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ORIGINAL ARTICLE **OPEN ACCESS**

Adsorption Isotherm Mechanism for Removal of Fluoride by Using Microwave Assisted and Acid-Base Impregnated Biomaterial Prepared from *Tamarindus Indica* Seed

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ABSTRACT

The acid-base impregnated activated carbon derived from Tamarindus indica seed waste was used in the present study to remove fluoride ions from water. The adsorbent were prepared by activating the selected biomass in muffle furnace and then in microwave and subsequently with sodium hydroxide and sulphuric acid. The developed carbon material was assigned as MACTIS. The effects of different operating parameters including adsorbent dose, initial concentration of fluoride, contact time, solution pH and temperature on the removal of the fluoride ions, have been studied. Optimum conditions were observed for the prepared carbon content, such as pH 5, adsorbent dosage of 3.0 g/L, and agitation rate of 120 strokes/min and contact time of 180 min at a temperature of 303 K. The isotherms of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich have been studied to explain the adsorption mechanism on the adsorbent surface. The Langmuir isothermal model agreed to a greater extent with the equilibrium results, suggesting monolayer adsorption of fluoride ions on MACTIS. The fluoride uptake potential for MACTIS by the Langmuir isotherm was found to be 1.222 mg/g. Thermodynamic experimentation found that the mechanism of adsorption in nature was feasible, exothermic and spontaneous. With a rise in temperature from 303 K to 333 K, the elimination efficacy of the defluoridation process was reduced. These results provide insights to further explore the adsorption method for fluoride ion removal using impregnated acid-base and microwave-assisted carbon materials derived from other plant based bio waste.

Keywords: *Adsorption, Fluoride, Equilibrium, isotherm, Tamarindus indica Seed*

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INTRODUCTION

Pure drinking water is inadequate and not readily accessible to everyone. Natural sources or industrial effluents can contaminate the water. Fluoride, found in groundwater and surface water, is one such contaminant. The main source of fluoride in the groundwater is geological formation. Fluoride, the 13th most common element on Earth, is a naturally occurring compound derived from fluorine. It can be found in rocks, soil, fresh water and ocean water. Fluoride occurs naturally as a consequence of runoff from weathering of rocks and soils containing fluoride and leaching from soil into groundwater in public water systems. In addition, the atmospheric deposition of fluoride-containing pollutants from coal-fired power plants and other industrial sources leads to the high fluoride concentrations in water, either by direct deposition or through soil deposition and subsequent water runoff [1].

The discharge of fluoride into groundwater and surface water is also involved in various industries such as semiconductor production plants, pharmaceutical firms, beryllium extraction units, smelters, aluminium, fertiliser manufacturing plants and mining industries are the sectors in question [2]. In several countries, including Benin, Algeria, Cameroon, Ethiopia, Egypt, Ghana, Kenya, Malawi, Libya, Nigeria, Morocco, Rwanda, South Africa, Tanzania, Sudan, Togo, Uganda, Tunisia, Zimbabwe, India, China, Indonesia, Pakistan, , Iran, Saudi Arabia, Turkey, South Korea, Yemen, Mexico, Canada, Argentina, USA, etc. the fluoride contamination and its associated diseases have been reported [3]. In different states of India, such as Andhra Pradesh, Haryana, Punjab, Rajasthan, Uttar Pradesh, Gujarat, Tamil Nadu, Maharashtra and Karnataka [4], the problems associated with fluoride contamination are more severe. If the level of fluoride in drinking water reaches 1.5 mg/L, then osteoporosis, skeletal fluorosis, dental fluorosis, Alzheimer's disease, neurological damage, male and kidney infertility, thyroid disorders, liver damage [5] are induced.

The use of groundwater has increased as a result of rapid growth and industrial demand among the global population, resulting in low water quality supply and a decrease in groundwater levels. Inorganic toxins, such as fluoride, heavy metals, etc., play a major role in groundwater pollution. Fluoride is such a contaminant that human beings face an extreme danger. Since drinking water is the primary source of fluoride ingestion, the Bureau of Indian Standards BIS, 2012 [6] has therefore placed a permissible value of 1 mg/L of fluoride in drinking water that, as suggested by WHO, is less than 1.5 mg/L [7].

Different analytical techniques have been used to extract residual fluoride from the fluoride contaminated water until it is released into the public water system. Coagulation-precipitation, ion-exchange, adsorption, nano-filtration, electro-dialysis, reverse osmosis and electrocoagulation are used in these techniques [8, 9, 10]. The adsorption process is a highly encouraging procedure, which usually uses natural or synthetic solid adsorbents, among all these techniques. This technique is highly appropriate because of its favourable economical cost, high removal efficiency, ease of use, and the reuse of the adsorbent used after its regeneration [11].

Several plant-based biomass products have also been used to extract fluoride from drinking water, such as leaves, seeds, eggs, peels, bark, etc., as illustrated in our previous review articles [12, 13, 14, 15]. Due to highly microporous composition, wide surface area, excellent surface reactivity and adequate availability of functional groups, activated carbon (AC) developed from plant based biomass is reflected as a versatile adsorbent material. Many researchers have used activated carbon extensively for the removal of fluoride from water.

Tamarindus indica has a place with the family Leguminosae (Fabaceae), commonly known as Tamarind tree, is one of the fruit tree species that is utilized as conventional medicine [16]. *Tamarindus indica* (T. indica) is evergreen tree that can achieve 24 m height and 7 m size that has light yellow and pink flowers [17]. Tamarind tree is found particularly in the Indian subcontinent, Africa, Nigeria and largely in the tropical countries. All part of *Tamarindus indica* plant (root, fruit, body and leaves) has high nutritional value and wide medicinal usage. It moreover has industrial and economic importance. World Health Organization report determines, tamarind fruit is an ideal source of all vital amino acids except tryptophan (82%) [18] and it also contains phenolic compounds like, mucilage, procyanidin B_2, catenin, arabinose, tartaric acid, xylose, galactose, epicatechin, pectin, glucose, uronic acid and triterpen [19].

Many works have been recently published with the primary goal being the investigation of removal of different pollutants using seed based adsorbent materials [20, 21]. Seed based materials are of low economic value, so inexpensive and abundantly available and composed different chemical compositions which make them effective adsorbents for a wide range of pollutants due to the presence variety of functional groups that participates in binding with the pollutants [22]. Thus, this article aimed at studying the adsorption behaviour of chemically activated *Tamarindus indica* seed for the removal of fluoride from aqueous solution.

MATERIAL AND METHOD

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

Tamarindus indica seeds were collected from the local area and washed several times with water to remove dust and other impurities and kept for sun dry. The procedure of preparation of material was followed as that reported in previous work [23]. The carbon obtained from the seed of *Tamarindus indica* was hereafter referred as microwave assisted *Tamarindus indica* seed **(MACTIS).**

Batch adsorption experiments

The developed MACTIS 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):

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

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):

% Removal of fluoride $= \frac{(\mathrm{Co-Ce})}{\mathrm{Co}} \mathrm{X}\ 100$ (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 MACTIS 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	$q_e = B\ ln\ A_T + \mathrm{B}\ \ln\ C_e$	[24]
Dubinin-Radushkevich isotherm	$lnq_e = lnq_D - (K_D)\ \varepsilon^2$	[24]

RESULT AND DISCUSSION

Fluoride batch adsorption experiments:

Effect of pH

In order to study the impact of pH on fluoride removal from aqueous solution, batch experiment was performed with changing initial pH value from 2 to 10 at 303 K **(Fig. 1(a))**. The initial concentration of fluoride and agitation speed was fixed at 2 mg/L and 120 strokes/min, respectively. The amount of the adsorbent dose was taken as 3 g/L and contact time was maintained as 180 min. It could be observed that the removal of fluoride increases with increment of initial pH from 2 to 5 and it nearly achieves a highest removal around pH 5. Therefore, the optimum fluoride removal consider at pH 5. At low pH, the concentrations of hydrogen ions are high, so adsorbent surface sites become positively charged and then hydrogen and fluoride ions compete for binding sites of the adsorbent which results the decrease in fluoride removal efficiency [25]. As pH increases in the ranges from 4 to 7, the fluoride removal efficiency are high and their after as pH increases removal efficiency diminishes. From above discussion, it is indicate that optimum pH 5 is required for later experiments for the successful removal of fluoride.

Effect of agitation speed

The impact of agitation speed on fluoride removal efficiency onto the MACTIS material was examined by changing the agitation speed from 20 to 180 strokes/min, while keeping the alternate parameters constant. As indicated by **Fig. 1(b)**, the removal of fluoride efficiency by and large increased besides increasing agitation speed. The fluoride removal efficiency of MACTIS adsorbent material increased from 53.00 % to 88.50 % when the speed of agitation of shaker increased from 60 to 120 strokes/min and the adsorption removal capacity shows up generally steady for agitation rates greater than 120 strokes/min. This outcome can be related to the fact that the expansion of the agitation speed enhances the diffusion of fluoride towards the adsorbent surface [26]. This additionally shows an agitation speed of 120 strokes/min is adequate to ensure that all the binding sites of adsorbent surface are made readily accessible for adsorption of fluoride.

Effect of adsorbent dose

The impact of adsorbent dosage on the removal of fluoride from aqueous solution are appeared in **Fig. 1(c),** by varying the amount of adsorbent dosage from 1 g/L to 6 g/L, by keeping 2 mg/L of initial fluoride concentration and equilibrium contact time for 180 min at 303 K. The agitation speed kept up at 120 strokes/min. The outcomes indicated that the fluoride removal capacity increases with increase of amount of adsorbent dose because of the more prominent accessibility of adsorption sites of adsorbent [27]. On the other hand, the percentage removal of fluoride was more at 3 g/L and the optimum was obtained at this dose and changes slightly with respect to adsorbent dose. Therefore 3 g/L was taken reasonably as the adsorbent dose for further experimental investigations.

Effect of initial fluoride concentration

The effect of initial concentration of fluoride was considered by ideal adsorbent dose of 3g/L onto distinctive initial concentration of fluoride arrangements (2 - 10 mg/L) at four unique temperatures (303K to 333K) by keeping other optimum parameters steady. The impact of initial fluoride concentration on the percent fluoride removal efficiency is shown in **Fig. 1(d)**. The results laid out that percent fluoride removal efficiency diminished with rising initial fluoride concentration at studied unique temperatures. This was might be because of the capacity of the adsorbent carbon material gets exhausted sharply with the rise in the concentration of fluoride [28]. Furthermore, it is probably due to the fact that for a predetermined adsorbent dosage, the entire active adsorption surface sites of the carbon material were constrained at higher initial fluoride concentration. Similar pattern has been reported for adsorption of fluoride by utilizing the various adsorbents [28, 29].

Effect of contact time

The investigation of impact of contact time for the adsorption of fluoride onto the MACTIS adsorbent material at different fluoride concentrations (2, 4, 6, 8 and 10 mg/L) with changing contact time from 30 to 300 min keeping every other parameters constant are appeared in **Fig 1(e).** It was seen that, fluoride adsorption by MACTIS carbon material was increased with time. In the beginning, fluoride adsorption on MACTIS material occurred rapid followed by slower fluoride adsorption up to the equilibrium. For MACTIS adsorbent, 88.50% of adsorption occurred for fluoride within 180 min contact time and equilibrium reached in 300 min, therefore contact time of 180 min was considered for further studies. It was observed that the adsorption efficiency of fluoride steadily increased with the increase in contact time. The steady rise shows the accessibility of adsorbent sites for adsorption of fluoride during the initial lower contact times [30]. On the other hand, adsorption site saturation arises after 180 min of contact time for MACTIS adsorbent material.

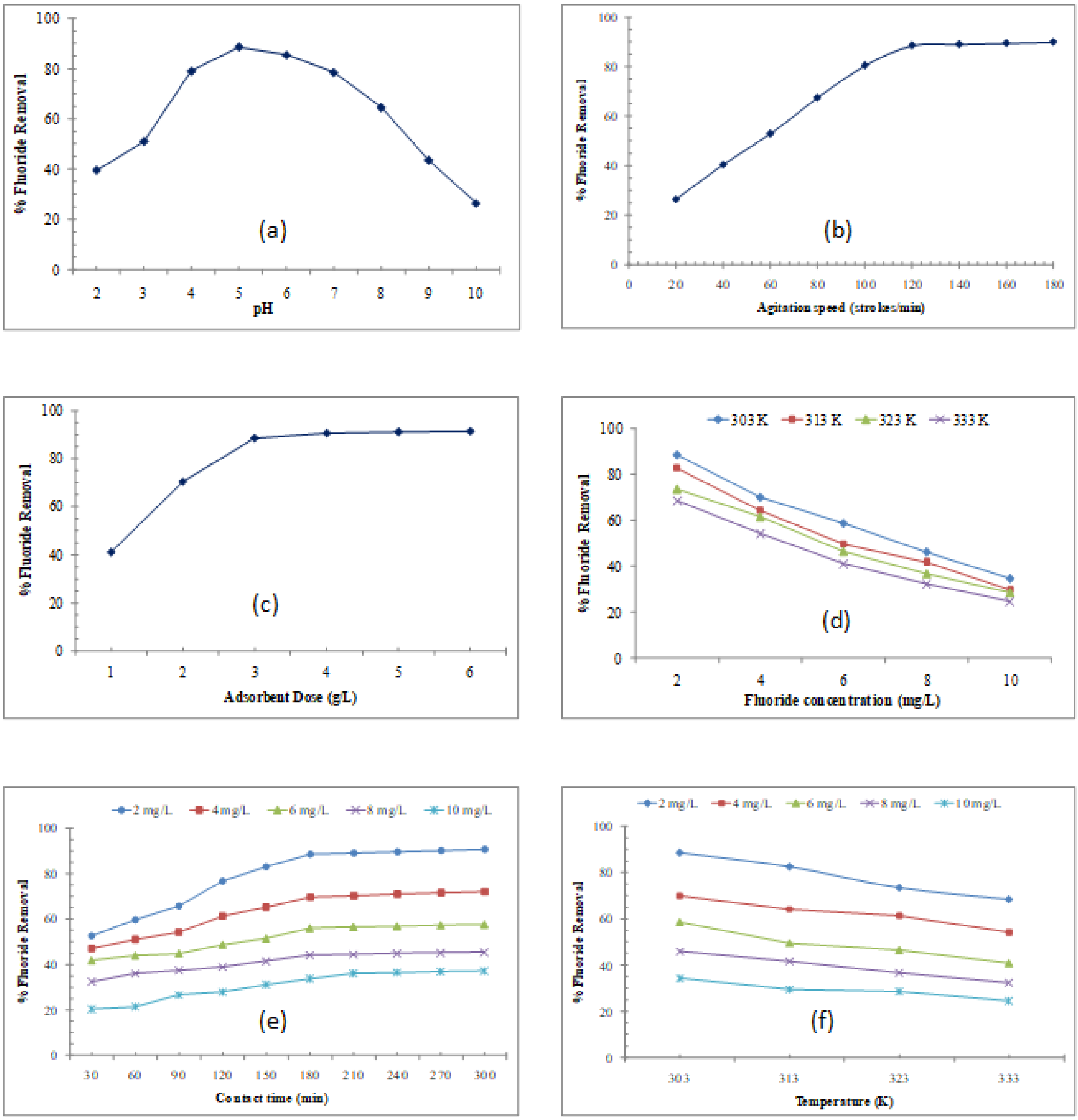

Fig. 1: Effect of (a) pH, (b) agitation speed, (c) adsorbent dose, (d) initial fluoride concentration (e) contact time and (f) temperature on the fluoride adsorption by MACTIS

Effect of temperature

It is well known that temperature is a supplementary factor significantly impacts the adsorption process. The impact of temperature on fluoride adsorption onto MACTIS from aqueous solution was investigated at 303, 313, 323 and 333 K for the initial fluoride concentration of 2–10 mg/L at optimized pH, agitation speed, adsorbent dose, and contact time. The plot presented in **Fig. 1(f)**, signifying the fluoride adsorption efficiency diminished with increase in temperature. Highest efficiency for fluoride removal (88.50 %) obtained at 303 K temperature for 2 mg/L fluoride concentration. This outcome shows low temperature supports the expulsion of fluoride and the adsorption process is exothermic in nature. The diminishing of expulsion of fluoride might be due to that at elevated temperature the thickness of the limit layer diminishes because of increased inclination of the adsorbate particles to escape from the adsorbent carbon surface to the aqueous phase, which results in a decrease in the fluoride adsorption efficiency as temperature is increased [31]. Comparative outcomes were previously reported by researchers [30, 31].

Adsorption isotherms study of fluoride onto MACTIS

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 MACTIS material at four unique temperatures has been examined by four well-known isotherms models, viz. Freundlich, Langmuir, Dubinin–Radushkevich (D-R) and Temkin **(Table 2)**.

Langmuir isotherm

The Langmuir adsorption isotherm plot of C_e/q_e versus C_e suggests the applicability of this isotherm model **(Fig. 2(a))**. Estimations of Langmuir parameters q_m (fluoride adsorption capacity) and K_L (Langmuir parameter) were calculated from the intercepts and slope of the plot and the data are exhibited in the **Table 2**. From the Table 2, it is indicates that the value of adsorption efficiency q_m and K_L of the MACTIS carbon material decreases on increasing the temperature from 303 K to 333 K. From the Langmuir parameters, it is noted that the most elevated fluoride adsorption communicates to a monolayer of fluoride particles on the adsorbent material surface with constant energy. Also, there is no spread of adsorbate in the plane of the adsorbent surface [30, 31]. The pattern demonstrates that the adsorbent likes to bind fluoride particles and that condition prevails on adsorbent characteristics, when ion exchange is the prime mechanism. Besides, it confirms the exothermic nature of the adsorption processes in the system. The calculated values of the separation factor (R_L) was seen to be somewhere in the range of 0 and 1 confirm that the Langmuir adsorption process is favourable [30, 31]. The correlation coefficient (R^2) values show a decent agreement between the parameters and confirm the monolayer adsorption of fluoride onto the adsorbent surface.

Freundlich isotherm

The Freundlich isotherm model was also utilized to investigate the adsorption of fluoride on the MACTIS adsorbent. Straight plot of log q_e versus log C_e appeared in **Fig. 2(b)**. The Freundlich isotherm parameters, K_F and N were determined by using slope and intercept. The experimental data obtained was presented in the **Table 2**. The outcomes demonstrate that the reduction in K_F values from 0.863 mg/g to 0.558 mg/g as temperature increases from 303 K to 333 K. This is a result of the adsorbent surface that diminishes the electrostatic force among the carbon surface of adsorbent and fluoride ions, which decreases the adsorption of fluoride with increase in temperature [32, 33]. The estimated values of $N > 1$ show that the adsorption process is much favourable for fluoride removal [34]. But, the values of the correlation coefficient, R^2, obtained in this case show that the Freundlich isotherm model gave a poor fit to the experimental data than the Langmuir model.

Temkin isotherm

Temkin isotherm model was applied to assess the adsorption potential of MACTIS adsorbent material for fluoride removal. The Temkin constants b_T, B and K_T are determined from the slopes and intercepts of the Temkin plot of q_e versus Log C_e **(Fig. 2(c))**. From the **Table 2**, the values of heat of adsorption and the equilibrium binding constant are appeared to the minimum during the adsorption of fluoride on MACTIS. The heat of fluoride adsorption (B) is decreased with increasing temperature from 0.191 to 0.158 J/mol. This demonstrates that the heat of adsorption of fluoride onto the surface of MACTIS decreases with increasing temperature from 303 to 333 K and the adsorption isotherm process is exothermic [28, 35]. Also, the b_T values is lower than 30 KJ/mol which indicating a physical adsorption process and dominating the chemisorptions and ion exchange. The correlation coefficients (R^2) are found to be the poor fit of all experimental data.

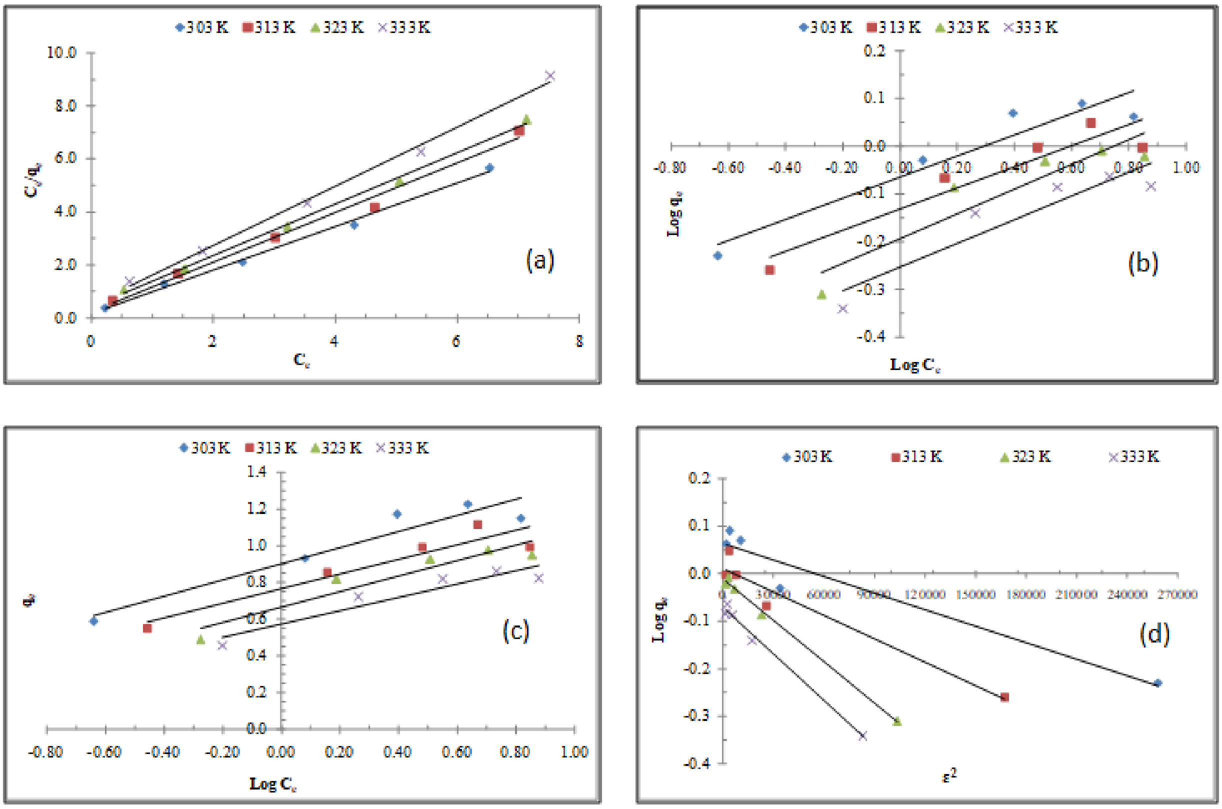

Fig. 2: (a) Langmuir, (b) Freundlich, (c) Temkin and (d) Dubinin-Radushkevich isotherm models for adsorption of fluoride by MACTIS at 303, 313, 323, 333 K.

Dubinin-Radushkevich (D-R) isotherm

Dubinin–Radushkevich isotherm model [344] was selected to study the adsorption potential of MACTIS adsorbent material for fluoride removal **(Fig. 2(d))**. It is an adsorption isotherm model that is commonly connected to express adsorption system with Gaussian energy distribution onto heterogeneous surfaces [35, 36].The model has often effectively fitted for high solute actions and the intermediate concentration range, but has unacceptable asymptotic properties and does not anticipate the Henry's law at low concentration [346]. The D-R isotherm was generally applied to make a distinction between the Chemical and physical adsorption of adsorbate [36]. From the results mentioned in **Table 2**, the values of q_D and the mean free energy (E) decreased with increase in temperature. The values of E are reveals the adsorption process follows physical adsorption process. The correlation coefficients for the D-R isotherm are highest for all temperature range (Table 2) proposes that the fluoride adsorption onto MACTIS is a physical process.

It is observed that fluoride equilibrium isotherm data fitted nicely to a majority of these isotherm models for MACTIS material. The correlation coefficients (R^2) values demonstrated that Langmuir adsorption isotherm gives a decent model for the adsorption of fluoride on MACTIS material, which depends on monolayer adsorption on to the surface limiting a finite number of identical adsorption sites. The appropriateness of the adsorption information to the Langmuir isotherm model suggests that the binding energy on the whole surface of the MACTIS adsorbent material was uniform and that adsorbate-adsorbate interaction was small. The values of various constants of four adsorption isotherm models were determined and were presented in the **Table 2**.

Table 2: Adsorption parameters for the removal of fluoride on MACTIS

Isotherm model	Adsorption Parameters	Temperature			
		303 K	313 K	323 K	333 K
Langmuir	q_m (mg/g)	1.222	1.068	1.034	0.898
	K_L (L/mg)	4.596	4.052	2.244	2.210
	R_L	0.098	0.110	0.182	0.184
	R^2	0.995	0.989	0.996	0.995
Freundlich	K_F (mg/g)	0.863	0.740	0.641	0.558
	1/n	0.220	0.221	0.258	0.247
	N	4.545	4.525	3.876	4.049
	R^2	0.912	0.886	0.861	0.863
Temkin	K_T (L/mg)	112.202	85.505	37.421	38.373
	B (J/mol)	0.191	0.172	0.184	0.158
	b_T (kJ/mol)	13.185	14.613	13.682	15.982
	R^2	0.911	0.881	0.894	0.887
Dubinin-Radushkevich	q_D (mg/g)	1.158	1.025	0.974	0.849
	K_D (mol^2/kJ^2)	2.66E-06	3.78E-06	6.69E-06	7.53E-06
	E (kJ/mol)	0.433	0.363	0.273	0.258
	R^2	0.938	0.944	0.996	0.995

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

The fluoride expulsion effectiveness of the adsorbent prepared from *Tamarindus indica* seed investigated in this present work has been matched up with other seed-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 MACTIS has comparable fluoride adsorption efficiency with other reported values. (Table 3).

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

Adsorbents	Maximum % removal of fluoride	Ref.
Activated carbon of *Phyllanthus emblica* seed	82.1	[38,39]
Seed extracts of *Moringa Oleifera* (Drum stick)	88	[21]
Activated carbon of *Punica granatum* seed	78.1	[40]
$CaCl_2$ treated activated carbon of *Phoenix Dactylifera* (Date Plam) seeds (Impregnation ratio's = 0.25)	88	[41]
$CaCl_2$ treated activated carbon of *Phoenix Dactylifera* (Date Plam) seeds (Impregnation ratio's = 0.50)	91	[41]
$CaCl_2$ treated activated carbon of *Phoenix Dactylifera* (Date Plam) seeds (Impregnation ratio's = 0.75)	93	[41]
Restructured lignite of *Cuminum cyminum* (Cumin) seeds	60	[42]
***Tamarindus indica* Seed (MACTIS)**	**88.5**	**This Work**

CONCLUSION

A new acid-base impregnated and microwave treated carbonized material from the seed of *Tamarindus indica* (MACTIS) has been prepared for removal of fluoride from aqueous solution. The association of fluoride adsorption and fluoride removal efficiency both were investigated by changing process parameters responsible for effective adsorption such as pH, initial fluoride concentration, contact time, adsorbent dose, temperature and agitation speed. The maximum removal of fluoride was achieved by MACTIS up to 88.50 % for initial fluoride concentration was 2 mg/L. The investigation was assessed with four different adsorption isotherm models among them; the Langmuir isotherm described the experimental outcomes better than other isotherm models. The maximum fluoride adsorption capacity (q_m) obtained from Langmuir plot was found to be 1.222 mg/g and moreover correlation coefficients values greater than 0.989. The thermodynamic study indicates the fluoride adsorption process is exothermic, feasible and favour at lower temperature. All the above observations show that the MACTIS carbon material prepared from seed of *Tamarindus indica* is a highly efficient adsorbent for the removal of fluoride from aqueous solution.

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