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Study of removal of fluoride and adsorption isotherm mechanism by using microwave-assisted and acid-base impregnated carbon material developed from *Ficus benghalensis* leaf

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Abstract
The adsorption of fluoride from the aqueous solution containing fluoride was investigated using modified carbon material developed from *Ficus benghalensis* leaf (MACFBL). The effect of different parameters such as adsorbent dose, pH, adsorption speed, contact time, initial fluoride concentration, and temperature has been explored by Batch adsorption experiments. Fluoride adsorption equilibrium was established after 150 min in the range of 2–10 mg/l of initial fluoride concentrations. The batch experiment result and the isotherm equilibrium data were studied by using the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models for the removal of fluoride. The results of the investigation obtained from the linear plots of isotherm models were fitted precisely by the Langmuir adsorption isotherm model with the correlation coefficients of 0.999, 0.991, 0.982 and 0.976 at 303K, 313K, 323K and 333K, respectively. The linear plots of the Temkin and Dubinin-Radushkevich isotherm models were also suitable and show acceptable results for fluoride adsorption especially at lower temperatures. Assessment of the experimental results of defluoridation using the Langmuir model made known that the highest fluoride adsorption capacity onto modified carbon material of *Ficus benghalensis* leaf (MACFB) was 0.808 mg/g at 303K.
Keywords: Adsorption, Fluoride, Equilibrium, isotherm, *Ficus benghalensis*

INTRODUCTION

The increase of high fluoride concentration within the groundwater could be a serious worldwide concern as a result of anthropogenic and natural activities which result in cause wellbeing and health hazards to the human populace [1, 2]. Fluoride in groundwater gets generally from the disintegration of characteristic common natural minerals present within the various soils and rocks with which the groundwater undergoes interactions [3]. Other than natural occurring sources, fluoride can like manner be originated in effluents from different fertilizers, metal processing, semiconductor, glass-manufacturing industries, etc. [4,5]. The World Health Organization (WHO) and also the Bureau of Indian Standards (BIS) set down the highest permissible limit of fluoride in the potable water for a human being is 1.5 mg/L [6,7]. Fluoride is a very poisonous ion for human health when its concentrations present above the permissible limit which will result in the muse of assorted health problems like osteoporosis, skeletal fluorosis, dental fluorosis, neurological harm, Alzheimer's disease, thyroid issues, male infertility, as well as kidney, liver damages [8].

The higher fluoride concentrations in groundwater have been documented in many developed and developing countries including Asia, USA, and Africa. It has been found that 17 different states of India are highly affected by excess fluoride concentration [9, 10]. Over a couple of decades, various strategies have been produced for the expulsion of fluoride from groundwater because of their harmful effects on the public health and environment. These comprise ultrafiltration, solvent extraction, sedimentation, coagulation, precipitation and co-precipitation, reverse osmosis, electrodialysis, adsorption, ion exchange method, etc. [11, 12, 13]. Among all these methods, adsorption is extensively considered and adopted in light of its low-cost installation, simple maintenance, efficient performance and easy operational process [12, 13].

The condition of higher fluoride concentration in the water is ever-increasing due to natural and industrial effluent interactions and thus the defluoridation was undertaken by frequently used adsorption techniques. Different carbon materials reported by researchers for defluoridation of water derived from *Aspergillus niger* (FS18) biomass[1], *Citrus limonum* (lemon) leaf [3], cattle bones [5], KOH-treated Syzygium cumini Seed [10], Sawdust [11], Activated Alumina, Alum and Brick Powder [13], sugarcane bagasse[14], hyacinth beads doped with hydrous oxides of aluminium and iron [15], aluminum impregnated coconut fiber [16], *Camellia oleifera* seed shell [17], *Santalum Album* Leaf Powder [18], Al-impregnated *Eucalyptus* bark [19], Tea waste biomass [12, 20], commercial activated carbon treated with quaternary ammonium salts [21], Azadirachta indica leaf [22], coconut root [23], etc. The objective of the current study is to examine the effectiveness of plant-based biomass non-conventional adsorbent material developed from the leaf of *Ficus benghalensis* for the expulsion of fluoride from water.

EXPERIMENTAL

Materials used: All chemicals used were of analytical reagent grade and these chemicals obtained from S-D Fine Chemicals Ltd or Merck India limited. All glassware used in the study were delivered using Borosil glass. Batch adsorption experiments were performed using double distilled water.

Preparation of Adsorbent: *Ficus benghalensis* leaf sample was gathered from the neighborhood local village. It was rinsed with water to get rid of dust particles and impurities. It was then dried on natural sunlight, crushed in small pieces, powdered using a home blender. The powder material was washed and dried in a vacuum oven for overnight at 80 ^{O}C. The subsequent dried *F. benghalensis* leaf powder was thermally activated in a muffle furnace at 500^{0}C for five hours. Then, this leaf powder again activated in a microwave oven (900MW) for 30 minutes with a one-minute gap. This thermally and microwave treated leaf powder was allowed for chemical impregnation first with 0.5 N sodium hydroxide and then with 0.5 N sulphuric acid for 24 hours independently. The resultant material was washed with water until a consistent pH of the filtrate was obtained. At the last the carbon material was dried in a vacuum oven, grind well, sieved through 330 mesh and kept in airtight plastic containers for the adsorption experiments. This activated material developed from the *Ficus benghalensis* leaf was referred to as microwave-assisted carbonized *Ficus benghalensis* leaf (MACFBL).

Batch adsorption experiments: The developed MACFBL carbon material was used for the defluoridation of water by batch adsorption experiments at different initial fluoride concentrations (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):

$$q_e = \frac{(Co - Ce)\, V}{m} \qquad (1)$$

Where m, V, C_0 , C_e and q_e are the mass of adsorbent (g), the volume of the solution (L), the initial fluoride concentration (mg/L), equilibrium fluoride concentration (mg/L) and fluoride adsorbed at equilibrium (mg/g), respectively. The fluoride removal efficiency from the water was evaluated by equation (2):

$$\%\ \text{Removal of fluoride} = \frac{(Co - Ce)}{Co} \times 100 \qquad (2)$$

The impacts of agitation speed, adsorbent dose, contact time, pH, temperature and initial fluoride concentration have been considered for fluoride removal from the aqueous solutions by utilizing MACFBL material. The fluoride adsorption isotherm mechanism was discussed by using well-known models e.g., Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms **(Table-1).**

Table-1: Empirical adsorption isotherm equations.

Isotherm Models	Isotherm Equations	Ref.
Langmuir isotherm	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	[24]
Freundlich isotherm	$lnq_e = lnK_F + (1/n)\ \ln C_e$	[24]
Temkin Isotherm	$q_e = B\, ln\, A_T + B\ \ln\, C_e$	[24]
Dubinin-Radushkevich isotherm	$lnq_e = lnq_D - (K_D)\ \varepsilon^2$	[24]

RESULT AND DISCUSSION

Fluoride batch adsorption experiments:

Effect of pH: The fluoride removal efficiency onto MACFBL carbon material at various pH values with a known initial fluoride concentration of 2 mg/L has appeared in **Fig. 1(a).** It was found that as the pH increase from 2 to 5, the degree of fluoride adsorption expanded and subsequently it diminished above pH 5. The most extreme fluoride removal efficiency was 86.5 % at pH = 5. For further investigation, pH maintained at 5. It is observed that acidic conditions (pH range 4 to 6) may support the adsorption of fluoride on the surface of MACFBL material [25, 26].

Effect of agitation speed: The agitation speed for the expulsion of fluoride from fluoride bearing solution was shifted from 20 strokes/min to 180 strokes/min, by keeping every other condition constant **(Fig. 1(b))**. The efficiency of fluoride removal increased from 54.50 to 86.5 % at the same time as the agitation speed increased from 20 to 120 strokes/min. The removal capacity of fluoride for adsorbent material remained constant for elevated agitation speed, because elevated agitation speed builds the level of physicochemical interaction among the surface of MACFBL carbon and fluoride, bringing about higher removal efficiency for fluoride [27].

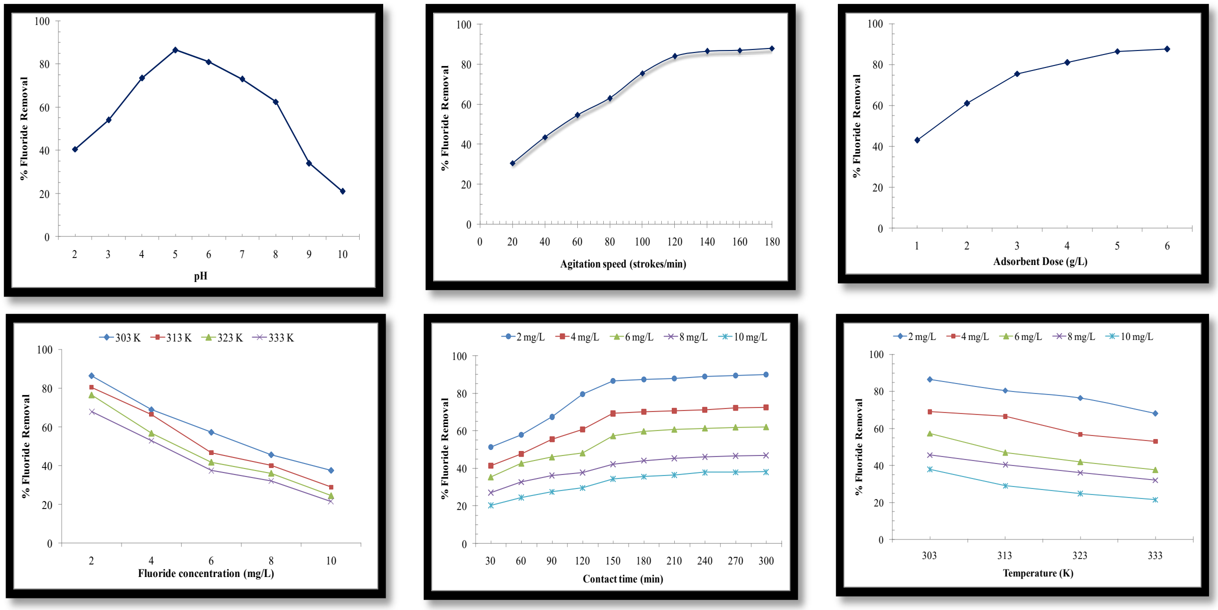

Fig. 1: Effect of (a) pH, (b) agitation speed, (c) adsorbent dose (d) initial fluoride concentration (e) contact time and (f) temperature on the fluoride adsorption by MACFBL

Effect of adsorbent dose: The investigations were performed to study the impact of adsorbent dose by changing dosage from 1 gm/L to 5 gm/L under the constant situation **(Fig. 1(c))**. The removal efficiency of fluoride increases by way of an increase in adsorbent dose, because contact surface of adsorbent material increased and it would be more likely for fluoride ions to be adsorbed on top of adsorption sites [38, 39]. The highest adsorption efficiency was seen at 5 g/L. It tends to be seen that percent removal of fluoride of the adsorbents usually improved with increasing the amount of adsorbent dose. It is because of the accessibility of interchangeable sites offered for the adsorbate [28].

Effect of initial fluoride concentration: The impact of the initial concentrations of fluoride onto MACFBL carbon material was well studied at four distinct temperatures (303 K – 333K) by maintaining other optimum parameters constants **(Fig. 1(d))**. As the underlying fluoride concentration was expanded from 2 mg/L to 10 mg/L, the quantity of fluoride adsorbed was increased from 0.346 mg/g to 0.754 mg/g (Table 3.6) at lower temperature 303K. This shows the measure of fluoride adsorbed was expanded by improving the underlying grouping of fluoride adsorbate. The percentage of fluoride expulsion diminishes with an expansion in the initial concentration of fluoride. It might be because of an expansion in the number of fluoride ions for the fixed quantity of MACFBL carbon material [29].

Effect of contact time: The impact of contact time on MACFBL was considered by varying contact time from 30 min to 300 min for 2mg/l -10 mg/L fluoride concentrations by keeping other adsorption parameters constants **(Fig. 1(f))**. 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 considerable change in fluoride adsorption was noticed after 150 min. The underlying fast rate of adsorption of fluoride was might be because 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 [30].

Effect of temperature: The impact of temperature on the removal of fluoride using MACFBL material was examined by performing the adsorption experiments at four distinct temperatures 303, 313, 323 and 333 K, by keeping other adsorption parameters constant for initial concentrations of fluoride (2 -10 mg/L). It has been seen that the adsorption limit diminished from 0.360 mg/g to 0.272 mg/g for initial concentrations of fluoride of 2 mg/L as the temperature was changed from 303 K to 333 K. **(Fig.1(e))**. Comparative patterns were found for higher fluoride concentrations. This indicates that the fluoride adsorption process onto MACFBL material is an exothermic process [43]. From figure 3 (e), it is confirmed that the low temperatures are in favours of fluoride removal. This may be a result of a tendency for the fluoride particles to split away from the solid phase to the bulk phase with an expansion in the temperature of the aqueous solution. [30, 31].

Adsorption isotherms study of fluoride onto MACFBL

The adsorption techniques are one of the significant processes for representing the fluoride adsorption capacity of the adsorbent material and it also demonstrates the mechanism of the fluoride adsorption process which communicates the specific relation between the concentration of the fluoride and its extent of accumulation onto the surface of the adsorbent material. The equilibrium data of fluoride adsorption onto MACFBL material at four unique temperatures has been examined by four well-known isotherms models, viz. Freundlich, Langmuir, Dubinin–Radushkevich (D-R) and Temkin (Table-1).

Langmuir isotherm: The Langmuir linear plot between C_e/q_e versus C_e appeared in **Fig. 2(a).** The most extreme adsorption capacity of fluoride on to MACFBL material was observed to 0.808 mg/g at 303 K. The dimensionless parameter (R_L) values lies in between 0.089 and 0.185 is reliable with the prerequisite for favourable adsorption [32, 33]. The value of correlation coefficient (R^2) obtained indicates good conformity between the Langmuir parameters and shows the monolayer fluoride adsorption on the surface of MACFBL carbon material.

Freundlich isotherm: The Freundlich plot (Log q_e versus Log C_e) determined the fluoride adsorption information by changing initial concentrations of fluoride (2 mg/L to 10 mg/L). The isotherm parameters with correlative coefficients (R^2) values appeared in **Table-2**. The adsorption capacity of fluoride (K_f) decreased (0.504 – 0.329 L/mg) with the expansion in temperature which confirms the exothermic nature of fluoride adsorption onto MACFBL material and the lower value for K_f demonstrates that the rate of fluoride adsorption is low [34].

Temkin isotherm: The direct plot of the Temkin model at various temperatures **(Fig. 2(c))** and experimental results have appeared in **Table-2**. The heat of fluoride adsorption (B) is specifically identified with the inclusion of fluoride onto MACFBL because of adsorbent-adsorbate interaction. The heat of fluoride adsorption (B) was decreased from 0.135 to 0.076 J/mol shows that the heat of fluoride adsorption on the MAFBL adsorbent surface decreases with expanding temperature starting from 303 K to 333 K and the fluoride adsorption process found to be exothermic [35]. Also, the b_T estimated values are lower than 50 KJ/mol which showing a physical adsorption process and dominating the chemical adsorption and ion exchange process. The correlation coefficients (R^2) are observed to be the poor fit of every experimental data.

Dubinin-Radushkevich (D-R) isotherm: D-R model [35] is an adsorption isotherm model to facilitate and commonly connected to articulate equilibrium adsorption systems with Gaussian energy dispersion on the heterogeneous surfaces of adsorbent material [36]. From the linear plot of D-R isotherm model **(Fig. 2(d))** and the results of D-R isotherm **(Table-2)**, the calculated values of q_D and the mean free energy (E) diminished with an increase in temperature. The estimated values of average free energy are indicated the fluoride adsorption process follows a physisorption mechanism. The findings of correlation coefficients (R^2) demonstrated the appropriateness of D-R isotherm model for the fluoride adsorption on MACFBL surface.

It is observed that fluoride equilibrium isotherm data fitted nicely to a majority of these isotherm models for MAFBL material. The values of correlation coefficients (R^2) indicates that Langmuir isotherm provides a viable model for fluoride adsorption on MACFBL surface, which relies on the adsorption of a monolayer on the surface and limits the number of identical adsorption sites. Adequate adsorption information for the Langmuir model shows that the binding energy is the same across the surface of the MACFBL adsorbent and that the interactions between adsorbate-adsorbate are low. The estimated values of different isotherm parameters are determined and are shown in Table 2.

Comparison of fluoride removal effectiveness of different leaf-based adsorbents:

The fluoride expulsion effectiveness of the adsorbent prepared from *Ficus benghalensis* leaf investigated in this present work has been matched up with other leaf-based adsorbent material that was accounted by researchers in the literature and the values of fluoride removal efficiency **(Table-3)**. The experimental data of the present research work were compared with reported values for the removal of fluoride. Results of this research work revealed that the adsorbent MACFBL has higher fluoride adsorption efficiency than other leaf-based adsorbents **(Table-3)**.

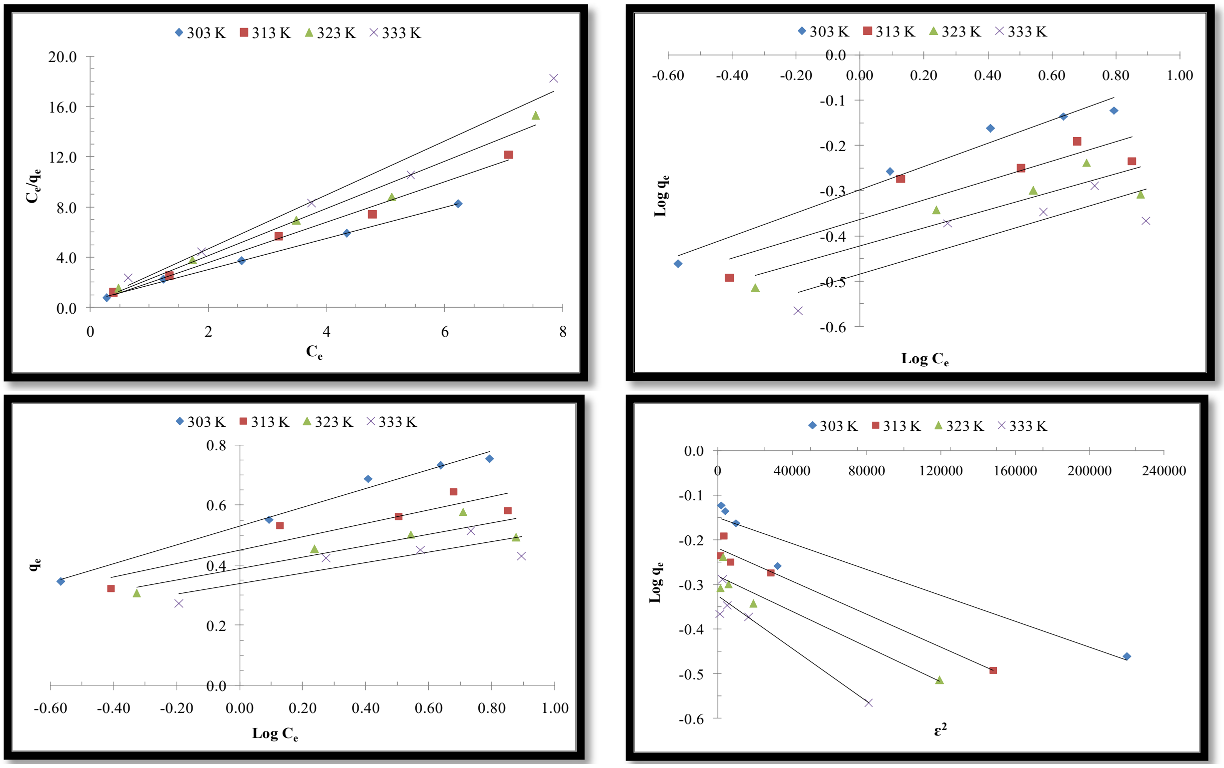

Fig. 2: (a) Langmuir, (b) Freundlich, (c) Temkin and (d) Dubinin-Radushkevich isotherm models for adsorption of fluoride by MACFBL at 303, 313, 323, 333 K.

Table-2: Adsorption parameters for the removal of fluoride on MACFBL

Isotherm model	Adsorption Parameters	Temperature			
		303 K	313 K	323 K	333 K
Langmuir	q_m (mg/g)	0.808	0.943	0.842	0.467
	K_L (L/mg)	2.207	2.625	3.095	5.147
	R_L	0.185	0.160	0.139	0.089
	R^2	0.999	0.991	0.982	0.976
Freundlich	K_F (mg/g)	0.504	0.434	0.378	0.329
	1/n	0.256	0.214	0.201	0.208
	N	3.906	4.673	4.975	4.808
	R^2	0.971	0.834	0.828	0.737
Temkin	K_T (L/mg)	50.230	101.033	114.341	85.394
	B (J/mol)	0.135	0.097	0.082	0.076
	b_T (kJ/mol)	18.654	25.899	30.696	33.151
	R^2	0.986	0.843	0.802	0.715
Dubinin-Radushkevich	q_D (mg/g)	0.708	0.605	0.524	0.474
	K_D (mol^2/kJ^2)	3.336E-06	4.254E-06	4.542E-06	6.792E-06
	E (kJ/mol)	0.387	0.343	0.332	0.271
	R^2	0.934	0.969	0.917	0.922

Table-3: Comparative reported details of different plant leaf-based adsorbents for the removal of fluoride.

Adsorbents	Maximum % removal of fluoride	Ref.
Citrus limonum leaf	70 .0	[3]
Ficusreligiosa leaf	85.7	[37]
Curly Kale (Borecole) leaf	83.7	[38]
Cynodon dactylon biomass	84.0	[39]
Polyalthia longifolia (Devdaru) leaf	77.0	[40]
Azadirachta indica (Neem) leaf	65.2	[41]
Acacia arabica (Kikar) leaf	68.8	[41]
Mixture of Azadirachta indica (Neem) and Acacia arabica (Kikar) leaves.	63.6	[42]
Terminalia chebula (Silikha) leaf	74.0	[43]
Shorearobusta (Sal) leaf	63.6	[44]
Ficus benghalensis leaf (MACFBL).	**86.5**	**This Work**

CONCLUSION

The equilibrium adsorption characteristics mechanism of fluoride onto the surface of MAFBL material developed from *Ficus benghalensis* leaves were studied. The adsorption is one of the most important techniques for representing the adsorption capacity of the adsorbent material and the mechanism of the adsorption system, which reveals the specific relationship between the adsorbate concentration and its accumulation rate on the adsorbent surface. MACFBL-fluoride adsorption equilibrium data at different temperatures (303, 313, 323 and 333 K) were analyzed using four known isotherm models. It is found that the experimental data fit to all of these isothermal adsorption models. The correlation coefficient (R^2) values indicate that the Langmuir model provides a viable model for fluoride adsorption on MACFBL materials, which relies on the adsorption of a monolayer on the adsorbent surface and limits the number of identical adsorption sites. The relevance of the adsorption information with the Langmuir isotherm model shows that the binding energy is the same across the surface of the MACFBL adsorbent and that the adsorbate-adsorbate interaction is low. The maximum fluoride removal efficiency for MACFBL was found to be 86.5%.

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