Defluoridation of Water by Using Modified Material Developed from *Ficus benghalensis* Leaf: Characterization, Kinetic and Thermodynamic Study

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Abstract. In the present study, microwave-assisted and chemically treated carbonized *Ficus benghalensis* leaf (MACFBL) material was used as an adsorbent material for the removal of fluoride from water. The results of the characterization of MACFBL carbon material exhibited ideal adsorbent properties. The fluoride adsorption experiments were performed under the batch mode to improve the different affecting parameters such as contact time (0-300 min) and temperature (303-343K) at predetermined pH (5), agitation speed (120 strokes/min), fluoride concentration (2 mg/L) and adsorbent dose (5 g/L). The maximum fluoride removal efficiency of fluoride on MACFBL material was found 86.5%. The fluoride adsorption data applied for four well known kinetic models such as pseudo first-order, pseudo second-order, intra-particle diffusion, and Elovich kinetic models. The pseudo second-order kinetic study shows the most favourable mechanism for the removal of fluoride. Thermodynamic investigation proposed that the fluoride adsorption process onto MACFBL was exothermic. The instrumental study of MACFBL adsorbent material before and after adsorption during FTIR, SEM, EDX and XRD techniques established the fluoride adsorption on the carbon surface. The developed adsorbent material (MACFBL) is efficient for the removal of fluoride.

1. Introduction

The rise in high concentrations of fluoride in groundwater is of significant concern worldwide due to natural and anthropogenic actions contributing to health threats for the human population [1,2]. In general, fluoride in ground is derived through the degradation of distinctive natural minerals found in the different soils and rocks with which the water interacts[3]. Fluoride can, other than natural sources, originate in effluents from the semiconductor, metal processing, fertilizer and glass manufacturing industries [4,5]. The maximum allowable limit of fluoride content in drinking water for a human being is 1.5 mg / L, as set by the Bureau of Indian Standards (BIS) and WorldHealth Organization (WHO) [6,7]. Fluoride is an extremely toxic ion at concentrations greater than the allowable level and may contribute to multiple health issues, such as skeletal fluorosis, dental fluorosis, neurological injury, osteoporosis, parathyroid damages, Alzheimer's disease, male infertility, thyroid and kidney problems, liver damage, etc.[8].

In many developed and developing countries, including Asia, the USA, and Africa, higher fluoride concentrations in groundwater have been recorded. It has been found that with excess fluoride concentration, 17 different states of India are strongly affected, particularly AndhraPradesh, Telangana, Rajasthan, Madhya Pradesh, Gujarat, Assam, Uttar Pradesh and Tamilnadu [9, 10]. Owing to their adverse effects on humanwellbeing and the environment, various methods for the expulsion of...
fluoride from water have been developed over a few decades. That includes ultrafiltration, separation of solvents, sedimentation, absorption, coagulation, reverse osmosis, electrodialysis, ion exchange, adsorption, etc. [11, 12, 13]. In view of its low-cost installation, quick and simple maintenance, effective efficiency and fast operating procedure, adsorption is extensively considered and adopted among all these methods [12, 13].

The condition of excess fluoride content in drinking water is increasing gradually, and commonly used adsorption methods have been used to conduct water defluoridation. In recent years, activated carbons and various unconventional biomass materials such as Citrus limonum (lemon) leaf [3], KOH-treated Syzygium cumini Seed [10], Sawdust [11], tree bark [14], leaves [15], fruit shell / peel [16] and fruit seed [17] have been investigated and recorded for fluoride removal due to their low cost, simple availability in large amounts and effective fluoride removal. Industrial activated carbon treated with sugarcane bagasse[18], Hyacinth beads [19], aluminium impregnated coconut fibre [20], Camellia oleifera seed shell,[21], Santalum Album Leaf Powder[22], Al-impregnated Eucalyptus bark[23], Tea waste biomass[12, 24] and various carbon material identified by researchers for defluoridation of water [25]. The purpose of the present study is to set up and investigate the kinetic and thermodynamic efficacy of non-conventional adsorbent material obtained for the removal of fluoride from the aqueous solution using Ficus benghalensis leaves.

2. Material and Method

Analytical grades chemicals were used in the present work, such as sodium hydroxide, acetic acid, hydrochloric acid, nitric acid, sulphuric acid, sodium fluoride, sodium bicarbonate, sodium sulphate, sodium chloride, sodium phosphate, potassium hydroxide, sodium nitrate, 1, 2-cyclohexane dianineteraactetic acid (CDTA) and these chemicals were acquired from S-D Fine Chemicals Ltd or Merck India Limite Ltd.

2.1. Preparation of Adsorbent

The Ficus benghalensis leaf collection was taken from the neighbourhood area. To extract dust and additional impurities, it was washed with water. It was ground using a home blender after air drying and then sieved through a mesh size of 300. The leaf sample was rinsed with double distilled water and was dried for 24 hours in an oven at 80 °C. The resulting dried leaf powder of Ficus benghalensis was carbonised in the muffle furnace at 500 °C for 5 hours. This carbonised leaf powder was again triggered for 30 minutes at one-minute intervals in a domestic microwave (900MW). The microwave-assisted carbonised leaf powder was then individually impregnated for 24 hours with 0.5 N sodium hydroxide and 0.5 N sulfuric acid. With double purified water, the resulting carbon material was washed until a stable pH of the slurry was produced. Finally, the carbon sample was dried in a vacuum oven at 110 °C, mashed well and kept for future use in airtight plastic containers. Microwave-assisted carbonised Ficus benghalensis leaf is the activated material developed from the Ficus benghalensis leaves and was referred to as MACFBL subsequently (Figure 1).

2.2. Characterization of adsorbent

2.2.1. Proximate analysis

Physico-chemical parameters of MACFBL were studied, like pH, moisture, ash, volatile matter, bulk density, fixed carbon, water, and acid-soluble matter of MACFBL were examined. The results of the ultimate analysis were summarized in Table 1. Using the Elico pH metre, model LI-120, the pH of the
MACFBL bio adsorbent material was determined and other parameters were evaluated by utilizing standard analytical test methods [28, 29, 30].

![Image of Ficus benghalensis leaves, dry crushed leaves, untreated leaf powder, and activated carbon](image)

**Figure 1:** Graphical representation of the development of carbon material (MACFBL)

### 2.2.2. Ultimate analysis.

The Brunauer-Emmett-Teller (BET) surface area pore characteristics were analyzed by using a Quanta Chrome Nova-1000 surface analyzer instrument using a computer and software-controlled nitrogen gas adsorption analyzer at -196°C. Using the Elementar Vario EL III model (C-H-N Analyser), the elements like C, H, N, and S were analysed. Scanning Electron Microscopy (SEM) (JEOL Model JSM-6390LV) was used for the study of MACFBL’s microstructure morphology. Electron dispersive X-ray (EDX) (JEOL JSM-7600F FEG-SEM model) was used for the element and chemical classification of the developed MACFBL material. The FTIR spectra were obtained by using Fourier-Transform-Infrared-Spectrophotometer (Thermo Nicolet, Avatar 370) with KBr. The FTIR spectra give information about the characteristic functional groups on the MACFBL bio-adsorbent material. The Structural integrity of the bio-adsorbent samples was checked by Powder X-ray diffraction (Model: Bruker AXS D8 Advance diffractometer).

### 2.3. Batch adsorption experiments

The developed MACFBL carbon material was used for the defluoridation of water by batch adsorption experiments at different initial concentrations of fluoride (2 mg/L to 10 mg/L). The 50 ml of known synthetic fluoride concentration solutions were taken for a batch test in 100 ml of Erlenmeyer flask and were shaken at 120 strokes/min for prearranged contact time, adsorbent dose, temperature and pH. The fluoride concentrations before and after adsorption were estimated by utilizing fluoride ion-selective electrode (HANNA Model No. H I 4110) and ion-selective meter (HANNA Model No. HI 4522). The adsorption capacities of fluoride were determined by the equation (1):

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

(1)

Where m, V, C0, Ce and qe are the mass of adsorbent (g), the volume of the sample solution (L), initial concentration of fluoride (mg/L), fluoride concentration at equilibrium (mg/L) and amount of fluoride adsorbed at equilibrium (mg/g), respectively. The fluoride removal efficiency from the water was evaluated by equation (2):

$$\text{% Removal of fluoride} = \frac{(C_0 - C_e)}{C_0} \times 100$$  

(2)

The impacts of agitation speed, adsorbent dose, contact time, pH, temperature and initial fluoride concentration have been considered for fluorideremoval from the aqueous solutions by
utilizing MACFBL material. The kinetic of fluoride adsorption was studied by applying four different models, e.g., pseudo first-order, pseudo second-order, Elovich and Intra-particle diffusion models\[Table 1\]. The thermodynamic analysis for enthalpy change, entropy change and free energy change was carried out on the fluoride adsorption on MACFBL carbon material. Finally, fluoride desorption study and impact of various counter anions has been investigated for the removal of fluoride onto MACFBL material.

\[Table 1.\] Empirical kinetic equations and its parameters [31, 32].

| Kinetic Models | Kinetic equations | Equation Numbers |
|----------------|-------------------|------------------|
| Pseudo first-order kinetic model | \( \log(q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t \) | (3) |
| Pseudo second-order kinetic model | \( \left( \frac{t}{q_t} \right) = \left( \frac{1}{k_2 q_e^2} \right) + \left( \frac{1}{q_e} \right) t \) | (4) |
| Intra-particle diffusion model | \( q_t = k_d t^{1/2} + C \) | (5) |
| Elovich kinetic model | \( q_t = \left( \frac{1}{B} \right) \ln AB + \left( \frac{1}{B} \right) \ln t \) | (6) |

4. Result and Discussion

4.1. Characterization of adsorbent material
Table 2. provides the physicochemical characterization results of the chemically activated microwave-assisted carbonized Ficus benghalensis leaf (MACFBL), i.e. the proximate and ultimate analysis. The Physico-chemical results obtained by characterization of MACFBL shows that the chemical activation and microwave treatment achieves the tremendous adsorbent carbon material required for fluoride adsorption.

4.2. Fourier transforms infrared (FTIR) study
Figure 2(a) displays the FTIR spectrum of the MACFBL carbon material before and after fluoride adsorption. The number of peaks reflects MACFBL's adsorptive existence. The peaks in the region 3700 to 3400 cm\(^{-1}\) is because of the existence of \( –N-H \) and \( –O-H \) stretching vibrations. The peaks in the region 2900 to 2500 cm\(^{-1}\) represents the \( –CH_2 \) symmetrical and asymmetrical stretching. The peak region from 1700 to 1400 cm\(^{-1}\) reveals the appearance of the carbonyl group of ketones, esters and amide. The peaks due to \( –N-H \) deformation and bending were observed in the region 1400 to 1500 cm\(^{-1}\). Around 1200 to 500 cm\(^{-1}\) position, peaks observed due to the existence of \( –C=S, -C-N, –C-H \) -C-O and -C-C- stretching vibrations and deformations. The shift in peak values and intensity band decrease might be because of the appearance of a chemical relationship between the functional groups which is in attendance on the surface of MACFBL. The shifts in the spectra demonstrate that MACFBL will be a helpful adsorbent material in the fluoride adsorption process. The IR band which either disappeared or decreases/increases in intensity after adsorption may engage in fluoride binding. Similar perceptions are accounted for by various scientists for fluoride adsorption [29, 30, 31, 32].
Table 2. Proximate and Ultimate analysis of MACFBL material

| Sr. No. | Parameters                          | Values  | Sr. No. | Parameters          | Values  |
|---------|-------------------------------------|---------|---------|---------------------|---------|
| 1       | Bulk density (gm.cm⁻³)              | 0.39    | 1       | Carbon %            | 39.74   |
| 2       | Moisture content %                  | 4.28    | 2       | Hydrogen %          | 1.09    |
| 3       | Ash content %                       | 14.73   | 3       | Nitrogen %          | 0.55    |
| 4       | Volatile matter content %           | 32.65   | 4       | Sulphur %           | 00      |
| 5       | Fixed carbon content %              | 48.34   | 5       | Oxygen %            | 58.62   |
| 6       | pH                                  | 7.63    | 6       | Surface Area (m².g⁻¹)| 109.41  |
| 7       | Water Soluble Matter (%)            | 1.24    | 7       | Average Pore Diameter (Å) | 90.72  |
| 8       | Acid soluble matter (%)             | 3.73    | 8       | Total Pore Volume (cc.g⁻¹) | 0.248  |

4.3. X-ray diffraction (XRD) study
The XRD spectrum of MACFBL adsorbent before and after the removal of fluoride as presented in Figure 2(b). The strong main peak indicates the existence of a very much organized crystalline structure and noises in the XRD patterns show the amorphous nature of carbon material before and after fluoride adsorption. The strength of the well-structured peaks is also diminished to some extent. The XRD spectrum shows the fluoride adsorption was recognized by the physisorption process on the upper part of the MACFBL surface [32, 33].

![Figure 2](image1.png)  
**Figure 2.** (a) Fourier-Transform-Infra-red (FTIR) spectra, (b) X-ray diffraction spectra of MACFBL before and after removal of the fluoride.

4.4. Scanning electron microscope (SEM) study
SEM micrographs of the MACFBL material before and after the adsorption of fluoride are seen in Figure 3 (a, b). SEM pictures of MACFBL shows that the adsorbent material has a rough surface with nearly non-compact structure. It is apparent that the adsorbent has a significant number of pore spaces, where proper conditions exist for fluoride ions to be caught and adsorbed into these pores. The bright spot demonstrates the existence of tiny holes on the crystalline structure of activated carbon material and after handling with fluoride the bright spots converts the black suggests the adsorption of the fluoride on the carbon surface through the physisorption process [30, 32, 33, 34].
4.5. Energy-Dispersive X-ray (EDX) study
The EDX outcomes of the MACFBL material shown in Figures 3(a) and 3(b) indicate the variations between the number of elements in the adsorbent carbon material before and after adsorption of the fluoride. The fluoride content found in the EDX pattern for adsorbent material after contacting with adsorbate in aqueous solution indicates towards the adsorption of fluoride.

![Figure 3. SEM-EDX monograph of MACFBL (a) before and, (b) after fluoride adsorption.](image)

4.6. Effect of the contact time
The impact of the contact time on MACFBL was considered by varying the contact time from 30 min to 300 min for 2mg/l -10 mg/L fluoride concentrations by keeping other adsorption parameters constants (Figure 4). Adsorption of fluoride started at 30 min with 51.50 % and reached 86.50% at 150 min and the amount of fluoride adsorbed was 0.360 mg/g. No major improvement in the adsorption of fluoride was detected after 150 min. The underlying fast rate of adsorption of fluoride was might be due to the existence and of the availability of the extensive surface of the adsorbent material for fluoride particles present in the aqueous solution. The later moderate fluoride adsorption rate was might be because of the electrostatic obstruction due to already adsorbed fluoride ions and moderate pore diffusion of the particles [35,36]. So up to the contact time of 150 min the 86.50 % fluoride adsorption happens and after 150 min, the adsorption was expanded but the rate of adsorption was moderate as compared with the early rate of adsorption and the equilibrium point was occurred after 300 min. As a result, the minimum contact time for maximum fluoride reduction on the MACFBL adsorbent material was set at 150 minutes. A similar interpretation was achieved for the fluoride removal for initial concentrations of fluorides of 4mg/L, 6mg/L, 8 mg/L, and 10mg/L, but, there was a decline in per cent removal efficiency of fluoride.
Figure 4. Effect of contact time on the fluoride adsorption by MACFBL.
(pH: 5, adsorbent dosage: 5 g/L, agitation speed: 120 strokes/min, initial fluoride concentration: 2 - 10 mg/L, temperature: 303 K)

4.7. Kinetics study for fluoride adsorption
The kinetic examination into the adsorption of fluoride from water plays an important role since it gives a significant understanding into the response pathways and mechanisms of the adsorption process of fluoride. With pseudo first-order, pseudo second-order, Intra-particle diffusion and Elovich models, the potential rate-restricting strides and probable kinetic mechanism of the adsorption of fluoride on MACFBL carbon material were investigated. Table 1 describes the observed kinetic equations and kinetic parameters of adsorption kinetic models for fluoride removal.

4.7.1. Pseudo first-order kinetic model for fluoride adsorption
Figure 5 presents a plot of log (q_e - q) against t. The plot shows a straight line for the first-order kinetics process, and Table 3 shows the outcomes of the fluoride adsorption on MACFBL. Using equation 3, the pseudo first - order rate constant (k_1) and the equilibrium adsorption power (q_e) were determined at different fluoride concentrations along with the correlation coefficients (R^2). The first-order rate constant (k_1) values are extending from 0.520 to 0.620 min^{-1} over the fluoride concentration range from 2 mg/L to 10 mg/L. A wide dissimilarity involving between the theoretical values and experimental values of equilibrium fluoride adsorption capacity, q_e, is seen from the kinetic results (Table 3) in the fluoride concentration range (2 mg / L-10 mg / L), suggesting weak applicability of the pseudo first - order kinetic model to the experimental results.

4.7.2. Pseudo second-order kinetics model for fluoride adsorption
The pseudo second-order kinetic model parameters of fluoride adsorption were estimated by utilizing empirical equation 4. The linear plot of t/q against t at various fluoride concentrations (from 2 mg/L to 10 mg/L) is made known in Figure 6. The second-order rate constant (k_1) for fluoride adsorption, and the equilibrium fluoride adsorption capacity (q_e) are calculated from the plot of t/qt against t. Table 3 describes the respective approximate parameters of the second order kinetic model. It is evident from the kinetic results that, relative to the pseudo-first - order kinetic model, the pseudo-second - order kinetic model displayed excellent linearity with admirable correlation coefficient
values (R² > 0.992) at the fluoride concentration tested. With only minor variations, the qₑ values calculated from the second-order kinetic plots are incredibly similar to the experimental values of qₑ. This demonstrates that the mechanism of fluoride adsorption fits the kinetic pseudo second-order relation. The pseudo second-order fluoride adsorption rate constant, k₂, values ranging in between 0.322 g mg⁻¹ min⁻¹ to 0.899 g mg⁻¹ min⁻¹.

Figure 5. Linear Plots of the Pseudo first-order kinetic for fluoride adsorption on to MACFBL.

4.7.3. Intra-particle diffusion model for fluoride adsorption
The relationship based on the elimination of contaminants from aqueous solution was examined using the Weber-Morris intra-particle diffusion model. The linear plot results (Figure 7) obtained by the use of equation 5 and Table 3 refer to the external take-up of the surface. It may suggest that intra-particle diffusion was involved in the adsorption of fluoride on the surface of MACFBL. Based on these findings, but it was not the sole rate-determining step and that during fluoride adsorption, various other system processes often took part. The kinetic plot in the present case shows reasonably high rate coefficients and also better linearity. The comparative pattern has been reported for fluoride adsorption by researchers [36, 37, 38].

4.7.4. Elovich kinetic model for fluoride adsorption
In order to validate the suitability of the Elovich kinetic equation (Figure 8 and Table 3), the adsorption of the fluoride from the aqueous solution into the MACFBL carbon material, a linear plot of qₑ versus Log t at various contact time for the removal of the fluoride is examined. From the intercept and slope of the linear plot, the parameters of the Elovich kinetic constants A and B were estimated. The correlation coefficient values (R² = 0.937-0.984) over the initial fluoride concentration range for the Elovich equation indicate that fluoride diffusion fits the kinetic process proposed by the Elovich model and the rate-deciding step is the diffusion in nature [39]. In fluoride adsorption to the surface of MACFBL adsorbent material, this diffusional rate-limiting mechanism is more clearly identifiable.
Figure 6. Linear plots of the Pseudo second-order kinetic for fluoride adsorption on to MACFBL.

Figure 7. Linear plots of the Intra-particle diffusion model for fluoride adsorption on to MACFBL.
4.8. Effect of temperature on fluoride adsorption
The analysis of the impact of temperature variation is significant in order to find out the viability of the fluoride adsorption process. The impact of temperature on the evacuation of the fluoride using MACFBL material was examined by performing the adsorption experiments at four different temperatures 303, 313, 323 and 333 K, by keeping other parameters constant for initial concentration of the fluoride from 2 mg/L to 10 mg/L. The fluoride adsorption potential was found to decrease from 0.360 mg/g to 0.272 mg/g with an initial fluoride concentration of 2 mg/L as the temperature increased from 303 K to 333 K. (Table 4 of Figure 9). Comparative patterns were found for higher fluoride concentrations. This indicates that the mechanism of the fluoride adsorption is an exothermic process [40]. It is seen in Figure 3.21 that low temperatures favour the elimination of fluoride. This may be due to the tendency for the fluoride ions to break apart with an expansion of the aqueous solution temperature from the solid phase to the bulk phase [36, 40].

4.9. Thermodynamic study
Thermodynamic parameters such as free energy change (ΔG), enthalpy changes (ΔH) and entropy change (ΔS) can be calculated by using equations (7), (8), (9) for the thermodynamic analysis to learn the feasibility of the adsorption of fluoride. In order to discover the values of ΔS and ΔH from the slope and intercept (Figure 10), a linear plot of Log K versus 1/T can be applied. Table 4 displays the Gibbs free energy (ΔG) for the adsorption of fluoride on MACFBL carbon content at all temperatures. The outcomes of the thermodynamics investigation describe the estimated values of ΔH, ΔG, and ΔS. The negative values of enthalpy change have shown the exothermic and random existence of the mode of adsorption[41], and the negative values of entropy change have shown that the process of adsorption is enthalpy-driven[41]. For the lower temperatures and lower fluoride concentrations, the ΔG values observed in the present sample were negative. The change in free energy (ΔG) values was positive as the temperature expanded and the adsorption turned out to be less ideal. The present research showed that at a lower temperature, the fluoride adsorption mechanism was more favourable.
and feasible. Comparable negative and positive estimates of $\Delta G$ for adsorption of fluoride on various adsorbents have been reported by researchers [41, 42].

![Figure 9. Effect of the temperature on the fluoride adsorption by MACFBL.](image)

**Figure 9.** Effect of the temperature on the fluoride adsorption by MACFBL.

- **Initial concentrations:** 2 – 10 mg/L
- **pH:** 5
- **AdSORbent doses:** 5 g/L
- **Agitation speed:** 120 strokes/min
- **Contact time:** 150 min

| Kinetic model         | Kinetic parameters                                      | Initial concentrations of fluoride (mg/L) |
|-----------------------|---------------------------------------------------------|-------------------------------------------|
|                       |                                                         | 2  | 4  | 6  | 8  | 10 |
| Pseudo-first-order    | $q_e$ (mg/g) [Plot]                                      | 0.352 | 0.621 | 1.035 | 0.787 | 1.064 |
|                       | $q_e$ (mg/g) [Expt.]                                    | 0.360 | 0.580 | 0.746 | 0.750 | 0.764 |
|                       | $k_1$ (min$^{-1}$)                                      | 0.567 | 0.573 | 0.620 | 0.520 | 0.571 |
|                       | $R^2$                                                    | 0.978 | 0.953 | 0.943 | 0.947 | 0.925 |
| Pseudo-second-order   | $q_e$ (mg/g) [Plot]                                      | 0.354 | 0.591 | 0.735 | 0.758 | 0.761 |
|                       | $q_e$ (mg/g) [Expt.]                                    | 0.360 | 0.580 | 0.746 | 0.750 | 0.764 |
|                       | $k_2$ (g/mg min)                                        | 0.899 | 0.515 | 0.377 | 0.397 | 0.322 |
|                       | $h$ (mg/g min) (10$^{-1}$)                              | 0.113 | 0.180 | 0.210 | 0.228 | 0.187 |
|                       | $R^2$                                                    | 0.994 | 0.995 | 0.992 | 0.997 | 0.994 |
| Intra-particle diffusion | $k_d$ (mg/g min$^{0.5}$)                              | 0.014 | 0.220 | 0.029 | 0.027 | 0.032 |
|                       | $C$                                                      | 0.142 | 0.231 | 0.284 | 0.310 | 0.247 |
|                       | $R^2$                                                    | 0.887 | 0.912 | 0.935 | 0.917 | 0.958 |
| Elovich               | $A$ (mg/g min $10^{-1}$)                                | 0.349 | 0.583 | 0.718 | 0.892 | 0.534 |
|                       | $B$ (g/mg)                                               | 13.160 | 8.314 | 6.433 | 6.813 | 5.801 |
|                       | $R^2$                                                    | 0.937 | 0.954 | 0.952 | 0.984 | 0.973 |

**Table 3.** Kinetic parameters of fluoride adsorption on MACFBL.
\[ \Delta G = -R \cdot T \cdot \ln K \]  

(7)

\[ \Delta G = \Delta H + T \cdot \Delta S \]  

(8)

\[ \ln K = \frac{\Delta S}{R} - \frac{\Delta H}{R \cdot T} \]  

(9)

**Figure 10.** Linear plots of Log K against 1/T for fluoride adsorption by MACFBL.

4.10. Effect of counter anions on fluoride removal

Removal of fluoride was performed experimentally in the presence of typical counter ions, such as sulphate, bicarbonate, chloride, nitrate, and phosphate, which are normally found in water. The counter ion concentration ranged from 0 to 500 mg/L at an initial dosage of 2 mg/L at a set pH 5 and a contact time of 150 min at a dosage of 5 g/L, retaining an agitation speed of 120 strokes/min at a temperature of 303 K. Figure 11 showed that there was a significant effect on the removal of fluoride in the presence of these counter ions. The presence of bicarbonate and phosphate ions, however, resulted in a drop in the fluoride removal percentage. This may be a direct result of the opposition of these counter ions with fluoride for adsorption sites [43, 44]. The unique selective nature of the adsorbent material depends on the various properties of the counter ions such as polarizability, size, electronegativity difference charge of ions, etc. [45, 46]. The descending hindrance observed for different counter ions for removal of fluoride onto MACFBL material is in the following order, Bicarbonate > Phosphate > Nitrate > Sulphate > Chloride.
Table 4. Thermodynamic properties for adsorption of fluoride onto MACFBL

| C₀ (mg L⁻¹) | ΔH (kJ mole⁻¹) | ΔS (kJ mol⁻¹ K⁻¹) | ΔG (kJ mole⁻¹) |
|-------------|----------------|-------------------|----------------|
|             | 303 K | 313K | 323 K | 333 K |
| 2           | -29.754 | -0.082 | -4.680 | -3.690 | -3.170 | -2.087 |
| 4           | -20.544 | -0.061 | -2.016 | -1.784 | -0.729 | -0.332 |
| 6           | -22.095 | -0.071 | -0.744 | 0.330 | 0.885 | 1.414 |
| 8           | -16.007 | -0.054 | 0.429 | 1.028 | 1.530 | 2.071 |
| 10          | -21.961 | -0.077 | 1.265 | 2.317 | 3.008 | 3.586 |

Figure 11. Impact of Counter anions on fluoride removal ability of MACFBL

(pH: 5, adsorbent doses: 5 g/L, agitation speed: 120 strokes/min, contact time: 150 min, temperature: 303 K, fluoride concentrations: 2 – 10 mg/L)

4.11. Desorption Study

A desorption or regeneration study is also essential since it is valuable in the recycling of the MACFBL material and recovery of the fluoride. Desorption of fluoride utilizing with 0.1 & 0.2 mol/L of NaOH, KOH and Na₂CO₃ alkali solutions was considered for the investigation. The desorption arrangement was operated at the optimum condition based on the batch experiment results. 50 ml test solution was taken from the effluent during desorption study and estimate for fluoride by using an ion-selective method. Figure 12, demonstrates the increase in desorption from 0.1M to 0.2 M alkali solutions. Results indicate that 0.2 mol/L alkali solutions regenerate fluoride-rich carbon up to 69.5 – 62.5 %. It was found that the MACFBL carbon material has been effectively regenerated with alkali solutions [47-50].
Figure 12. Desorption ability of MACFBL using alkali solutions. (pH: 5, adsorbent doses: 5 g/L, agitation speed: 120 strokes/min, contact time: 150 min, temperature: 303 K, fluoride concentration: 2 mg/L)

5. Conclusion
In the current investigation, a new chemically impregnated carbon material from leaves of *Ficus benghalensis* (MACFBL) has been developed for expulsion of fluoride from synthetic solution of fluoride. The adsorbent material could be simply prepared from leaves *Ficus benghalensis* that are locally available everywhere. It has developed as an efficient, porous and economically reasonable carbon material which demonstrated the highest percentage removal of fluoride i.e. 86.5%. The developed microwave treated and chemically activated adsorbent material (MACFBL) was characterized to investigate properties of adsorbent material by proximate analysis like bulk density, volatile matter, ash content, moisture content, water and acid soluble matter, and fixed carbon; ultimate and instrumental analysis like C, H, N, S element analysis, BET surface analysis, SEM, FTIR, EDX and XRD study. The characterization results show tremendous adsorbent properties for MACFBL carbon material. The fluoride adsorption rate was additionally examined with pseudo first-order model, pseudo second-order, Intra-particle diffusion, and Elovich kinetic models. The experimental finding was found to suit superior to pseudo second-order over other kinetic models. Thermodynamic investigation shows that fluoride adsorption favours at the lower temperature and the adsorption of fluoride was spontaneous, feasible and exothermic. Finally, it was concluded that MACFBL carbon material has adequate potential to extract fluoride from water and also 69.50% fluoride can be recovered from the adsorbent surface by using a 0.2 M NaOH solution.

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