Removal of fluoride using bagasse adsorbent: Process optimization using response surface methodology

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Abstract. The high fluoride (F-) content in drinking water is highly hazardous to human health. Bagasse is a solid waste generated in the cane-based sugar industry. It can be used to get energy after firing in boilers or used to produce activated charcoal. The activated carbon is used as an adsorbent material to remove pollutants from water. In the present study, the activated carbon prepared from bagasse was used to remove F- contain in water. Batch adsorption studies were performed to examine the effect of temperature (T), treatment time (tR), and initial fluoride concentration (Fi-) on F- removal. Response surface methodology (RSM) was used to generate a mathematical model and for the optimization of parameters. The optimum operating condition was evaluated to be T = 26°C, treatment time (tR) = 3.5 h, and Fi- = 25.14 mg/L, at which F- concentration in solution after treatment reached to 0.8 mg/L. The predicted values of F- in the solution obtained from the quadratic model were found to be well-matched with the experimental data. The model gave significant coefficients of determination R2 = 99.61%, R2 (adjusted) = 99.11%, and R2(predicted) = 97.71%, which shows that the model developed from RSM is highly accurate and well represents the process with its process parameters.

Keywords: de-fluoridation, water purification, bagasse adsorbent, optimization

1. Introduction
Most of the Indian population living in rural areas rely on groundwater for their drinking water need. F- may enter into groundwater by weathering rocks, industrial effluent discharge, and geochemical reactions [1]. While F- is an essential element to be present in water in a small amount for bones and dental enamel, its high concentration (>1.5 mg/L) can lead to several health disorders such as dental fluorosis, irreversible demineralization of bones, damage of brain tissues, the adverse effect over kidney and liver, etc.[2,4]. It is highly electronegative and usually found in a combined state because of its high chemical reactivity.

In India, the F- concentration in groundwater ranges from 4.21 mg/L to 48 mg/L [5], which is well above the limit of F- in the water of 1.0 mg/L to 1.5 mg/L, as specified by the Bureau of Indian Standards [6]. Needless to say, it poses a significant threat to health. This necessitates the removal of F- from water through a cheap and effective method to bring its concentration within the specified limit.
Adsorption provides a flexible way of treating wastewater due to the large variety of adsorbents available and ease of operation. However, an adsorbent with high adsorbent capacity, easy regeneration, and low cost has always focused on research in water treatment. In this lead, researchers have explored brick powder[7], ionic liquid functionalized alumina [8], microorganism [9], bone char [10], alum [11], metal-organic frameworks [12], furnace slag[13], fly ash [11,14], bagasse [15], bark of Phyllanthus emblica (amla) tree [16], etc.to remove F- from wastewater.

Response surface methodology (RSM) is a powerful tool for generating a mathematical optimization model and getting the optimized operating condition with a minimum number of experimental runs [17]. The application of RSM has been reported for fluoride removal to optimize the operating parameters [18,19]. The use of RSM and artificial neural network (ANN) for optimization has been reported to remove methylene blue dye, but the RSM was found to be better than the ANN [20]. Nobbou et. al. (2019) used one parameter at a time method to optimize fluoride removal using Kaolinite [21]. Asgari and coworkers have used the Taguchi method to optimize process conditions for the pyrolysis of bone char to be used in fluoride removal [22]. In the present study, bagasse a solid waste of the cane-based sugar industry has been selected as an adsorbent to remove F- content in water. The RSM studies based on the central composite design (CCD) using MINITAB have been performed to optimize the process.

2. Material and methods

2.1. Preparation of activated carbon
In this study, the activated carbon prepared from bagasse was used for the adsorption process, produced through the chemical activation process. Sugarcane bagasse waste was collected from the local market. Firstly, bagasse was washed thoroughly with tap water to remove dust particles, then it was dried at 120 °C in a hot-air oven for 24 h, ground, and sieved. Dried bagasse was crushed in a blender and sieved to obtain a uniform grain size. The sieved sugarcane bagasse was transformed into carbon by heating in a muffle furnace at the temperature of 300 °C without the addition of any chemical agent for 2 h. By carbonization, most of the noncarbonated elements, hydrogen, and oxygen, are removed in gaseous form and the remaining carbon atoms are grouped into an organized crystallographic formation known as elementary graphitic crystallites. The carbonization step usually results in an inert material with a specific surface area and low adsorption capacity. Produced carbon was then treated with 30% aqueous phosphoric acid (H3PO4) solution in a weight ratio 1:1 for 24 hr and then washed with double-distilled water several times and dried. The carbonized material was stored in vacuum desiccators for further use.

2.2. Adsorption of Fluoride
Adsorptive treatment of F- bearing water was carried out in a water bath shaker (Remi made) with a speed of 1200 rpm. 50 ml of Sodium F- solution (50 mg/L F-) was taken in a 100 ml conical flask (made of polymer). The required amount of adsorbent was added and kept for shaking. About 3 ml samples were taken at a certain time interval in a plastic test tube, and the adsorbent was allowed to settle for about 1.5 h. The supernatant was taken to determine F- using Merck made chemical kit. After adding the chemicals in F bearing, watercolor was developed. The adsorption of developed color, and consequently, F concentration was determined using Merck made spectrophotometer (model Spectroquant Prove 300). Effect of pH, adsorbent dose (mg), F- concentration, temperature, and contact (shaking) time on F- removal was estimated. Analytical grade regents made of Merck limited were used to estimate F-.

3. Result and Discussion

3.1. Statistical analysis and modeling
RSM is a useful tool used for the design and optimization of process variables. The F removal experiments were performed at pH 4 and bagasse activated carbon (BAC) adsorbent dose of 5 g/L. The other parameters like temperature, initial concentration of F-, and t_r were analyzed using MINITAB
based on a central composite design (CCD). Table 1 presents the chosen variables and their level. Here level selects are from -2 to +2, which having a wide range, could give a better representation of experimental data for modeling and statistical analysis. The data used for statistical analysis and corresponding F removal obtained from experiments are presented in Table 2. A set of data has been designed as per the earlier report by Mook et al., 2013 [23].

| Table 1. Process parameters and their level used for RSM studies |
|---------------------------------------------------------------|
| Variables | Factors | Range and levels |
|-----------|---------|-----------------|
| Temp, °C  | X₁, ₂  | -2  16  26  36 |
| F Conc., mg/L | X₂, ₂ | -2  10  30  50 |
| Time, h   | X₃, ₂  | 0.5  1.25 2  3.5 |

| Table 2. Design of RSM and its actual and predicted values |
|----------------------------------------------------------|
| Standard order  | X₁, ₂  | X₂, ₂  | X₃, Temp. (°C) | X₂, Conc. (mg/L) | X₃, Time (Min) | F° Actual | F° Predicted |
|---------------|--------|--------|----------------|-----------------|----------------|------------|-------------|
| 1             | -2     | -2     | +2  16          | 10              | 3.5            | 2.7        | 3.0791      |
| 2             | 0      | 0      | +1  26          | 30              | 2.45           | 6.5        | 7.0239      |
| 3             | -2     | -2     | -2  16          | 10              | 0.5            | 7.5        | 7.7319      |
| 4             | +2     | +2     | +2  36          | 50              | 3.5            | 16         | 15.7423     |
| 5             | +2     | -2     | +2  36          | 10              | 3.5            | 1.8        | 1.8452      |
| 6             | 0      | 0      | -1  26          | 30              | 1.25           | 13         | 12.9776     |
| 7             | 0      | +1     | 0   26          | 40              | 2.0            | 13         | 14.2473     |
| 8             | 0      | -1     | 0   26          | 20              | 2.0            | 5.8        | 4.2238      |
| 9             | -2     | +2     | +2  16          | 50              | 3.5            | 9.6        | 9.5761      |
| 10            | -2     | +2     | -2  16          | 50              | 0.5            | 34         | 33.9289     |
| 11            | -1     | 0      | 0   21          | 30              | 2.5            | 8.6        | 7.4858      |
| 12            | +2     | -2     | -2  36          | 10              | 0.5            | 7          | 7.0909      |
| 13            | 0      | 0      | 0   26          | 30              | 2              | 9.2        | 9.2247      |
| 14            | 0      | 0      | 0   26          | 30              | 2              | 9.2        | 9.2247      |
| 15            | 0      | 0      | 0   26          | 30              | 2              | 9.2        | 9.2247      |
| 16            | 0      | 0      | 0   26          | 30              | 2              | 9.2        | 9.2247      |
| 17            | +2     | +2     | -2  36          | 50              | 0.5            | 41         | 40.6879     |

3.2. Polynomial equation formation and its validation

Various models that can be used for polynomial studies are linear, interactive, quadratic, and cubic. In the present study, the quadratic model has been undertaken. The response output (Y) of input parameters can be represented by the quadratic model, which is given by Eq. 1 [24].

\[ Y = a_0 + \sum a_i x_i + \sum a_{ii} x_i^2 + \sum a_{ij} x_i x_j + \epsilon \]  

(1)

Where Y is the response, \( a_i, a_{ii} \) and \( a_{ij} \) are the coefficient of linear, interaction and quadratic terms, \( \epsilon \) is the residual error, and \( x_i, x_j \) are independent variables, values of which have an impact on the response (Y). Using the analysis of variance (ANNOVA), the regression method was used to fit the second-order
polynomial with experimental data. The relation obtained among the variables in terms of a coded factor representing F\(^{-}\) remaining in solution after Eq.2 presents its removal.

\[
F^{-}\text{after treatment (mg/L)} = 34.8 - 2.97 x_1 + 0.583 x_2 - 0.13 x_3 + 0.0548 x_1^2 + 0.00011 x_2^2 + 0.09 x_3^2 + 0.00925 x_1 x_2 - 0.0099 x_1 x_3 - 0.1642 x_2 x_3
\] (2)

After the statistical modeling, the predicted values calculated from Eq. 2 are presented in Table 2. The predicted and calculated values are very close to each other with a maximum of 1.6 mg/L error, as shown in the Table. The experimental values and predicted values are also presented in Fig 1. In this, it can be seen that dotes are very close to the line, which shows the result of the ANNOVA analysis is correct.

The statistical model of RSM give coefficient of determination \(R^2 = 99.61\%\), \(R^2\) (adjusted) = 99.11\% and \(R^2\)(predicted) = 97.71\%; which shows validation of model as large value of \(R^2\) is desirable. In the present case, the values of \(R^2\) is sufficiently high. The values are comparable to various earlier reports used for RSM statistical analysis [24,25]. The regression model's significance is also evaluated in terms of Fischer distribution (F value) and a null hypothesis test (P-value). There is an interrelation between F and P, a high value of F gives a low value of P. The ANNOVA for the quadratic (second-order) equation fitted for \(F^{-}\) remaining in solution after its removal is presented in Table 3. The overall value of F obtained in the regression is 199.89 and P-value is 0.0, which shows the model's statistical significance [25].

![Figure 1](image_url)

**Figure 1** Graph for actual versus predicted value for \(F^{-}\) removal

The ANNOVA analysis also shows values of \(F = 473.56\) and \(P = 0.0\) for linear, \(F = 45.31\) and \(P = 0.0\) for square, and \(F = 78.91\) and \(P = 0.0\) for interaction effect on \(F^{-}\) removal. In ANNOVA analysis, for best fit, the value of F should be large (>5) and p should be low (< 0.05). The large value of F and low value of p in the present case shows that the regression can explain most of the variation in response. Our values are better to F = 16.50 and P = 0.001 reported by Thakur et al., 2009 [24], and F =16.55 and P = 0.0001 obtained by Asaithambi et al.,2011 [25]. Among the various sets of experiments \(A^2\), \(B^2\), \(C^2\), and BC interaction effects are found less significant. Many authors have removed the less significant parts from the quadratic model. However, in the present case, it has been retained in the model. Removing the less significant parts increases the error between experimental and predicted values to some extent. It was targeted to remove \(F^{-}\) till its concentration in the treated solution reached 0.8 mg/L, because 0.5-1.0 mg/L \(F^{-}\) is acceptable concentration limit [26]. Overall \(T = 26^\circ C\), \(F_{\text{max}} = 25.13\) mg/L \(F^{-}\).
and $t_R = 3.5$ h were evaluated as optimum for the process. The results are presented in Fig. 2 and Table 4.

### Table 3. Anova for analysis of variance using the quadratic model

| Source        | DF | Sum of square | Mean square | F     | P   |
|---------------|----|---------------|-------------|-------|-----|
| Regression    | 9  | 1683.99       | 187.11      | 199.89| 0   |
| Linear        | 3  | 1329.84       | 443.282     | 473.56| 0   |
| A             | 1  | 16.15         | 16.153      | 17.26 | 0.004|
| B             | 1  | 854           | 854.005     | 912.33| 0   |
| C             | 1  | 454.85        | 454.852     | 485.92| 0   |
| Square        | 3  | 127.24        | 42.412      | 45.31 | 0   |
| A$^2$         | 1  | 4.05          | 4.047       | 4.32  | 0.076|
| B$^2$         | 1  | 0             | 0           | 0     | 0.985|
| C$^2$         | 1  | 0.01          | 0.005       | 0.01  | 0.943|
| Interaction   | 3  | 221.6         | 73.867      | 78.91 | 0   |
| AB            | 1  | 27.38         | 27.38       | 29.25 | 0.001|
| AC            | 1  | 0.18          | 0.176       | 0.19  | 0.678|
| BC            | 1  | 194.04        | 194.045     | 207.3 | 0   |
| Error         | 7  | 6.55          | 0.936       |       |     |
| Lack-of-Fit   | 5  | 6.55          | 1.31        |       |     |
| Pure Error    | 2  | 0             | 0           |       |     |
| Total         | 16 | 1690.54       |             |       |     |

### Figure. Plot for the optimum value of the process determined from RSM.

### Table 4. Response optimization to determine residual F, by RSM

| Response | Goal | Lower | Target | Upper | Weight | Importance |
|----------|------|-------|--------|-------|--------|------------|
| Residual F, mg/L | Target | 0.72 | 0.8    | 41    | 1      | 1          |

### Solution

| Solution | Temp, oC | Concentration, mg/L | Time, h | Residual Fit, mg/L | Composite Desirability |
|----------|----------|---------------------|---------|--------------------|------------------------|
| 1        | 26       | 25.14               | 3.5     | 0.8                | 1                      |

### 3.3. Effect of variables on fluoride removal

The surface response plots and contour plots in a three-dimensional form obtained from RSM studies for F$^-$ concentration remain in solution during the treatment are presented in Fig. 3. Figures 3a and 3b show the effect of time and initial F$^-$ concentration on the amount of residual F$^-$ present in solution at 26
Figure 3 Response surface plot and contour plot for F\textsuperscript{2} removal.
°C. Figure shows, as the initial concentration is less, the residual F⁻ is also less. The initial concentration of 10 mg/L of F⁻ has been removed completely in 1.6 h, and 20 mg/L in 3.5 h. As the treatment time is more, and F⁻ concentration is less, the F⁻ left in solution is also less. The F⁻ of 40 mg/L reached to < 5 mg/L in 3.5 h treatment time. For lower values of F⁻, the removal was high due to the large active surface available per gram of F for the adsorption process. Figure 3c and 3d show the effect of temperature and initial F⁻ concentration on its removal for 2 h treatment period. It can be seen that medium temperature (22-27°C) is favorable; at this temperature range, less than 5 mg/L fluorides has remained in solution after 2 h treatment. Figure 3c-d also shows that removal was increased as the temperature was increased up to 26°C. After that, the removal decreased as the temperature was increased further due to the desorption of fluoride at elevated temperatures. Effect of temperature and time on the removal of F⁻ at constant F⁻ concentration of 30 mg/L is shown in Fig 3e and f. Between temperature 17 to 30°C, the 30 mg/L F⁻, decreased to less than 5 mg/L in 3.5 h. The figure also shows that the highest removal rate is at about 25°C. At all the temperatures, the F⁻ removal was increased with an increase in time, which is due to much contact time available for contact F⁻ with the adsorbent.

4. Conclusions

Following conclusions can be drawn from the studies

The activated carbon prepared from bagasse has been found as an effective adsorbent for the removal of F⁻. The optimum operating condition from RSM is evaluated to be T = 26°C, tₙₐₜ = 3.5 h, and F⁻ 25.14 mg/L, to reach F⁻ in the solution 0.8 mg/L. The quadratic model developed using RSM is highly accurate as the experimental data was very close to the data predicted by the quadratic model. The model gave significant coefficients of determination R² = 99.61%, R² (adjusted) = 99.11%, and R²(predicted) = 97.71% also, a high value of F (199.89) and a low value of P (0.0) obtained by ANNOVA shows that the model is statistically accurate.

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