Research Article

Exclusion of Chromium(VI) Ion in Grueling Activated Carbon Fabricated from *Manilkara zapota* Tree Wood by Adsorption: Optimization by Response Surface Methodology

S. Sujatha, R. Sivarethinamohan, A. Oorkalan, V. Senthilkumar, B. Anuradha, B. Veluchamy, P. Prabhu, Magda H. Abdellatif, and Abdulmohsen Khalaf Dhahi Alsukaibi

1Department of Civil Engineering, K.Ramakrishnan College of Technology, Tiruchirapalli, Tamilnadu, India
2CHRIST (Deemed to be University), Bangalore Karnataka, India
3Department of Civil Engineering, M.Kumarasamy College of Engineering, Karur, India
4Department of Civil Engineering, Chennai Institute of Technology, Chennai, India
5Department of Mechanical Engineering, K.Ramakrishnan College of Engineering, Trichy, India
6Department of Mechanical Engineering, College of Engineering and Technology, Mettu University, Ethiopia
7Department of Chemistry, College of Science, Taif University, P.O. Box 11099, Taif 21944, Saudi Arabia
8Department of Chemistry, College of Sciences, University of Hail, Hail-2440, Saudi Arabia

Correspondence should be addressed to P. Prabhu; drprabhu@meu.edu.et

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The current paper makes obvious the elimination of chromium(VI) ion, from wastewater via adsorption technique with activated carbon generated from *Manilkara zapota* tree (MZTWAC). Preliminarily MZTWAC has undergone characterization studies which uncovered the suitability of MZTWAC to expel chromium(VI) from aqueous solution. Batch adsorption experimentation was premeditated with the competence of central composite design (CCD) and it was executed. Response surface methodology (RSM) was the key optimization software to appraise the adsorptive chattels of MZTWAC engaged in removing chromium(VI) ion in aqueous solution which explored the interactions flanked between four expounding variables explicitly initial concentration of chromium(VI) ion, pH of the solution, MZTWAC dose and time of exposure, and contact time. The response variable that was concentrated in the study was adsorption capacity. It was deduced a polynomial in quadratic equation was documented amid the adsorption capacity and variables influencing the adsorption with $R^2 = 0.9792$ which was projected as the best suit for the adsorption process. ANOVA that is expanded as analysis of variance judged the connotation of adsorption process variables. 0.2 g of MZTWAC dosage has removed 87.629% chromium(VI) from aqueous solution. The enhancement of adsorption process reclined on the attainment of maximum adsorption capacity which further depends on the optimization of variables under consideration. This criterion was accomplished by the desirability function optimizing the process variables.

1. Introduction

Rapid increase in population and modern innovative technology and its progression guide environment towards the polluted scenario reported during the history of the last few decades [1]. Natural resources are extensively used and exploited nowadays abruptly deteriorating the atmosphere and thereby the lives on the earth in turn. The metals like chromium, copper, lead, and arsenic are naturally occurring objects whose usage increases randomly in many industrial operations. These metals are universally accepted as heavy metals which hold a 5 g/cm$^3$ specific density more than that of water. Though these metals are inherent to the functioning of the physiological
2. Materials and Methods

Activated carbon was prepared from Manilkara zapota tree wood. The process remained encrypted in the authors’ original article [20]. To get to know the presence of functional groups that favour chromium(VI) ion adsorption and to have an idea on the surface morphology, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) analysis were performed.

2.1. Experimentation. Optimize the process variables of the least experiments by employing the response surface methodology (RSM) technique. The main intent here is in the direction of upgrading the response on which the chosen process variables have much impact. It too computes the association amid the chosen inputs and the response. A set of advanced design of experiment (DoE) techniques is said to be a response surface design that helps to understand better and to optimize the response. The design procedure [21] for RSM follows four stages as listed below.

(i) Experimental design for satisfactory and trustworthy extent of the response by central composite design
(ii) Emergence of the second-order mathematical response model by means of the best fit
(iii) Establishing the optimal solution for investigational variables producing a maximum response
(iv) Two- and three-dimensional (3D) charts are used to represent the collaborative impacts of process factors

The requisite experimental figures are reliant on the elected design in central composite design [22, 23]. CCD gives ample facts and figures as a multilevel factorial which entails considerably littler experiments more than a complete factorial that are satisfactory to pronounce the majority of steady-state course responses. The factors (variables) investigated were initial concentration, pH, MZTWAC (adsorbent), and interaction time, with adsorption capacity as response. The objective of this current study is to see how the factors interact, and a four-factor second-order polynomial equation was employed in the determination of those statistics. Batch adsorption process is affianced in adsorbing chromium(VI) ion from wastewater. As a result, the process design is more solidified. Table 1 lists the variables and investigational values utilized in the rotatable CCD.

As a result, the design of the process has become more defined. In a summary, the variables and experimental settings utilized in the rotatable central composite design are listed in Table 1 (CCD).

2.2. Batch Adsorption Studies. To build up a 1000 mg/L concentration of chromium(VI) stock solution, dissolve 2.89 g of K₂Cr₂O₇ in 1 L of distilled water [24, 25]. Dilution with distilled water is used to create any remaining solutions. Batch adsorption mode experiments were carried out for the specified time duration at a constant rpm using a shaker (manufactured by Remi). Batch adsorption investigations were conducted with chains of conical flasks containing 100 mL chromium(VI) solution. At ambient conditions, the reaction of concentration, pH, adsorbent dosage, and contact time were investigated, culminating in filtration using Whatman filter paper no. 41 [16], and filtrate was stacked to determine the equilibrium concentration of chromium(VI) with the support of a UV/Vis spectrophotometer.
The proportion of chromium(VI) removed was calculated using the equation below [26].

\[
\% \text{removal of chromium(VI) ion by adsorption} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100, \tag{1}
\]

where \( C_0 \) denotes the initial chromium(VI) content in mg/L and \( C_t \) denotes the chromium(VI) equilibrium concentration in milligrams per litre. The following equation [23, 27] was utilized to compute adsorption capacity of the adsorbent:

\[
q_e = \frac{(C_0 - C_t)W}{V}, \tag{2}
\]

where \( q_e \) represents the quantity of chromium(VI) adsorbed in mg/g, \( V \) denotes the solution volume represents in L, and \( W \) denotes the adsorbent weight in grams.

### 3. Results and Discussion

#### 3.1. Properties of MZTWAC

The SEM exhibited in Figure 1 MZTWAC reveals the availability of irregular and porous surface that facilitates the adsorption process to take place [20]. From Figure 2 [19], it is visible that MZTWAC possessed broad peaks, -OH stretching from hydroxyl to phenolic groups [28–30], C-H stretching of aliphatic acids, C-O stretching of alcohols [28, 29], and C-O stretching of carboxylic acid [7] and alcohols.

#### 3.2. Experimental Design and Model Development

**3.2.1. Mathematical Model Development and Design of Experiments.** The mathematical-statistical quadratic model was assessed by analysis of variance (ANOVA). Critical parameters taken into account have been experimented for their optimized values in adsorption which were figured using the models that may fit and the same were validated. The current experimental work hired fourteen experiment variables: \( A, B, C, D, AB, AC, AD, BC, BD, CD, A^2, B^2, C^2, \) and \( D^2 \), where \( A \) is the beginning concentration, \( B \) is the pH, \( C \) is the adsorbent dosage, and \( D \) is the contact period. At this point, the Design Expert has a variety of modeling options for fitting the response, including linear, two-factor interaction (2FI), quadratic, and cubic polynomials, and the evaluation was done to confirm the best model fit based on the \( R^2 \) value obtained from sequential model sum of squares. Table 2 is in charge of compiling a model evaluation summary. The programme selected the optimal model for the research project. When compared to other models, the quadratic model was suggested, while the cubic model was aliased; thus, it must not be used.

**3.3. Validation of Quadratic Model.** Multiple regression analysis was applied to figure out the coefficients of quadratic model that was intended to fit the results. The noteworthy connotation of autonomous process parameters was studied with 29 batch experiments. From Table 3, the model’s \( F \) value of 1292.46 entailed that the model is...
There is only 0.01% chance that an \( F \) value is large, and this could occur due to noise. Values of “Prob > \( F \)” less than 0.0500 indicate the model terms are significant. Here, \( A \), \( B \), \( C \), \( D \), \( AB \), \( AC \), \( AD \), \( BD \), \( CD \), \( A^2 \), \( B^2 \), and \( C^2 \) are significant model terms. The rest of the source term values, which are larger than 0.1000 signpost, are not noteworthy and are deliberated as eliminating terms. The “lack-of-fit \( F \) value” entails the lack of fit is not significant.

In addition, the ANOVA in Table 4 is supplemented by a variety of indications provided by the Design Expert. Low experimental variance is shown by the standard deviation of 0.247295. The 0.9955 “Pred. \( R^2 \)” and the 0.9984 “Adj. \( R^2 \)” have an excellent correlation, with a difference of less than 0.2. The tolerable precision of 163.9238 indicates that the signal is viable. The signal-to-noise ratio is measured by “Adeq. precision,” and a number greater than 4 is preferable. In summary, the \( R^2 \) statistics are excellent since they are near to 1, implying that the regression model offers a substantial connection amid the observed and anticipated values. As a result, this model may be utilized to traverse the design.

The second-order polynomial equation is derived based on RSM results. Equation (3) shows how a particular component and the interaction between the four independent process parameters impacted the adsorption process [22].

\[
\text{Adsorption Capacity } Y = \frac{12.200 + 2.895 A - 0.598 B - 5.219 C + 0.630 D + 0.241 AB - 0.752 AC + 0.621 AD - 0.490 B^2 - 0.417 C^2 + 0.282 A^2 - 0.199 B^2 + 2.709 C^2}{1} \tag{3}
\]
Equation (3), when used with coded variables, may predict the response for different degrees of each element. Obviously, the process variables’ higher levels are entered as +1, and the variables’ low degrees are coded as -1. When looking at the factor coefficients, the coded condition is expedient for detecting overall influence of variables. Negative and positive coefficients show how considerable metal particles are ejected in a negative or positive way. An optimistic consequence of a factor indicates that response improves as the factor level increases, whereas a negative effect indicates that the reaction does not improve as the factor level increases.

As the circumstances show, starting concentration and contact duration have a beneficial impact on chromium(VI) retention, but pH and adsorbent percentage have a negative impact. As a result, as IC increased, so did adsorption ability. In any instance, when the pH and adsorbent fraction increased, the adsorption rate lessened. The relapse equation is graphically shown in the 3D response surface plots shown below (Figures 3–5). The adsorption limit widened as the underlying fixation was amplified from 40 mg/L to 60 mg/L and the pH declined from 6 to 4, as shown in Figure 6. The addition of the adsorption limit was suggested by the high initial fixing of initial concentration and the low pH values. The adsorption limit grew in lockstep with the experiment, even if not as dramatically (Figure 4). Similarly, a large adsorbent dosage did not support the adsorbent’s adsorption limit, as shown in Figure 4. Low pH and long contact duration, as seen in Figure 5, resulted in a remarkable adsorption limit for the MZTWAC.

3.4. Capability of Model. Analytic plots, with predicted versus definite and normal probability plot that has studentized residuals, are used to assess the adequacy of the numerical model and to analyse the relapsing model’s sufficiency. Figure 6 depicts the association amid the actual and projected adsorption limits. The graph demonstrates proclivities in straight relapse fit, and the model effectively describes the trial run under consideration. Furthermore, it establishes a strong link between the data gathered through testing and the predictions made by the regression model meant for the chromium adsorption process (VI).

The normal probability plot (Figure 7) is also regarded as the most appropriate graphical method for verifying and

<table>
<thead>
<tr>
<th>Table 4: Post-ANOVA statistics.</th>
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</thead>
<tbody>
<tr>
<td>Std. dev.</td>
</tr>
<tr>
<td>Mean</td>
</tr>
<tr>
<td>C.V. %</td>
</tr>
<tr>
<td>PRESS</td>
</tr>
<tr>
<td>$R^2$</td>
</tr>
<tr>
<td>Adj. $R^2$</td>
</tr>
<tr>
<td>Pred. $R^2$</td>
</tr>
<tr>
<td>Adeq. precision</td>
</tr>
</tbody>
</table>

![Figure 3](image1)

**Figure 3:** Upshot of interface connecting pH and the initial concentration of chromium(VI).

![Figure 4](image2)

**Figure 4:** Upshot of interface connecting MZTWAC (adsorbent dose) and the initial concentration of chromium(VI).

![Figure 5](image3)

**Figure 5:** Upshot of interface connecting pH and the contact time.
Figure 6: Interface connecting the actual and anticipated figures of adsorption capacity.

Figure 7: Normal probability design.

Figure 8: Leverage vs. run.

Figure 9: Cook’s distance.

Figure 10: DFFITS vs. run number.

Figure 11: Perturbation plot.
evaluating normality of the residual. The aforementioned depicts residual behaviour that tracks a normal distribution and is straight, i.e., dispersal of residuals in a regular manner with minimal divergences. It is discovered that the model is suitable meant for the evacuation of chromium(VI) during the adsorption method when MZTWAC is used.

3.5. Influence Plots. The model’s residuals are roughly parallel to the straight line. Although they appear to follow a normal probability distribution, the residuals explicit minimal deviation from normalcy. To examine the impact of outliers, it is never needed that the mistakes be genuinely regularly distributed in general terms. In this examination, Design Expert is used to create several graphical representations of the residuals. Estimates of the leverage (influence), Cook’s distance, and DFFITS plots are requested to examine the regression model’s exactness to discover the statistical features of the experimental model. Figure 8 shows that the influence statistics were all in the range of 0 to 1 [31]. There is no information which emphasizes that there is an unreasonably negative impact on the model fit because the effects of all run values in the current evaluation are less than 1. Figure 8 shows that the influence values were all within the range of 0 to 1 [31]. There are no information foci that have an unreasonably negative impact on the model fit because the effects of all run values in the current evaluation are less than 1.

Additionally, Cook’s distance (Figure 9) estimates the impact of erasing a certain observation and is used to govern the outlier in the data (data). It must fall between the ranges of +1 and −1. Apart from DFFITS plots, Figure 10 assesses the influence of observed values on its projected value, and its run is in the centre of the typical farthest that reaches +2 to −2.

3.6. Outcome of Independent Variables. Tsai and Wu [32] used a case-weight perturbation plan in 1992 to get an elective nearby impact indicator that considers the Jacobian perturbation consequences. However, in this study, a perturbation diagram (Figure 11) was plotted to consider the relationship between four independent factors, pH, adsorbent dose, contact time, and initial concentration, in the adsorption procedure aimed at the removal of chromium(VI), as well as their contrasting impact on the response.

The response acquired by operation Design Expert is assessed by altering only one variable while keeping the other components constant. Although the starting concentration (A) line goes upward on the opposite side, the perilous slant down of adsorbent dosage (C) and pH (B) reveals that adsorption capacity is subtle to adsorbent dose

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbate</th>
<th>Initial concentration (mg/L)</th>
<th>pH</th>
<th>Adsorbent dose (g)</th>
<th>Contact time (min)</th>
<th>Predicted adsorption capacity (mg/g)</th>
<th>Desirability value</th>
<th>%removal (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MZTWAC</td>
<td>Chromium(VI)</td>
<td>59.98</td>
<td>4.08</td>
<td>0.2</td>
<td>80</td>
<td>26.279</td>
<td>0.694</td>
<td>87.629</td>
</tr>
</tbody>
</table>

Figure 12: RAMP plot for adsorption of chromium(VI) by MZTWAC.

(C) followed by pH (B) for expulsion. It shows that adsorption capability for removing chromium(VI) increases with increasing chromium(VI) concentration (A), but declines with growing adsorbent dosage (C) and pH (B).

Initial concentration (A) and adsorbent dosage (C) were additionally profound to the adsorption process than changing pH (B) and contact duration, according to the perturbation plot (D). Nevertheless, the perturbation plot reveals that pH, adsorbent dosage, contact duration, and beginning concentration all have a significant influence on adsorption capacity in the chromium(VI) expulsion proficiency.

3.7. Optimization of the Process Variable. Exploratory data is used to ensure the most accurate estimates of variables for chromium(VI) expulsion by MZTWAC from the model. The optimization of multiple response models is done using the desirability function. It is filled out as target work and used to create a custom mix of process parameters ahead of time. For each element and reaction, Design Expert provides five alternative objectives: maximize, reduce, target, in range, and set to a precise number. In this current study, the desired target for adsorption capacity was set to 1 maximum and “in the range” for four independent variables such as starting concentration, pH, contact duration, and adsorbent dosage.

The analysis of desirability predicted that the desirability for the response function selected is furnished in detail in Table 5. The RAMP plot (Figure 12) depicts that 26.279 mg/g is an optimized response while the independent variables are 59.98 mg/L (initial concentration), 4.08 (pH), 0.2 g (adsorbent dosage), and 80 minutes at maximum desirability.
4. Concluding Remarks

The high match was established among the experimental value and predicted value of the adsorption capacity in the optimization procedure of chromium(VI) adsorption by MZTWAC which recommended that the model chosen was an excellent fit. Auxiliary inference was that the optimized outcome acknowledged from the plots of RAMP that the activated carbon fabricated from Manilkara zapota tree is the best choice in removing chromium(VI) ion from aqueous solution and it is economically worthy too. The inclusion of central composite design in the experimental study reduced the experimentation work, and the optimum results were arrived for the chosen process parameters. The response surface methodology conferred a clear picture between the process parameter interactions through the three-dimensional images. Many adsorbents such as aluminum–lanthanum mixed oxyhydroxide (ALMOH), chitosan/aluminum–lanthanum mixed oxyhydroxide (CSALMOH), ionic solid impregnated phosphate chitosan, and PAN–CNT/TiO2–NH2 have been involved in the removal of chromium ion with the adsorption capacity of 49.8, 78.9, 266.67, and 714.27 mg/g, respectively. The more water pollution, the more there is a want of a new adsorbent to treat polluted water to make safe water either to be disposed of or be reused. In this context, MZTWAC is best suited which costs low and is efficient as well.

Data Availability

The data used to support the findings of this study are included within the article. Should further data or information be required, these are available from the corresponding author upon request.

Disclosure

The study was performed as a part of the employment of Mettu University, Ethiopia.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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