobility and easy reduction [6]. The toxic effect of Cr (VI) is due to oxidizing nature and the formation of free radicals, resulting from the reduction of Cr (VI) to Cr (III) occurring inside the cell [8]. According to World Health Organization (WHO), it is recommended that the toxic limit of chromium (VI) in waste water is at the level of 0.05mg/l [7].

Conventional methods used for the removal of chromium from the industrial wastewater include reduction followed by chemical precipitation [9], ion exchange [10], reduction [11], electrochemical precipitation [12], solvent extraction [13], membrane separation [14], evaporation [15] and foam separation [16]. Above cited conventional chromium elimination processes are ineffective for diluted solutions. In recent years, much focus is given on biosorption using readily available biomass for the removal of heavy metals. This process can be used in economic way for purifying the industrial waste water whereby drinking water quality can be improved and impact on animals, aquatic species and humans may be reduced. A considerable research was carried out by various researchers using bio-adsorbent materials for the removal of heavy metals from industrial effluents. Since this noble approach is effective and cheap, many researchers have been investigating the various kinds of biomaterials that effectively remove Cr (VI) from aqueous solutions [17, 18]. Various kinds of adsorbents like tamarind seeds [19], rice husk [20], azadirachta indica [21], maize bran [22], red saw dust [23], wall nut hull [24], groundnut hull [25], limonia acidissima hull powder [26], Ragi husk powder [27] and custard apple peel powder [28] were reported in literature for removal of chromium.

The technique used for optimizing a multivariable system by traditional conventional optimization is not only time consuming but also often easily misses the interactions between the components. Also, this method requires a large number of experiments to determine the optimum levels when the interactions are significant [29]. In order to overcome this problem, many statistical experimental design methods have been employed in chemical process optimization. These methods involve mathematical models for designing chemical processes and analyzing the process results. Among them, response surface methodology (RSM) is one suitable method utilized in many fields. The main objective of RSM is to determine the optimum operational conditions for the system or to determine a region that satisfies the operating specifications [30]. The application of central composite design for the removal of heavy metals by various kinds of biosorbents such as Treated Sugarcane bagasse [31], Tamarind wood activated carbon [32], Hypnea Valentiae [33], Sand [34], Rice husk [35], Activated carbon from tamarind wood [36], Sugarcane bagasse waste [37], Activated rubber wood sawdust [38], Dried yeast biomass [39], Hazelnut shell [40], Ragi husk powder [41] are described in separation technology.

In the present investigation, the results obtained through the batch experimentations [28] on removal of chromium

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from waste water by custard apple peel powder are used for optimization of process parameters. The input parameters are initial chromium (VI) concentration, adsorbent dosage and pH and the output is the percentage removal of chromium (VI). The process optimization has been carried out using CCD for maximum chromium (VI) removal. However there is no information available in the literature regarding the optimization of chromium adsorption by central composite design (CCD) on custard apple peel powder. Therefore, we decided to study more thoroughly the phenomenon of adsorption of chromium in custard apple peel powder using CCD in response surface methodology.

## 2. Materials and methods

### 2.1Summary of Experimental investigations

A 0.25% W/V solution of diphenylcarbozide was prepared in 50% acetone. 15 ml each of the sample solutions containing various concentrations of Cr (VI) were pipette out into 25 ml standard flasks. To this 2 ml of 3M $H_2SO_4$ was added followed by 1 ml of diphenylcarbozide and total volume was made up to 25 ml using deionised, double distilled water. Chromium (VI) concentrations estimated by the intensity of the red brownish color complex formed, was measured using UV- spectrophotometer at 540nm. The absorbance was measured indicating adherence to the Beer Lambert's law (0 to 30 mg/l).

The Custard apple peel was collected from local markets; materials were washed, dried, and crushed in primary crusher and air dried in sun for several days until its weight remains constant. After drying, it was grounded into powder. This powder was screened through BSS meshes. Finally the products obtained were stored to do experimentation. The average particle sizes were maintained in the range of 63 to 125 µm.

2.835 g of 99% $K_2Cr_2O_7$ is added in distilled water of 1.0 L volumetric flask to obtain 1000 ppm (mg/l) of chromium (VI) stock solution. Synthetic samples of various concentrations of solutions are prepared.

The batch experimental studies [28] were used to investigate the effect of various process parameters like adsorbate concentration (5-30 mg/l), adsorbent dosage (0.1-0.6g in 50ml of solution), agitation time (0-120 min), temperature (303-323 K), adsorbent particle size (63µm, 89µm and 125µm) and pH(1-0)

### 2.2 Central composite design method for optimization of adsorption parameters

Response surface methodology (RSM) is a collection of mathematical and statistical techniques for modeling and analysis of problems in which a response of interest is influenced by several variables [30]. A standard RSM design called central composite design (CCD) was applied in this work to study the variables for adsorption of chromium.

The optimization of Cr (VI) uptake was carried out by three chosen independent process variables using central composite non-factorial surface design with 15 unique runs including 4-replicates at center points. The amount of percentage metal adsorption was taken as the response of the design experiments. Three factors were studied and their low, medium and high levels are given in table 1. Percentage adsorption was studied with a standard RSM design called central composite design (CCD). Nineteen experiments were conducted in duplicate according to the scheme mentioned in Table 2. Design expert version 6.0 (StatSoftware) was used for regression and graphical analysis of the data obtained. The optimum values of the selected variables were obtained by solving the regression equation [30].

**Table 1. Coded and actual values of variables of the experimental design.**

| Factor | | Coded levels of variables | | |
|---|---|---|---|---|
| | | -1.00 | 0 | 1.00 |
| Initial concentration (mg/l) | $X_1$ | 15 | 20 | 25 |
| pH | $X_2$ | 2 | 3 | 4 |
| Biomass loading (g/l) | $X_3$ | 1.6 | 2 | 2.4 |

**Table 2. CCD Experimental design for the chromium removal.**

| Ru N | Coded Values | | | Actual values | | | Cr(VI) removal | |
|---|---|---|---|---|---|---|---|---|
| | X 1 | X 2 | X 3 | X 1 | X 2 | X 3 | observe d | Predicte d |
| 1 | -1 | -1 | -1 | 15 | 2 | 6 | 80.24 | 80.0869 |
| 2 | -1 | -1 | 1 | 15 | 2 | 10 | 89.09 | 89.0259 |
| 3 | -1 | 1 | -1 | 15 | 4 | 6 | 77.83 | 77.6859 |
| 4 | -1 | 1 | 1 | 15 | 4 | 10 | 86.47 | 86.7819 |
| 5 | 1 | -1 | -1 | 25 | 2 | 6 | 78.01 | 77.8479 |
| 6 | 1 | -1 | 1 | 25 | 2 | 10 | 86.85 | 86.7819 |
| 7 | 1 | 1 | -1 | 25 | 4 | 6 | 75.59 | 75.4419 |
| 8 | 1 | 1 | 1 | 25 | 4 | 10 | 84.23 | 84.1709 |
| 9 | -1 | 0 | 0 | 15 | 3 | 8 | 88.18 | 88.5913 |
| 10 | 1 | 0 | 0 | 25 | 3 | 8 | 85.91 | 86.3473 |
| 11 | 0 | -1 | 0 | 20 | 2 | 8 | 85.79 | 86.2373 |
| 12 | 0 | 1 | 0 | 20 | 4 | 8 | 83.33 | 83.7313 |
| 13 | 0 | 0 | -1 | 20 | 3 | 6 | 80.81 | 81.4173 |
| 14 | 0 | 0 | 1 | 20 | 3 | 10 | 90.01 | 90.2513 |
| 15 | 0 | 0 | 0 | 20 | 3 | 8 | 87.21 | 88.0526 |
| 16 | 0 | 0 | 0 | 20 | 3 | 8 | 88.91 | 88.0526 |
| 17 | 0 | 0 | 0 | 20 | 3 | 8 | 88.54 | 88.0526 |
| 18 | 0 | 0 | 0 | 20 | 3 | 8 | 88.88 | 88.0526 |
| 19 | 0 | 0 | 0 | 20 | 3 | 8 | 88.42 | 88.0526 |

## 3. Results and Discussions

### 3.1CCD experimental results

The results of the each experiments performed as per the software are given in table 2. Empirical relationships between the response and the independent variables have been expressed by the following quadratic model adsorption

$$Y=88.0526-1.122X_1-1.253X_2+4.417X_3-0.5833X_1^2-3.0683X_2^2-2.2183X_3^2-0.00125X_1X_2-0.00125X_1X_3-0.05125X_2X_3$$

Where Y is the percentage removal of Chromium (VI) and $X_1$, $X_2$ and $X_3$ are the scaled input variables. Regression coefficient of full polynomial model is given in Table 3. The analysis of variance for the response has been given in Table 4 to analyze the model. To evaluate the goodness of the model, the coefficient of variation and F-value tests has also been performed. The F value in the ANOVA table is the ratio of model mean square (MS) to the appropriate error mean square. The larger the ratio, the larger the F value and the more likely that the variance contributed by the model is significantly larger than random error. As a general rule, if P-value is less than 0.05, model parameter is significant (refer to Table 3). On the basis of analysis of variance, the conclusion is that the selected model adequately represents the data for chromium (VI) removal. The experimental values and the predicted values are in perfect match with $R^2$ value of 0.989 (refer to Figure 1). This methodology could therefore be successfully employed to study the importance of individual, cumulative, and interactive effects of the test variables in biosorption. The optimum values of initial concentration of chromium (VI), pH and adsorbent dosage from CCD were found to be 15.18693 mg/l, 2.78767 and 9.99661 g/l respectively.

**Table 3. Regression coefficient of full polynomial model. ( $^*$significant<0.05).**

| Coefficient | Parameter estimate | T | Standard error of coefficient | P-Value |
|---|---|---|---|---|
| β0 | 88.05258 | 372.2256 | 0.236557 | $0^*$ |
| β1 | -1.122 | -5.4909 | 0.204338 | $0.000385^*$ |
| β2 | -1.253 | -6.132 | 0.204338 | $0.000172^*$ |
| β3 | 4.417 | 21.6161 | 0.204338 | $0.0000^*$ |
| β11 | -0.5833 | -1.4922 | 0.390911 | 0.169857 |
| β22 | -3.0683 | -7.8491 | 0.390911 | $0.000026^*$ |
| β33 | -2.2183 | -5.6747 | 0.390911 | $0.000304^*$ |
| β12 | -0.00125 | -0.0055 | 0.228457 | 0.995754 |
| β13 | -0.00125 | -0.0055 | 0.228457 | 0.995754 |
| β23 | -0.05125 | -0.2243 | 0.228457 | 0.827510 |

**Table 4. ANOVA test results.**

| Sources | Sum of squares | df | Mean square | F-Value | Parameters |
|---|---|---|---|---|---|
| $X_1$ | 12.5888 | 1 | 12.5888 | 26.1412 | $R^2$=0.98929 |
| $X_1^2$ | 0.9297 | 1 | 0.9297 | 1.9305 | Adj $R^2$=0.97858 |
| $X_2$ | 15.7001 | 1 | 15.7001 | 32.6019 | MS pure error=0.48157 |
| $X_2^2$ | 25.7240 | 1 | 25.7240 | 53.4170 | |
| $X_3$ | 195.0989 | 1 | 195.0989 | 405.1309 | |
| $X_3^2$ | 13.4457 | 1 | 13.4457 | 27.9206 | |
| $X_1X_2$ | 0.0000 | 1 | 0.0000 | 0.0000 | |
| $X_1X_3$ | 0.0000 | 1 | 0.0000 | 0.0000 | |
| $X_2X_3$ | 0.0210 | 1 | 0.0210 | 0.0436 | |
| Lack of fit | 1.8316 | 5 | 0.3663 | 0.7607 | |
| Pure error | 1.9263 | 4 | 0.4816 | | |
| Total SS | 350.8176 | 18 | | | |

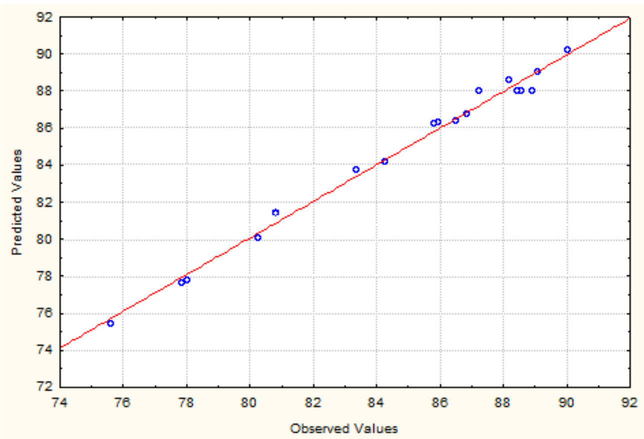


**Figure 1. Distribution of experimental vs predicted data values of percentage removal of chromium (VI).**

The maximum predicted adsorption of chromium (VI) was found to be 90.93039 %.

**3.2 Effect of various process parameters on removal of Cr (VI) in Three dimensional graph**

The percentage removal of Cr (VI) with custard apple peel powder was studied by pre-selected range of pH, biosorbent dosage and initial concentration of chromium (VI). The results have been depicted in Figure 2, Figure 3 and Figure 4 and maximum percentage removal of chromium (VI) was 90.93with custard apple peel powder at preselected ranges of process parameters i.e. pH of 3, adsorbent dosage 10 g/l and at lower concentration of metal ion. On the basis of these results, the optimum conditions for Cr (VI) removal by ragi husk powder are initial concentration of chromium (VI)- 15.18693 mg/l, pH- 2.7877 and adsorbent dosage- 9.9966 g/l.

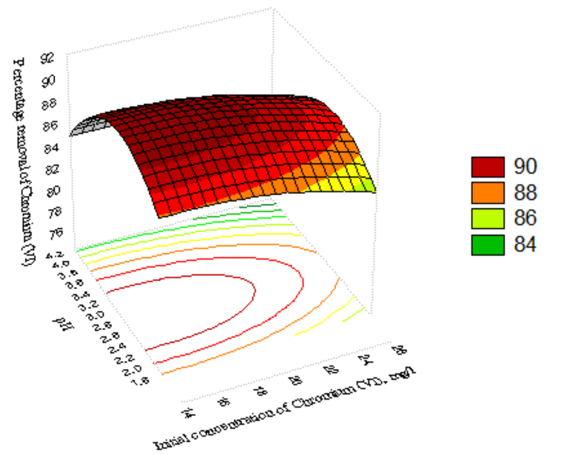


**Figure 2. 3D plot indicates the effect of interaction between initial concentration and pH on removal of Chromium (VI) while holding the biomass loading at 9.9966 g/l.**

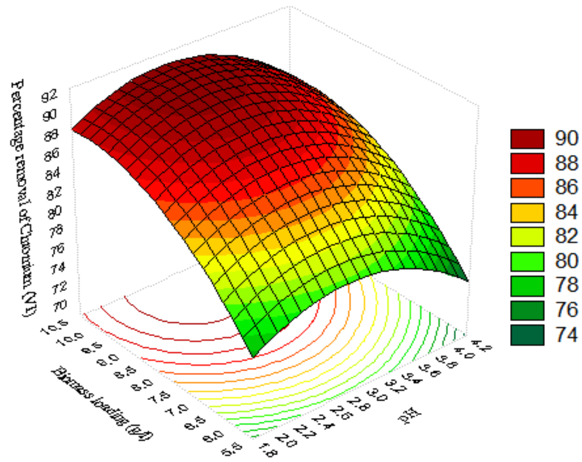


**Figure 3. 3D plot indicates the effect of interaction between Biomass loading and pH on removal of Chromium (VI) while holding initial concentration at 15.1869 mg/l.**

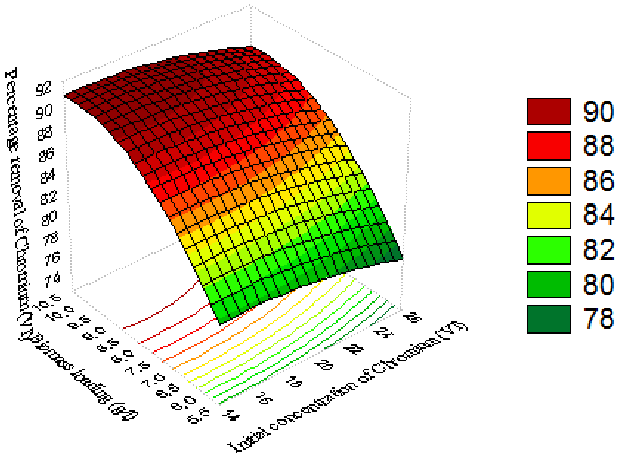


**Figure 4. 3D plot indicates the effect of interaction between Biomass loading and initial concentration of Chromium (VI) on removal of Chromium (VI) while holding the pH at 2.7877.**

## 4. Conclusions

The objective of the present study was to find out the optimum process conditions, using CCD in response surface methodological approach for the removal of chromium (VI) from waste water by custard apple peel powder as adsorbent. Response surface methodology using central composite design proved very effective and time saving model for studying the influence of process parameters on response factor by significantly reducing the number of experiments and hence facilitating the optimum conditions. This methodology could therefore be successfully employed to study the importance of individual, cumulative, and interactive effects of the test variables in biosorption. Process optimization was carried out and the experimental values obtained for the adsorption of chromium (VI) are found to agree satisfactorily with the values predicted by the models. The optimal adsorption of chromium (VI) was obtained as initial concentration of chromium (VI), pH and adsorbent dosage and these were found to be 15.18693 mg/l, 2.7877 and 9.9966 g/l respectively resulting in 90.93039% of maximum predicted adsorption of chromium (VI).

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