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Defluoridation of wastewater using powdered activated carbon developed from *Eichhornia crassipes* stem: optimization by response surface methodology

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ABSTRACT

The present investigation describes the removal of fluoride from synthetically fluoridated water using powdered activated carbon (PAC) developed through steam activation of carbonized *Eichhornia crassipes* stem by series of batch sorption experiments. Process is optimized by response surface methodology and experimental matrix is developed by central composite rotatable design. Influence of five different parameters viz. pH, adsorbent dose, temperature, contact time, and revolutions per minute (RPM) were studied in the range of 2–12, 2–12 g/L, 20–60˚C, 20–180 min, and 100–300, respectively. Prepared PAC was characterized to obtain physical properties and instrumentally analyzed to observe surface texture of raw PAC and spent PAC with fluoride using methods viz. SEM, EDAX, and XRD. Physical properties, such as surface area and total pore volume, obtained equal to 97.68 m^2/g and 0.5185 cm^3/g, respectively. From the performed experiments for fixed initial concentration of 10 mg/L, maximum fluoride removal (70%) was obtained at a pH of 5 and it took 133 min to attain this state with activated carbon dose, temperature, and RPM of 9 g/L, 48˚C, and 240, respectively. Second regression model equation was derived to study analysis of variance showing significance of the process parameters. Results of the performed study reveals that the adsorption of fluoride over AC prepared from *E. crassipes* stem can be cost-effective and prominent for the treatment of fluoridated waste water.

Keywords: *Eichhornia crassipes*; Fluoride; Adsorption; Response surface methodology; Analysis of variance

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1. Introduction

Fluoride is recognized as an essential micro-nutrient in the human diet for the formation of dental enamel and normal mineralization of bones. Fluoride ingestion through drinking water and food is beneficial within the permissible limits of 0.5–1.5 mg/L prescribed by World Health Organization, but the dietary intake of fluoride with concentration more than 1.5 mg/L may be detrimental to human health leading to dental or skeletal fluorosis [1]. The impacts on human health of fluoride with different concentration are represented in Table 1. Fluorides can occur in the environment due to both natural and anthropogenic activities. Inorganic fluorides are broadly distributed in the geological location and generally released into the groundwater by slow degradation of

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Table 1
Health impacts of fluoride in water with different concentrations

Fluoride concentration (mg/L)	Effect
Nil	Limited growth and fertility
0.5–1.0	Promotes dental health, prevents tooth decay
1.0–3.0	Dental fluorosis (discoloration, mottling and pitting of teeth)
3.0–4.0	Skeletal fluorosis (stiffened and brittle bones and joints)
4.0–6.0 and above	Crippling fluorosis (deformities in knee and hip bones)

fluoride-containing sedimentary and igneous rocks. Fluoride releases through minerals viz. fluorspar (CaF_2), cryolite (Na_3AlF_6), fluorapatite $CaF_2 \cdot 3Ca3 (PO_4)_2$, sellaite ($MgF_2$), etc. present in the rock is nearly insoluble but can be soluble in certain favorable conditions. Thus, the groundwater used for drinking purpose is a prime source of fluoride intake to the human health. It is noticeable that the extent of fluoride content in groundwater varies from 0.2 to 44 mg/L [2]. On the other hand, fluoridated compounds as raw materials find huge applications in various industries such as semiconductor manufacturing, electroplating, phosphate fertilizer production, steel and rubber manufacturing, coal power plants, glass and ceramic industries, etc. [3]. Consequently, the surface water is also getting polluted due to toxic wastes containing fluoride released from the industries. Thus, fluoride contamination in water has been a burning environmental issue and subject of worldwide attention over the past few decades.

The fluoride is endemic in nearly 23 countries across the globe. India also figures in this list and is suffering from fluoride epidemic fatally having increasing concentration of fluoride in groundwater. In India, peoples belonging to 150 districts of 19 states affected with dental, skeletal and non-skeletal fluorosis due to intake of fluoride-rich water are estimated to be 66 millions [4]. The endemic states, where the excess fluoride in ground water has been detected so far, are Maharashtra, Orissa, Himachal Pradesh, Punjab, Rajasthan, Tamil Nadu, Andhra Pradesh, Bihar, Gujarat, West Bengal, Uttar Pradesh, Haryana, Karnataka, Kerala, Madhya Pradesh, and five blocks of Delhi. In view of this alarming problem, development of economically viable technique for the treatment of fluoride-laden water towards mitigation of the menace and obtaining the fluoride-free drinking water is the need of the hour.

It is worth mentioning that fluorine is a highly electronegative element. So, it has a greater tendency to get attracted by positively charged ions like calcium. Excess amount of calcium intake reduces the risk of dental fluorosis, but this solution is not practical. Defluoridation is the feasible solution of this problem. Moreover, skeletal and dental fluorosis is irreversible in nature and no treatment exists for complete curing of fluorosis. The only remedy is prevention by keeping fluoride intake within the safe limits [5].

Till date, several methods of deflouridation have been reported to remove excessive fluoride from water, namely, adsorption, ion exchange, precipitation–coagulation, membrane process, bioremediation, etc. [6]. Membrane process is carried out based on the principle of electrolysis, electro-dialysis, reverse osmosis, ultra-filtration, etc. The selection of a promising technique depends greatly upon so many factors like ease of availability of raw materials, operating cost, installation space requirement, maintenance, technical versatility, mode of waste disposal, materials properties, etc. Membrane filtration employing reverse osmosis technique has been effective in defluoridation, but it is not cost-effective [7]. Precipitation–coagulation technique is claimed to be very effective but the major drawbacks are high initial and maintenance cost, routine addition of chemicals, production of larger quantity of sludge, regular analysis of feed and treated water, low fluoride removal in the form of precipitate (18–33%), less acceptability of treated water for alkaline pH, etc. Bioremediation using micro-organisms has received a greater momentum in terms of removal of fluoride content from the media, localization of contaminants, and cost-effectiveness, but the major limitation of this process is prolonged operation time requirement [8]. Adsorption seems to be one of the more widely used effective, socially acceptable, and efficient method for deflouridation of water because of its operation simplicity and cost-effectiveness [9]. In the recent years, this alarming situation has forced the scientists to focus on the study of various kinds of materials such as saw dust, tree bark, rice husk, activated alumina, manganese oxide-coated alumina, coconut shell-based activated carbon, zeolite, red mud, fly ash, synthetic resins, carbon Nano-tube, double-layered hydroxides, bone charcoal, hen feathers, bottom ash and de-oiled soya, bleaching earth, titanium-rich bauxite, titanium oxide, clay, carbon slurry, materials from agricultural waste, biosorbent, Nano-sorbent, and other waste materials to evaluate their fluoride sorption capacity at varying parameters [10–37].

Owing to its metal-sequestering capability, biosorbent material prepared from biomass can be employed for diminution of the fluoride concentration in groundwater. Biosorption technique has an edge over conventional methods in terms of its low cost, easy availability, high efficiency, minimization of chemical and/or biological sludge, no additional nutrient requirement, and regeneration of biosorbent [38]. The pore size distribution of sorbent is one of the stringent characterizations which can be engineered subjected to physical, chemical or physico-chemical condition. Pore size can also be encouraged by microwave treatment of biosorbent. It is well established that the chemical treatment can intensify the adsorbent pore size appreciably more than physical treatment, but physical treatment is used much more than the chemical method due to its operation simplicity. Physical treatment is a single step methodology and there would be no chance for any chemical coming out in the effluent.

In the present study, an attempt has been made to investigate the efficiency of a biosorbent derived from steam activation of carbonized *Eichhornia crassipes* [39–41] stem in decontaminating fluoride from water as a novel, potential, environment-friendly, and low cost material. Removal process has been optimized using response surface methodology (RSM). Second-order regression model equation has been developed and analysis of variance (ANOVA) analysis has been performed to check the fitting of the chosen model using Design Expert software 8.0.

2. Materials and methods

2.1. Materials

Materials used for the experiments were sodium fluoride Pure (NaF) (Merck, India) as a source of fluoride and steam-activated *E. crassipes* stem carbon as an adsorbent. Other chemicals used in the study were sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) (Merck, India). Deionized water was obtained from the Arium 611 DI ultra-pure water system (Sartorius A.G., Gottingen, Germany). For measuring the final concentration of fluoride in the wastewater, TISAB buffer was used.

2.2. Preparation of adsorbent-activated carbon

The manufacturing process of AC mainly consists of two steps:

(1) Carbonization of the stem of *E. crassipes* (commonly known as water hyacinth, floating water hyacinth, water orchid, or jacinthe D'eau, a floating uncultivated monocotyledonous fern belonging to the family Pontederiaceae is a submerged aquatic autotrophs, originated abundantly in various tropical and sub-tropical countries of South America, Africa, Australia, Southeast Asia, and Pacific) at a particular temperature in a closed atmosphere

(2) Physical activation of the carbonized char to get the final product.

2.2.1. Carbonization

Young aquatic weeds *E. crassipes* were collected from nearby ponds. Stems of *E. crassipes* were cut into 5–10 mm size, then washed with tap water followed by distilled water, and then placed it in trays to make it dry in laboratory temperature. After 24 h, it was placed in hot air oven and kept at 110℃ for 12 h. Superheated stem was then placed in furnace which was set in 600℃. The quality and yield of carbonized char depends on heating time and rate, final temperature, the soaking time at the final temperature, and the physical state of starting material [42].

2.2.2. Activation

As the carbonization process cannot remove appreciably part of hydrocarbons, which are assumed to be bonded chemically to the edge carbon atoms and metallic compounds or crystallites formed during carbonization, activation is done to eliminate them by employing "activating agent" e.g. air O_2, CO_2, and superheated steam not only to break up these bonds with carbon atoms but also to enhance the volume by creating and enlarging more and more macro- and micro-pore vacancies caused during the carbonization process. Carbonized biochar was activated by passing superheated steam at pressure of 1.5–2.0 kg/cm^2 (1.5–2.0 MPa) at 800℃ (1,073 K) for 1.5 h to produce activated carbon as the desired optimum product. At last, the steam-activated biochar was grinded in BOSS portable hand blender to obtain the powdered form. The complete process is shown by flow chart shown in Fig. 1.

2.3. Characterization of activated carbon

Physical properties of derived powdered-activated carbon viz. micro-pore volume, total pore volume, hardness, surface area, and iodine number were determined by characterizing the steam-activated char using standard methods.

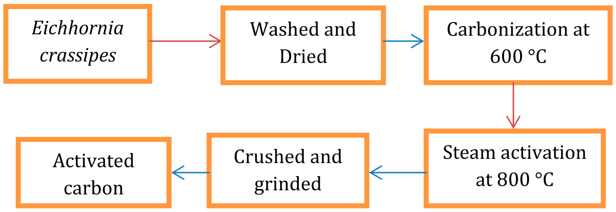

Fig. 1. Flow chart for preparation of activated carbon.

Hardness of AC was estimated following the standard codes of Bureau of Indian Standard IS 877:1989, while other properties such as micro-pore volume and specific surface area were determined using Dubinin–Radushkevich equation, BET method, respectively [42,43]. A standard method suggested by (ASTM D4607-94) was used to evaluate iodine number which indicates adsorption capacity of iodine on AC. Quanta chrome autosorb automated gas adsorption system (ASORB 2 PC VERSION 1.05) was used employing nitrogen adsorption technique for calculation of total pore volume.

2.4. Instrumental analysis of activated carbon

To study the surface micro-morphology of AC, prepared sample was analyzed instrumentally using SEM (JEOL JSM 6360 India). First, the sample was coated with palladium coating having thickness of 8 nm under condition of 30 mA in 30 s to increase the conductivity of the sample. Sample was first dried under an IR lamp and then was mounted on the SEM stub for micro-structural analysis.

X-ray energy dispersive analysis (EDAX) done using OXFORD Instrument INCAX-sight was used for analyzing elements present in the samples following the same procedure like SEM was followed.

XRD pattern of the sample was recorded at room temperature on a Rigaku X-ray Diffractometer ULTIMA III using Cu target with parallel beam. The scan was recorded in the 2θ range between 10 and 90˚ using sampling width of 0.02˚ and scan speed of 5.0000˚/min.

A JR Prestigi-21 SHIMADZU was used to know the functional group of the sample. First, KBr was used for the initialization of machine. Then sample was taken and mixed with KBr and same procedure was followed. It was then quantified with respect to KBr.

3. Experimental methodology

3.1. Preparation of synthetic adsorbate solution

For the experimental work, adsorbate solution has been prepared synthetically of matching concentration with contaminated ground water i.e. a stock solution of 10 mg/L was prepared by dissolving 0.022 g of NaF in 1 L of distilled water. Among various fluoridated compounds, sodium fluoride is less expensive and less hygroscopic than the related salt potassium fluoride. Solubility of sodium fluoride in water is much higher as compared with calcium fluoride. Because of these advantages over other fluoridated compounds, sodium fluoride was used as the source of fluoride. Final concentration of the prepared stock solution was measured using selective ion electrodes.

3.2. Experimental procedure

For performing the batch adsorption experiment of fluoride onto biochar, a magnetic stirrer (REMI, India) was used. The temperature of the solution was maintained using a water bath. Initially, 10 ppm fluoridated solution was taken and its concentration was confirmed by ion selective electrode. Adsorption experiments were carried out by taking the same concentration of fluoride solution for every run and varying other parameters viz. pH (2–12), adsorbent dose (2–12 g/L), temperature (20–60˚C), contact time (20–180 min), and revolutions per minute (RPM) (100–300) as per designed matrix. After completion of the experiments, samples were collected with time and filtered through 40 micron filter paper. Ten milliliters of each filtered solution was taken and mixed with 1 ml of TISAB buffer for taking the reading of final concentration of fluoride in the wastewater by ion-selective electrode. In the ion-selective electrode, result was shown in millivolt which was equivalent with the concentration. Finally, the obtained concentration value was used to calculate the fluoride percentage removal using Eq. (1)

$$\%\ \text{removal} = \frac{C_0 - C_i}{C_0} \times 100 \tag{1}$$

where C_0 is initial fluoride concentration and C_i is equilibrium fluoride concentration.

3.3. Design of experimental matrix

Quantitative data obtained from the appropriate experiments is used by RSM to estimate the operating condition and regression model equation. It consists of two principle RSMs i.e. central composite rotatable design (CCRD) [44] and Box–Behnken and Doehlert designs among which CCRD finds wide application for designing of an experimental matrix, because it requires minimum number of experimental runs for optimization of independent variables and it is suitable for fitting quadratic surface [45,46]. In general, CCRD consists of 2^k factorial runs with $2k$ axial runs and n_0 center runs and each variable is checked at two levels. Meanwhile, the number of runs for a complete replicate of the design increases steeply with increase in the number of variables k. Individual second-order effects are well estimated by CCRD and it is highly efficient, hence recommended for $k = 5$ in batch study as compared with factorial design; therefore, this method is employed in present study for optimization of the process.

Experimental error and the reproducibility of the data were determined by the center points. The independent variables are coded to the $(-\alpha, \alpha)$ interval where the low and high levels are coded as −1 and +1, respectively. Thus to estimate the influence of various operating parameters, CCRD has been used. The variables studied in batch experiment were pH of the solution (X_1), adsorbent dose (X_2), temperature (X_3), contact time (X_4), and RPM (X_5). For the present study, since the number of independent variables is five, so for each categorical variable, a 2^5 full factorial CCRD consisting of 32 factorial points, 10 axial points and 8 replicates at the center points was employed, indicating that altogether 50 experiments were required for batch study as calculated from the equation given below

$$N = 2^k + 2k + n_0 = 32 + 2 \times 5 + 8 = 50 \tag{2}$$

where N is the total number of experiments and k is the number of factors. Five different levels for each experiment in coded form are $+\alpha$, −1, 0, +1, and $-\alpha$. The value of α depends on the number of points in the factorial portion of the design. α value was fixed as $\alpha = 2.3784$. The relationship between the coded and uncoded form of the variables is

$$\text{Coded value} = x_i = \frac{X_i - \bar{X}_i}{\Delta X} \tag{3}$$

where X_i is actual value of the ith factor in the uncoded units, $\bar{X}_i$ is the average of the low and high values for the ith factor, and ΔX represents the step change.

3.4. Development of an empirical model

Basically, RSM optimization process involves three important steps, performing the designed experiments, estimating the coefficients in a mathematical model, and predicting the response and validation of the model. For batch experiments, the behavior of the system is generally explained by the quadratic equation given below.

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} b_{ij} X_i X_j \tag{4}$$

where Y is the predicted response, b_0 is the offset term, b_i is the linear effect, b_{ii} is the squared effect, b_{ij} is the interaction effect, and X_i and X_j represent the coded independent variables. In this study, a second-order polynomial equation was obtained using the uncoded independent variables as below.

$$\begin{aligned} Y = {} & b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_5 + b_{11}X_1^2 \\ & + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 + b_{55}X_5^2 + b_{12}X_1X_2 \\ & + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{15}X_1X_5 + b_{23}X_2X_3 \\ & + b_{24}X_2X_4 + b_{25}X_2X_5 + b_{34}X_3X_4 + b_{35}X_3X_5 \\ & + b_{45}X_4X_5 \end{aligned} \tag{5}$$

Multiple regression analysis was done to estimate the coefficient of the model equation. Statistical parameters were determined using ANOVA study. Optimization of the present study was done using Design Expert software 8.0 (Stat Ease, USA).

4. Results and discussion

AC prepared from *E. crassipes* stem was characterized and instrumentally analyzed to study its characteristics.

4.1. Physical properties of an adsorbent

Physical properties obtained by the characterization of prepared AC were tabulated in Table 2.

Surface area gives complete idea about adsorption capacity and it was analyzed using gas mixture having composition N_2 29.77% and He 70.23%. Micro-pore volume of an adsorbent significantly affects adsorption and desorption process as compared with total pore volume. It was estimated by changing the composition of a gas mixture (N_2 94.96%, and He 5.04%). Size of adsorbate molecule adsorbing on adsorbent surface was limited by pore volume and the amount of adsorbate molecules adsorbing were limited by the surface area of the adsorbent. Thus, obtained physico-chemical properties of AC prepared from *E. crassipes* stem suggests that it could be a promising adsorbent for the fluoride removal from the wastewater.

Table 2
Physical properties of PAC

Adsorbent	Properties	Results
Activated carbon from *Eichhornia crassipes* stem	Total pore volume	0.3568 cm^3/g
	Micro pore volume	0.2153 cm^3/g
	Surface area	97.68 m^2/g
	Iodine number	654 g/m^3
	Hardness	76.5

4.2. Instrumental analysis of an adsorbent

4.2.1. SEM and EDAX

Surface morphology of AC can be seen from the scanning electron micrographs taken at different magnifications and graph at 5 μm is shown in Fig. 2. Following figures confirm that the activation process was quite effective in developing micro-pores on the external surface. According to the theory of filling, developed micro-pores are directly proportional to the adsorption of fluoride on the surface. Hence, higher the number of micro pores, higher percent removal can be obtained. Energy dispersive analysis of prepared AC was shown in Fig. 3. From graph, it can be revealed that the presence of alkali metals such as calcium, magnesium, and potassium is higher, which helps in the removal of fluoride ion due to its high electronegativity

4.2.2. XRD

XRD pattern of the sample was recorded at room temperature shown in Fig. 4. The inbuilt software package was used to determine the wavelength to compute d-spacing, which was here 1.54059 Å (Cu/K-alpha1). The DIFFRAC^{plus} EVA software uses the fundamental parameter approach and is therefore capable of estimating the instrumental influence. Here, X-ray was passed at an average voltage of 40 kV/30 mA. Attachment used here was standard sample holder. K-beta filter was used. Slit was used at an angle of 2/3° for focusing. Data generated by the software was finally cross-checked with the ICPDE Data Card.

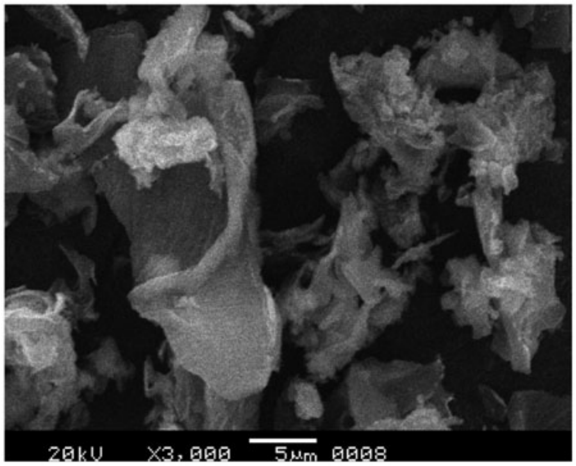

Fig. 2. Scanning electron micrographs of *Eichhornia crassipes* based active carbon at X3,000 5 μm.

4.3. Effects of individual parameters

Literature suggests that removal of F^- from wastewater over activated carbon using adsorption depends very much on the factors such as pH, adsorbent dose, temperature, contact time, and RPM. Therefore, the influences of these parameters were investigated by varying any one of the process parameters and holding the other parameters constant.

4.3.1. Effect of pH

The stability of F^- is dependent on the pH of the system. The effect of solution pH on F^- adsorption was studied using biochar as adsorbent. The experimental results showed that the adsorption was favorable in acidic condition and decreased with increasing

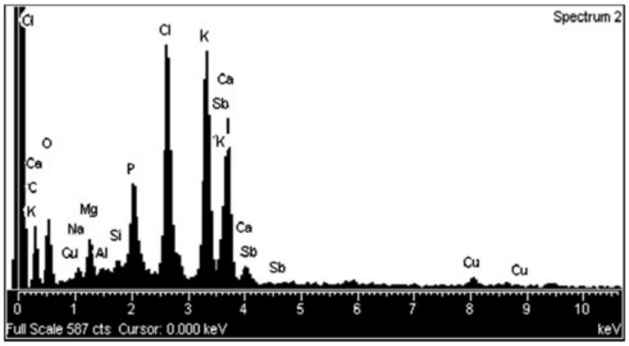

Fig. 3. EDAX of *Eichhornia crassipes* based activated carbon.

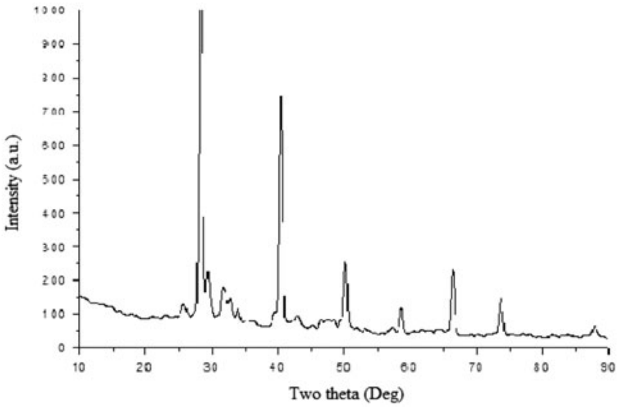

Fig. 4. XRD graph of thermally activated *Eichhornia crassipes*.

pH. The percentage of F^- adsorbed by biochar decreased from 71.74 to 64%, when the pH was increased from 2 to 12. The maximum percent removal was obtained at pH 2. All these experiments were done when the remaining factors were constant such as AC Dose (7 g/L), temperature (40˚C), contact time (100) min, and RPM (200). At lower pH, the F^- ion can easily bind with the H^+ ion. That is why lower pH is suitable for this experiment. But, with the increase in solution's pH, adsorption decreases. This is due to electrostatic repulsion between negative ions at higher pH.

4.3.2. Effect of adsorbent dose

To remove the F^- from wastewater, adsorbent dose is another important factor. With increasing adsorbent dose, percent removal was also increased. Side by side, it can also be seen up to certain level that the removal efficiency was increasing and then it started decreasing. Here, the maximum removal i.e. 65.06% was occurring when the dose was 7 g/L. But, it decreases when the dose was changed up to 12 g/L. In this experiment, the other factors such as pH = 7, temperature = 40˚C, contact time 100 min, and RPM 200 were constant. This may be due to the overlapping of active sites at higher dosage. So, there is no any appreciable increase in the effective surface area resulting due to the conglomeration of particles, thus in lower F^- adsorption.

4.3.3. Effect of temperature

Effect of temperature was same as adsorbent dose. When initially temperature was low, percent of removal was also low. Gradually, it started increasing with increase in temperature showing maximum removal at 40˚C. Then it started decreasing and at 59.03˚C, it removed 63.8% fluoride from the wastewater. Other factors which remain constant during the experiment were pH = 7, adsorbent dose = 7 g/L, contact time = 100 min, and RPM = 200. At lower temperature, Vander wall's forces works slowly. Interaction was not proper between the adsorbent and adsorbate. It can only be possible at medium range of temperature. Likewise, at higher temperature, ionic bond breaks and adsorption efficiency decreases.

4.3.4. Effect of contact time

Time is also a considerable factor in this experiment. When the experiment was run for 100 min, it removed maximum F^- and it was 65.6%. Lowest amount of fluoride was removed at 21.51 min contact and it was 35%. Here the constant factors were pH = 7, adsorbent dose = 7 g/L, temperature = 40˚C, and RPM = 200. At higher contact time, F^- ions get sufficient time to bond with adsorbent surface and as Vander wall's forces are responsible for the binding of adsorbate over adsorbent surface, it requires enough time for the maximum removal, which is not possible at lower contact time.

4.3.5. Effect of RPM

RPM is also having great impact on removal efficiency as contact time. From the experiments, it has been observed that when the pH, adsorbent dose, temperature, and contact time were fixed and set at 7, 7 g/L, 40˚C and 100 min, respectively, then at 200 RPM, it shows maximum fluoride removal. But if RPM increased above 200, then due to weak binding forces between adsorbate and adsorbent some adsorbed F^- ions gets detached from the surface resulting in decreased removal efficiency.

4.4. Combine effects of process parameters

Probable permutations and combinations obtained through design matrix developed by CCRD shown in Table 3 were used to perform batch-wise experimentation for deflouridation of waste water.

4.4.1. Response surface plots

To study the interaction of independent process parameters from the graphical interpretation of the parameters vs. responses, it is highly recommended to use 3D plots of regression model equation. Circular

Table 3
Experimental design matrix

Run no.	pH	AC dose (g/L)	Temp. (˚C)	Contact time (min)	RPM	Removal %
1	9.00	9.00	32.00	133.00	160.00	52.09
2	9.00	9.00	32.00	67.00	240.00	52.79
3	7.00	7.00	40.00	100.00	200.00	65.96
4	7.00	7.00	40.00	100.00	200.00	65.28
5	5.00	5.00	32.00	67.00	240.00	49.79
6	9.00	9.00	48.00	67.00	160.00	56.1
7	9.00	9.00	48.00	67.00	240.00	59.54
8	7.00	7.00	40.00	100.00	200.00	65.2
9	9.00	5.00	48.00	67.00	240.00	61.15
10	7.00	7.00	59.03	100.00	200.00	68.1
11	5.00	9.00	48.00	133.00	160.00	64.27
12	5.00	9.00	32.00	133.00	160.00	61.74
13	9.00	9.00	48.00	133.00	160.00	59.52
14	7.00	7.00	40.00	100.00	200.00	65.76
15	5.00	5.00	48.00	67.00	160.00	49.46
16	7.00	7.00	40.00	21.51	200.00	39.38
17	7.00	7.00	40.00	100.00	295.14	51.58
18	5.00	5.00	48.00	133.00	160.00	52.79
19	9.00	9.00	32.00	133.00	240.00	55.4
20	5.00	5.00	48.00	67.00	240.00	51.46
21	5.00	5.00	32.00	133.00	160.00	51.02
22	9.00	5.00	48.00	67.00	160.00	58.76
23	5.00	5.00	32.00	67.00	160.00	47.39
24	7.00	11.76	40.00	100.00	200.00	60.97
25	9.00	5.00	48.00	133.00	240.00	64.76
26	7.00	7.00	40.00	100.00	200.00	65.76
27	5.00	9.00	32.00	67.00	240.00	60.41
28	7.00	7.00	40.00	100.00	200.00	65.28
29	2.24	7.00	40.00	100.00	200.00	68.24
30	5.00	9.00	48.00	67.00	160.00	61.65
31	7.00	7.00	40.00	100.00	104.86	45.43
32	5.00	5.00	48.00	133.00	240.00	54.81
33	9.00	5.00	32.00	67.00	240.00	55.26
34	5.00	9.00	32.00	67.00	160.00	58.61
35	11.76	7.00	40.00	100.00	200.00	66.2
36	5.00	5.00	32.00	133.00	240.00	47.19
37	9.00	9.00	32.00	67.00	160.00	49.98
38	9.00	5.00	32.00	133.00	240.00	58.06
39	7.00	7.00	20.97	100.00	200.00	57.64
40	9.00	5.00	32.00	133.00	160.00	54.17
41	7.00	7.00	40.00	100.00	200.00	66.54
42	5.00	9.00	48.00	67.00	240.00	63.3
43	7.00	7.00	40.00	100.00	200.00	65.76
44	7.00	7.00	40.00	178.49	200.00	46.45
45	5.00	9.00	32.00	133.00	240.00	62.91
46	9.00	5.00	32.00	67.00	160.00	52.76
47	9.00	9.00	48.00	133.00	240.00	62.25
48	5.00	9.00	48.00	133.00	240.00	70.09
49	7.00	2.24	40.00	100.00	200.00	49.25
50	9.00	5.00	48.00	133.00	160.00	60.98

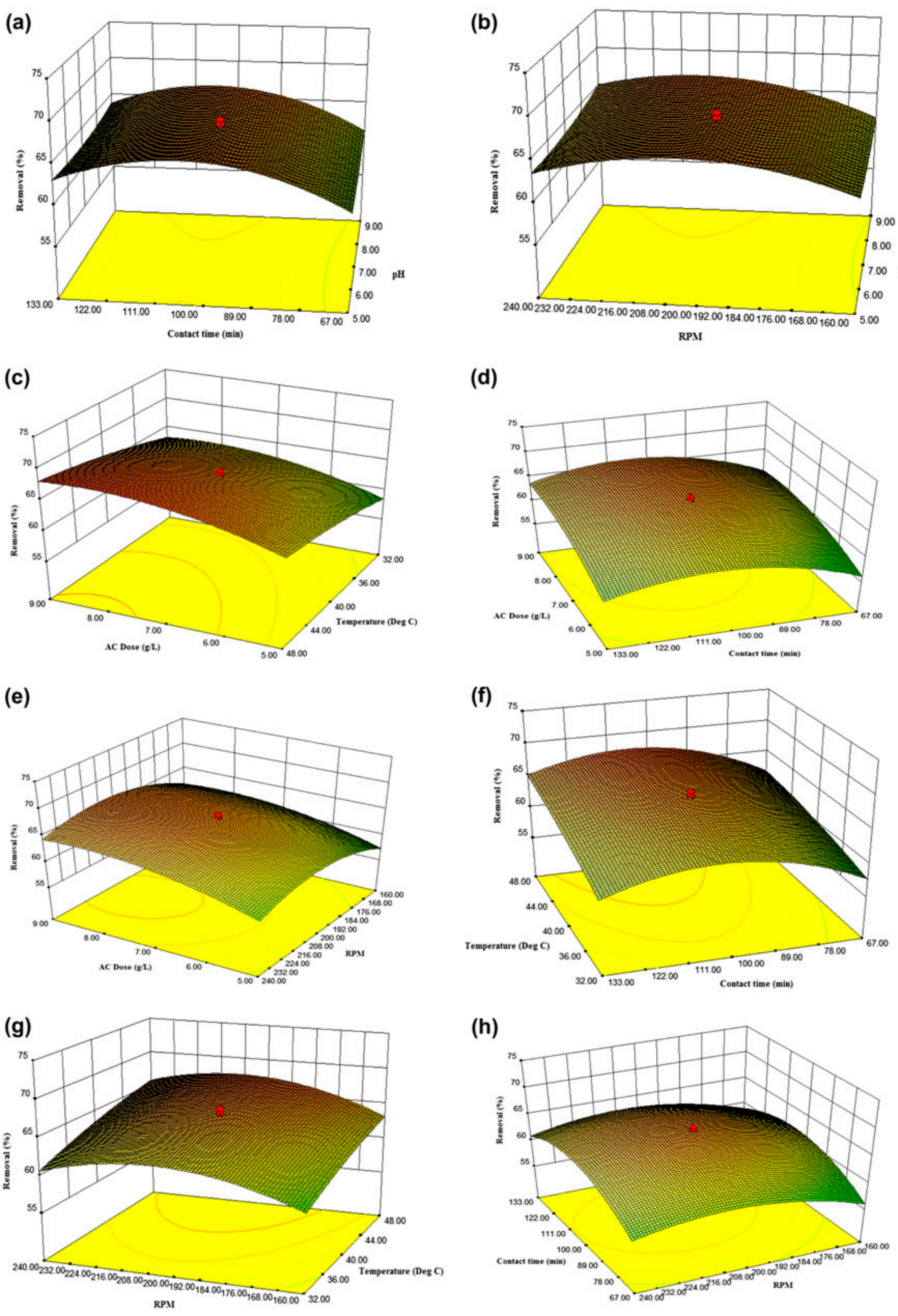

Fig. 5. (a–h) Response surface plots to study combined effects of process parameters on removal efficiency.

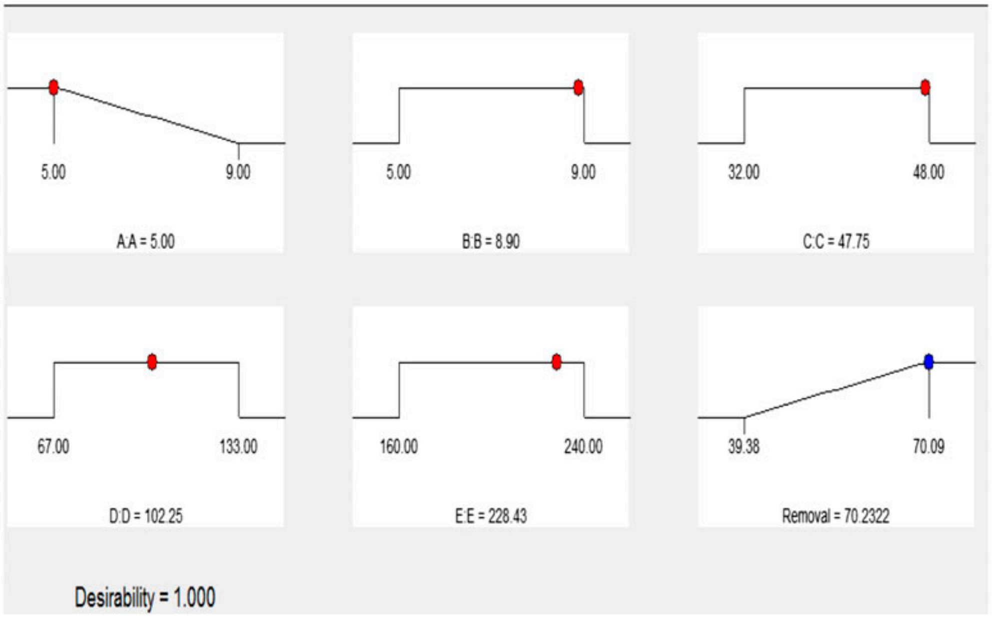

Fig. 6. Optimized process conditions.

Table 4
Model validation parameters vs. % removal

Model validation parameters					% Removal	
pH	AC dose (g/L)	Temp. (℃)	Contact time (min)	RPM	Predicted	Actual
5	9	48	117	208	70.301	70.136

contour plots obtained imply that the interactive effects between the parameters were difficult to predict and optimize.

Combined effects of two independent parameters on removal efficiency were clearly shown by surface plots in Fig. 5(a)–(h). Rate of fluoride removal is significantly dependent upon pH and RPM, and it has been observed that at nearly neutral pH values and RPM of 196, maximum fluoride removal was about 65–70%. When the effect of contact time was observed in combination with pH, then maximum removal was obtained nearly 70% at contact time of 110 min and pH (8–9). As adsorbent dose and temperature also have severe impact on the percent removal, hence the combined effect of these two parameters were studied and 3D surface plot shows that maximum removal of 60–65% can be obtained at a combination of temperature 40℃ and adsorbent dose of 7 g/L. Surface plot, obtained to study the effect of adsorbent dose and contact time shows that maximum removal can be observed at 7 g/L and 100 min, respectively. Combination of parameters such as contact time and RPM having less impact on the removal efficiency and maximum value can be obtained at 100 and 200 min, respectively.

4.5. Optimum condition

From the above study, it was found that the maximum adsorption of F^- from the simulated feed was achieved by varying pH, AC dose, temperature, contact time, and RPM. The initial fluoride concentration and temperature does not contribute much to the process and can be ignored. Thus in order to remove F^- from aqueous solutions efficiently by adsorption onto AC, a low pH and high AC dose is needed. Finding the optimum batch time is also vital for batch adsorption study. The optimum operating conditions suggested by DOE model for the five variables are shown in Fig. 6.

pH: 5, AC dose: 8.51 g/L, temperature: 47.77℃, contact time: 116.84 min, RPM: 207.76, removal: 70.301, and desirability: 1.000.

Table 5
ANOVA for response surface quadratic model

Source	Sum of squares	df	Mean square	*F*-value	*p*-value	Prob > *F*
Model	2,548.16	20	127.41	190.55	<0.0001	Significant
A-A	4.78	1	4.78	7.15	0.0122	
B-B	256.51	1	256.51	383.63	<0.0001	
C-C	244.40	1	244.40	365.52	<0.0001	
D-D	75.39	1	75.39	112.76	<0.0001	
E-E	55.88	1	55.88	83.57	<0.0001	
AB	406.05	1	406.05	607.29	<0.0001	
AC	22.93	1	22.93	34.30	<0.0001	
AD	0.066	1	0.066	0.098	0.7562	
AE	7.15	1	7.15	10.70	0.0028	
BC	0.028	1	0.028	0.042	0.8387	
BD	0.73	1	0.73	1.09	0.3050	
BE	0.57	1	0.57	0.85	0.3636	
CD	2.62	1	2.62	3.91	0.0575	
CE	1.31	1	1.31	1.96	0.1725	
DE	0.36	1	0.36	0.54	0.4669	
A2	20.26	1	20.26	30.30	<0.0001	
B2	196.58	1	196.58	294.00	<0.0001	
C2	14.40	1	14.40	21.54	<0.0001	
D2	905.46	1	905.46	1,354.19	<0.0001	
E2	516.40	1	516.40	772.32	<0.0001	
Residual	19.39	29	0.67			
Lack of fit	18.00	22	0.82	4.13	0.0304	Significant
Pure error	1.39	7	0.20			
Cor. total	2,567.5	49				

4.6. Model validation by experiments

Taking this optimum condition, three runs were performed in laboratory and the results are shown in Table 4. From the values obtained, it can be said that the chosen model is valid to perform the deflouridation experiment.

4.7. Development of regression model equation

An experimental result reveals that all the five parameters viz. pH, AC dose, temperature, contact time, and RPM significantly affect removal efficiency. Hence, all these parameters were considered for the development of regression model equation. Correlation between independent parameters and removal efficiency was developed by CCRD approach and numerical values of coefficients of equation were tabulated in Table 5.

$$
\begin{aligned}
\%\ \text{removal} = {} & -115.04090 + 0.91968 \times A + 13.39700 \\
& \times B + 0.31520 \times C + 0.73333 \times D \\
& + 0.72026 \times E - 0.89055 \times A \times B \\
& + 0.052910 \times A \times C + 6.86553E - 004 \\
& \times A \times D + 5.91016E - 003 \times A \times E \\
& + 1.85547E - 003 \times B \times C + 2.28693E \\
& - 003 \times B \times D + 1.66797E - 003 \times B \times E \\
& + 1.08310E - 003 \times C \times D + 6.31836E \\
& - 004 \times C \times E - 8.07292E - 005 \times D \times E \\
& + 0.15094 \times A^2 - 0.47021 \times B^2 \\
& - 7.95385E - 003 \times C^2 - 3.70673E - 003 \\
& \times D^2 - 1.90528E - 003 \times E^2
\end{aligned}
\tag{6}
$$

Table 6
Statistical parameters

Std. dev.	0.82	*R*-squared	0.9924
Mean	58.00	Adj. *R*-squared	0.9872
CV %	1.41	Pred. *R*-squared	0.9753
Press.	63.34	Adeq. precision	56.947

4.8. Analysis

ANOVA study was done to estimate the significance of process variables and to check the validity of regression model equation. From the Fisher's statistical test (*F*-test) value of ANOVA study, significance of the corresponding parameters can be stated. When the *F*-value

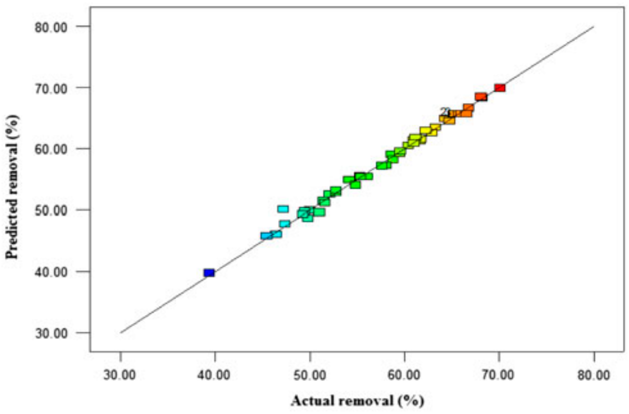

Fig. 7. Actual vs. predicted data.

is higher, its corresponding variable is said to be more significant. Probability *p*-value was determined and its lower value implies high significance of its corresponding variable. In determination of significance of any variable, sum of squares also plays vital role and its higher value implies higher significance of its corresponding variable. From the ANOVA, all the above-stated variables are determined and tabulated in Table 5.

From the table, it is clearly observed that higher sum of squares (2,584.16), higher *F*-value (190.55), and lower *p*-value (<0.0001) states that pH is more significant. It noticeably indicates that model terms are highly significant that appreciably explains the interaction between pH and fluoride removal efficiency. Another approach for the analysis of the process is checking the lack of fit value and the present study shows LOF value 4.13, which implies that it is significant. There is a 3.04% chance for such large LOF value to occur. From Table 6, it was observed that adj. *R*-squared value (0.9872) is in reasonable agreement with pred. *R*-squared (0.9753). Adeq. precision value measures the signal-to-noise ratio and present analysis gives 56.946 adeq. precision which is much higher than the desired value that indicates much adequate signals. *R*-squared value obtained as 0.9924 is very near to unity and shows that regression model is much significant. The graph of predicted values from model equation and actual values of flouride removal calculated from Eq. (1) is shown in Fig. 7.

5. Conclusion

The present investigation was carried out to study the removal of F^- from aqueous solutions using adsorption over AC developed through steam activation of carbonized *E. crassipes* stem and to conduct batch process optimization using RSM for finding the optimum values of parameters affecting the process to achieve maximum removal efficiency. Study showed that in case of batch adsorption experiments, parameters like pH, powdered activated carbon (PAC) dose, temperature, contact time, and RPM highly influence the adsorption process.

Maximum fluoride removal by adsorption process was obtained at pH, temperature 40° C, AC dose 7 g/L, RPM 200, in 100 min. The parameters were also calculated using the experimental data. A CCRD was constructed to determine the effect of these five significant parameters on the adsorption of F^-. Combine effects of all the parameters on removal process were explained through response surface plots. The RSMs were thoroughly analyzed. ANOVA study showed that interaction terms were not important for regression model. ANOVA study also showed that the chosen model is significant to fit the experimental data. Model validation was also done by carrying out experiments, and results conclude that predicted result from the model and result obtained from the experiments are nearly equal which confirms the validity of chosen model.

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