

Article

Analysis of equilibrium, kinetic, and thermodynamic parameters for biosorption of fluoride from water onto coconut (*Cocos nucifera* Linn.) root developed adsorbent

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ABSTRACT

Drinking water with higher fluoride levels results in serious irremediable health problems that have attained a startle all over the world. Researches focused towards defluoridation through the application of biosorbents prepared from various plants are finding greater scope and significance. Present research is done on *Cocos nucifera* Linn. (coconut tree) one of the very commonly available plants throughout Kerala and around the globe. An adsorbent developed from the root portion of *C. nucifera* Linn. is used in the present study. Equilibrium study revealed that the fluoride uptake capacity is quite significant and linearly increases with initial adsorbate concentration. The adsorption data is analyzed for Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models at varying initial adsorbate concentrations (2–25 mg·L⁻¹). It is found that the adsorption of fluoride onto *C. nucifera* Linn. root adsorbent follows Langmuir isotherm. Langmuir isotherm constants “a” and “b” obtained are 2.037 mg·g⁻¹ and 0.823 L·mg⁻¹ at an adsorbent dose of 8 g·L⁻¹ and temperature (26 ± 1) °C. The mean free sorption energy, *E* obtained, is 9.13 kJ·mol⁻¹ which points out that the adsorption of fluoride onto *C. nucifera* Linn. root adsorbent is by chemisorption mechanism. The kinetic study also supports chemisorption with adsorption data fitting well with a pseudo-second-order kinetic model with an estimated rate constant *K*₂ of 0.2935 g·mg⁻¹ min at an equilibrium contact time of 90 min. The thermodynamic study indicated the spontaneous and endothermic nature ($\Delta H = 12.728$ kJ·mol⁻¹) of fluoride adsorption onto the *C. nucifera* Linn. root adsorbent. Scanning Electron Microscopy (SEM), BET, FTIR, and EDX methods were used to analyze the surface morphology of adsorbent before and after fluoride adsorption process. Experiments on defluoridation using *C. nucifera* Linn. root adsorbent application on fluoride contaminated ground water samples from fields showed encouraging results.

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1. Introduction

Exploration of defluoridation methods is one of the key areas requiring vital attention on water pollution point of view that consumption of water containing fluoride causes dreadful diseases [1]. Groundwater fluoride contamination is one major crucial growing problem throughout many parts of the world [2]. Among the various nations around the world, India is the one where elevated groundwater fluoride levels are creating serious health issues [3]. About 203 districts in 20 states of the country are affected by fluoride contamination. Fluoride is an indispensable element for human health, but in excessive concentration of above 1.5 mg·L⁻¹ [4], can lead to chronic fluoride poisoning, fluorosis, which harms teeth enamel and bone tissues because of its strong attraction with calcium present in teeth and bones, arthritis, and other consequences such as cancer, damage to brain, and thyroid disorders.

Many commercial adsorbents have been used for defluoridation of water. But these adsorbents are very costly, more energy utilizing, and environment unfriendly. Hence, studies are being made to find environmental-friendly, efficient, simple, and sustainable adsorbent for defluoridation of water.

Studies on various natural or non-conventional materials as adsorbents for defluoridation is a new field of research. The use of natural materials as adsorbents is very advantageous over conventional materials as they are much cheaper, locally available, environmentally friendly, sustainable and required fewer transportation costs. Biosorption is one of the recent trends focused upon having the potential for defluoridation and is strongly recommended by scientists as an efficient and economically sustainable technology for defluoridation [5]. Up till now defluoridation potential of a fairly good number of adsorbent materials has been done such as *Phyllanthus emblica* adsorbent [6], *Cynodon dactylon* [5], Neem and kikar leaf activated carbon [3], Activated vetiver roots [7], Guava seeds (*Psidium guajava*) [8], rice straw adsorbent [9], coffee husk and Banana peel [1], and *Acacia farnesiana* [10]. However, the in-depth studies on defluoridation using

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these biosorbents including preparation, development, characterization, and mechanism of adsorption are very limited and require further more investigation.

Hence, in the present study, a new biosorbent developed from *Cocos nucifera* Linn. root which is a natural material was used to study the fluoride removal through adsorption process and thereby sorption equilibrium, kinetic models, and thermodynamics parameters were evaluated from experimental data. Experiments are also done for application of *C. nucifera* Linn. root adsorbent for defluoridation of fluoride contaminated ground water samples from fields.

2. Materials and Methods

2.1. Details of plant

C. nucifera Linn. commonly known by the name coconut tree belonging to the family Arecaceae and is the only member of genus *Cocos*. The coconut palm is the most useful palm in the world. The coconut palm (Fig. 1) is found to grow under varying climatic and soil conditions. Unlike other plants, the coconut tree has neither a taproot nor root hairs but has a fibrous root system. Around the globe, more than 90 countries are having an annual production of coconut around 60 million tonnes.

2.2. Reagents and chemicals

All the chemicals utilized in the present study were of analytical reagent grade purchased from (E Merk Ltd.). Double distilled water is utilized throughout the study for preparing all the solutions. The stock fluoride solution of $0.1 \text{ g} \cdot \text{L}^{-1}$ was obtained by dissolving 0.221 g anhydrous NaF (E Merk Ltd.) in distilled water and dilute it to 1 L. The required working concentration of fluoride solution was prepared by the serial dilution of stock fluoride solution. SPADNS solution, Acid Zirconyl-SPADNS reagent, and reference solution were prepared as per the manual Standard Methods for Examination of Water and Wastewater [11].

2.3. Preparation of adsorbent

C. nucifera Linn., common name, coconut tree root, was collected in bulk from Kerala. The adsorbent was prepared from *C. nucifera* Linn. root. The root of *C. nucifera* Linn. was initially subjected to distilled water washing to get rid of free acids and other impurities. It is then completely air dried (under sunlight) for 2 days and then crushed into smaller pieces by using a grinder. The air desiccated matter was then chemically treated with $1 \text{ mol} \cdot \text{L}^{-1} \text{ HNO}_3$ at $80 \text{ }^\circ\text{C}$ for 30 min followed by washing with distilled water until the entire color had been removed. The chemically treated material is then dried converted into carbon in a muffle furnace at $700 \text{ }^\circ\text{C}$ devoid of air for 30 min. The

carbonized material obtained is cooled and further, the fraction of material passing through $600 \mu\text{m}$ was used as an activated adsorbent in the present study.

2.4. Adsorption experiments

Batch mode adsorption studies were conducted on samples of known initial concentration utilizing the Jar test apparatus with 1 L borosil beakers with the main aim to determine kinetic, equilibrium and thermodynamic parameters for fluoride adsorption onto activated adsorbent prepared from *C. nucifera* Linn. root. All sorption investigations were governed at room temperature. Variable doses of the adsorbent ($2\text{--}12 \text{ g} \cdot \text{L}^{-1}$) were added to the 1000 ml borosil beakers containing fluoride water samples of known concentration at room temperature to determine the optimum dose for fluoride elimination. The content was mixed at a rate of $80 \text{ r} \cdot \text{min}^{-1}$ for 90 min contact time. For isotherm study, $8 \text{ g} \cdot \text{L}^{-1}$ of adsorbent was stirred with fluoride solutions of known concentration 2, 5, 10, 15, 20, and $25 \text{ mg} \cdot \text{L}^{-1}$ for 90 min at room temperature ($26 \pm 1 \text{ }^\circ\text{C}$). The kinetic study was carried out by varying the time from 15 to 120 min, $8 \text{ g} \cdot \text{L}^{-1}$ of the adsorbent was added to 1000 ml of fluoride solution having $5 \text{ mg} \cdot \text{L}^{-1}$ concentration taken in series of beakers and stirred at $90 \text{ r} \cdot \text{min}^{-1}$ at room temperature [$(26 \pm 1 \text{ }^\circ\text{C})$]. The influence of temperature (T) on equilibrium sorption studies was carried out in the temperature span of 293 K to 323 K. After the stirring interval, the borosil jugs were slowly detached from the Jar test dais and thereafter settling of the contents of the beaker was permitted for 2–3 min. After the adsorbent settlement, the supernatants were cautiously transferred, strained via 42 No. filter paper and examined for remnant fluoride by a spectrophotometer (Systronics, portable) Model-169 as per the procedure mentioned in the manual of Standard Methods for Examination of Water and Wastewater at wavelength 570 nm. Fluoride adsorbed per unit mass of adsorbent and the percentage of fluoride adsorbed were computed, respectively according to a mass balance on the fluoride concentration using Eqs. (1) and (2) shown below:

$$q_e = (C_i - C_e)V/M \quad (1)$$

Percentage fluoride removal (A) was determined by applying equation:

$$A = (C_i - C_e) \times 100\% / C_i \quad (2)$$

where, q_e ($\text{mg} \cdot \text{g}^{-1}$) is the sorption capacity at equilibrium time, A is the percentage of fluoride sorption, C_i and C_e are the initial concentration of fluoride and the concentration of fluoride in the effluent solution at equilibrium time in aqueous phase, V (L) is the aqueous solution volume, and M (g) is the mass of *C. nucifera* Linn. root adsorbent used in the experiment.



Fig. 1. Coconut (*Cocos nucifera* Linn.) tree.

3. Results and Discussion

3.1. Characterization

3.1.1. Textual properties of *C. nucifera* Linn. root biosorbent (see Table 1)

Table 1
Textual properties of biosorbent developed from *Cocos nucifera* Linn. root [12–15]

Sr. no.	Parameter	Value	
I	Apparent density/g·ml ⁻¹	0.24	
II	Ash content/%	4.68	
III	Moisture content/%	6.43	
IV	Iodine number/mg·g ⁻¹	692	
V	Surface area/m ² ·(g BET) ⁻¹	Before	312.84
		After	110.38

3.1.2. Scanning Electron Microscopy

The SEM image of *C. nucifera* Linn. root activated adsorbent before adsorption of fluoride ions is shown in Fig. 2(a). It was revealed that the adsorbent has a structure consisting of pores and fissures. Fig. 2 (b) elucidates the SEM image of adsorbent after adsorption. From the SEM images of *C. nucifera* Linn. root adsorbent prior to and after sorption of fluoride, it is clear that there is a notable difference on the surface of the adsorbent. It is observed that a white coating of adsorbed fluoride is

formed over the activated carbon adsorbent developed from *C. nucifera* Linn. root. As a result, the surface area of *C. nucifera* Linn. root decreases after adsorption.

3.1.3. Brunauer–Emmett–Teller (BET) analyzer

The BET surface area of *C. nucifera* Linn. root activated adsorbent was found out to be 312.84 m²·g⁻¹. The BET surface area was determined at 77 K by nitrogen adsorption using a Micromeritics ASAP 2020 V3.04 H surface area analyzer. It was found that surface area of *C. nucifera* Linn. adsorbent before adsorption was 312.84 m²·g⁻¹ and after adsorption 110.38 m²·g⁻¹. This reduction in surface area is mainly due to the sorption of fluoride onto *C. nucifera* Linn. biosorbent surface.

3.1.4. FTIR

FTIR analysis on *C. nucifera* Linn. root developed adsorbent was done on an FTIR spectrometer with spectra measured from 4000 to 500 cm⁻¹ mainly to investigate the surface functional groups. FTIR spectral analysis of *C. nucifera* Linn. biosorbent before and after defluoridation was investigated and resulting spectra are shown Fig. 3. FTIR spectrum band distributions prior to treatment are: 1400 cm⁻¹, 1500 cm⁻¹, 1600⁻¹, 3100 cm⁻¹, 3500 cm⁻¹, and 3600 cm⁻¹ and after fluoride adsorption band assignments were found to be changing significantly with broad peak bands from 3100 cm⁻¹ to 3500 cm⁻¹. These most probably belong to O—H stretching vibrations in the alcohol group, N—H stretching in amine, amide or due to alkyne stretching. The peaks corresponding to 1600 cm⁻¹ imply stretching vibrations in C=O and C=C. The band be-

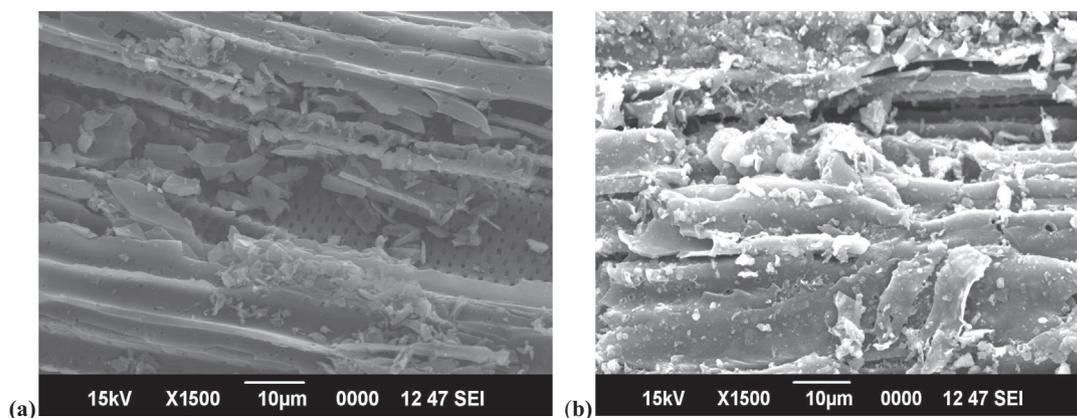


Fig. 2. SEM image of *Cocos nucifera* Linn. root activated adsorbent (a) before and (b) after adsorption.

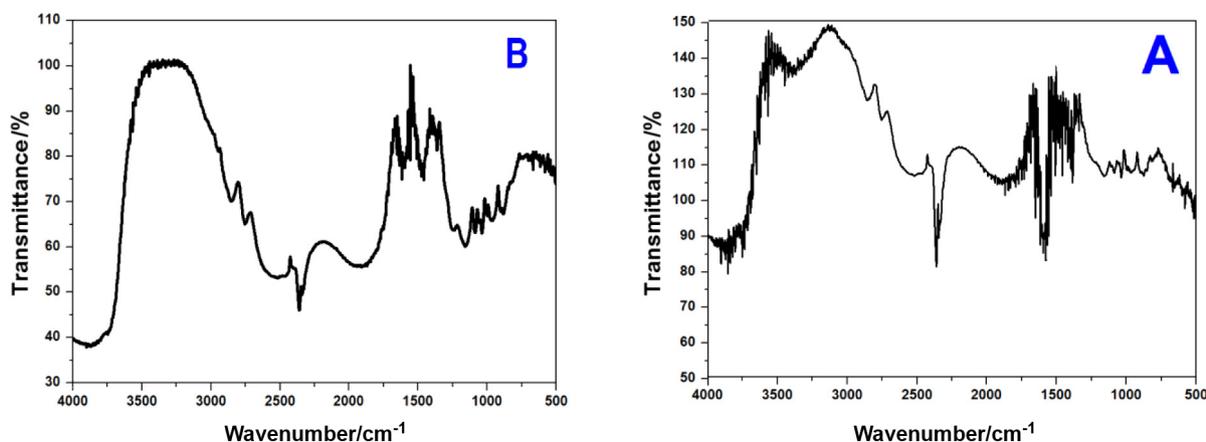


Fig. 3. FTIR image of *Cocos nucifera* Linn. root adsorbent before (B) and after adsorption (A).

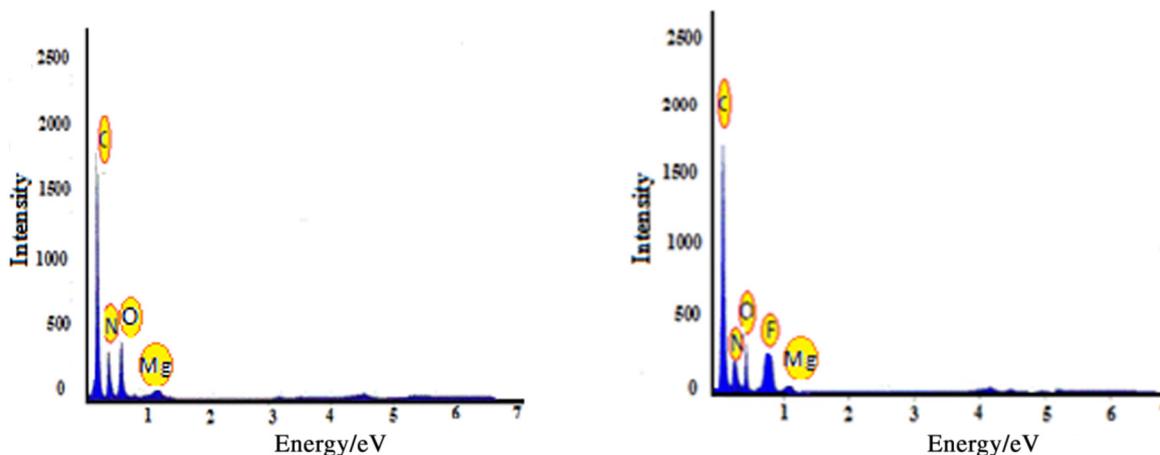


Fig. 4. EDX spectra of *Cocos nucifera* Linn. root adsorbent before and after adsorption.

tween 1400 cm^{-1} and 1500 cm^{-1} indicates the presence of O—H bonds. The peaks around 1000 cm^{-1} indicate mainly C—F stretching.

3.1.5. EDX

In the current work, EDX spectra were obtained for *C. nucifera* Linn. root adsorbent before and after fluoride sorption. The elemental analysis by Energy-dispersive X-ray spectroscopy showed the existence of carbon & oxygen molecules on the sample prior to and after sorption of fluoride (Fig. 4 & Table 2). The fluoride adsorbed after adsorption is shown in Fig. 4 whereas a small bump in both figures indicates the presence of magnesium as the roots of *C. nucifera* Linn. root are rich in magnesium and potassium. In comparison to carbon and oxygen, nitrogen is present in very small amount. It is very evident from the figure that after sorption fluoride peak appears in the EDX spectrum and this clearly suggests the sorption of fluoride onto *C. nucifera* Linn. root adsorbent. Furthermore, the percentage reduction in oxygen after sorption can be possibly because of substitution of some of the groups containing oxygen by fluoride ions at the surface of the adsorbent.

Table 2

Cocos nucifera Linn. root bio sorbent elemental composition

EDX of <i>Cocos nucifera</i> Linn. root adsorbent (before)		EDX of <i>Cocos nucifera</i> Linn. root adsorbent (after)	
Element	Mass fraction/%	Element	Mass fraction/%
C	84.38	C	84.15
O	13.56	O	10.52
N	1.92	N	1.68
Mg	0.14	Mg	0.10
		F	3.55
Total	100	Total	100

3.2. Optimization of adsorbent dose

The capacity of an adsorbent for adsorption for a given initial concentration of the adsorbate under a given set of operating conditions is decided on the basis of adsorbent dose. Studies on the upshot of the adsorbent dose were conducted by altering the dose of adsorbent from 2 to $12\text{ g}\cdot\text{L}^{-1}$. The upshot of adsorbent dose on fluoride adsorption is elucidated in Fig. 5.

By the analyses of adsorption data, it is clear that there is an increase in sorption of fluorides with a simultaneous increase in adsorbent dose. This increase in efficiency of adsorption with the corresponding increment in

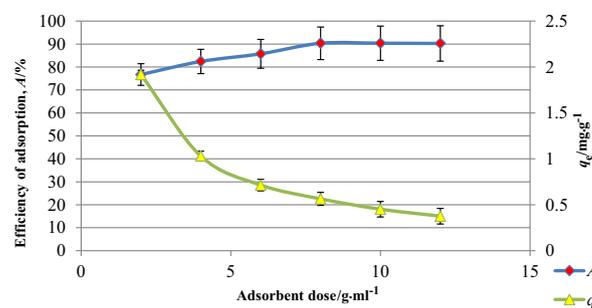


Fig. 5. Influence of adsorbent dose on sorption efficiency (A) and the equilibrium uptake (q_e) on *Cocos nucifera* root adsorbent. Initial adsorbate concentration — $5\text{ mg}\cdot\text{L}^{-1}$, contact period — 90 min, pH — 7, and stirring speed — $80\text{ r}\cdot\text{min}^{-1}$.

the dose of adsorbent is mainly because of greater adsorbent area and hence the presence of more active sites on adsorbent for the sorption of fluoride [16] meanwhile the adsorption capacity decreased from $1.918\text{ mg}\cdot\text{g}^{-1}$ to $0.376\text{ mg}\cdot\text{g}^{-1}$ with an increase in adsorbent from 2 to $12\text{ g}\cdot\text{L}^{-1}$. This decrease in the amount adsorbed could be due to a decrease in fluoride/active binding site ratio [17]. The percentage adsorption of fluoride on *C. nucifera* Linn. root activated adsorbent increases rapidly up to $8\text{ g}\cdot\text{L}^{-1}$ and more or less remains constant thereafter because of lack of availability of adsorbate around the adsorbent [16]. Maximum 90.32% removal of fluoride was obtained at $8\text{ g}\cdot\text{L}^{-1}$ adsorbent dose.

3.3. Adsorption isotherm

The adsorption isotherms were obtained by altering the initial adsorbate concentrations from $2\text{ mg}\cdot\text{L}^{-1}$ to $25\text{ mg}\cdot\text{L}^{-1}$ at $8\text{ g}\cdot\text{L}^{-1}$ adsorbent dose, contact time 90 min, pH 7, and stirring rate $80\text{ r}\cdot\text{min}^{-1}$ when room temperature was $(26 \pm 1)\text{ }^\circ\text{C}$. The plots of the amount of fluoride removed and efficiency of adsorption (% fluoride adsorbed) against initial fluoride concentration are given in Fig. 6.

It was observed that the fluoride sorption capacity gradually rises from 0.2305 to $1.765\text{ mg}\cdot\text{g}^{-1}$ with increment in the initial fluoride concentration from 2 to $25\text{ mg}\cdot\text{L}^{-1}$, which could be attributed to the presence of more fluoride ions for the adsorption at higher concentration.

The isotherm models employed in the present study are namely Langmuir, Freundlich, Temkin and D-R isotherm models. The adsorption data obtained from the experiment are fitted with the mentioned isotherm equations.

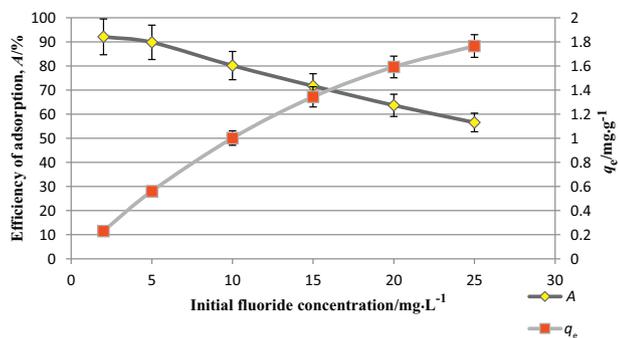


Fig. 6. Influence of adsorbate concentration on sorption efficiency (A) and equilibrium uptake (q_e) on *Cocos nucifera* root adsorbent. Adsorbent dose – $8 \text{ g}\cdot\text{L}^{-1}$, stirring speed – $80 \text{ r}\cdot\text{min}^{-1}$, pH – 7.0, contact period – 90 min.

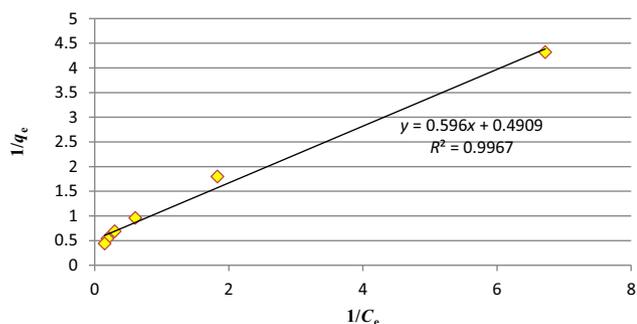


Fig. 7. Langmuir plot for sorption of fluoride on *Cocos nucifera* Linn. adsorbent. Adsorbent dose: $8 \text{ g}\cdot\text{L}^{-1}$, contact time: 90 min, stirring rate: $80 \text{ r}\cdot\text{min}^{-1}$, room temperature: $(26 \pm 1) \text{ }^\circ\text{C}$.

In the present study adsorption data obtained from the experiment are analyzed with the Freundlich, Langmuir, Temkin and D–R isotherm models. The dimensionless constant R_L related to the Langmuir adsorption isotherm indicates the shape of isotherm and the adsorption process nature and is expressed by the equation: $R_L = 1 / (1 + B C_e)$.

The process is irreversible if $R_L = 0$, favorable if $R_L < 1$, linear if $R_L = 1$ and unfavorable if $R_L > 1$ [1]. For *C. nucifera* Linn. root adsorbent, the R^2 value in the Langmuir isotherm was comparatively higher than the Freundlich isotherm, and the parameter (R_L) having a value of 0.195, which is in the range of 0 to 1 further suggests the Langmuir isotherm favorability than the Freundlich isotherm. Fig. 7 elucidates the Langmuir adsorption plot for *C. nucifera* Linn. biosorbent.

Furthermore, Temkin isotherm parameters A and B were obtained utilizing the equation, $q_e = B \ln C_e + B \ln A$, where $RT/b = B$ and D–R

isotherm parameters β and mean energy of sorption, E were obtained utilizing the equation $\ln(q_e) = -B\varepsilon^2 + \ln(q_m)$ and $E = (2\beta)^{-1/2}$ where $\varepsilon = RT \ln(1 + 1/C_e)$, R : gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), β : energy associated constant ($\text{J}\cdot\text{mol}^{-1}$), T : absolute temperature, ε : Polanyi potential, q_e : sorption capacity ($\text{mg}\cdot\text{g}^{-1}$) and C_e : equilibrium concentration of adsorbate in the solution in $\text{mg}\cdot\text{L}^{-1}$.

If the value of D–R mean free energy E is between 8 and $16 \text{ kJ}\cdot\text{mol}^{-1}$, the adsorption process is considered as chemisorption and if it is below $8 \text{ kJ}\cdot\text{mol}^{-1}$, the adsorption process is physisorption. The calculated mean free energy of sorption E ascertained to be $9.13 \text{ kJ}\cdot\text{mol}^{-1}$ for *C. nucifera* Linn. activated adsorbent. This observation is in agreement with the previously reported results with rice straw activated carbon [9], eggshell powder as adsorbent [18]. Table 3 shows the comparative isotherm constants for fluoride adsorption onto various adsorbents.

3.4. Kinetic study

Contact time plays a very prime part in adsorption, regardless of other experimental parameters which affect sorption kinetics. The kinetic study was conducted for the fluoride adsorption onto *C. nucifera* Linn. root activated adsorbent with a dose of adsorbent of $8 \text{ g}\cdot\text{L}^{-1}$ and initial adsorbate concentration of $5 \text{ mg}\cdot\text{L}^{-1}$. The sorption kinetic investigations were governed by altering the contact period between 15 and 120 min. The influence of contact period on percentage removal of fluoride is indicated in Fig. 8. From the analysis of the adsorption data obtained, it is observed that the fluoride removal increases with the rise in contact time. The fluoride removal capacity ($q_e, \text{mg}\cdot\text{g}^{-1}$) also increases with an increase in contact period. But after some time it reaches a steady value indicating the equilibrium attainment. As a result, the further increase in contact period does not add to further uptake mainly due to the accumulation of adsorbate in the present active sorption sites on the surface of *C. nucifera* Linn. root adsorbent [24]. All the adsorbent sites are vacant initially, and the solute concentration gradient is high which results in an initial high percentage of removal [21]. The equilibrium time for the present study was obtained for 90 min at which the graphs appear nearly asymptotic to the time axis and hence it is considered as optimum contact time for further study. The equilibrium contact time reported by previous researches are 120 min for rice husk [19], 120 min for Maize husk fly ash [25], 180 min for tea ash [26] and 90 min for chitosan coated silica [27]. The sorption capacity of fluoride at 90 min onto *C. nucifera* Linn. root adsorbent was found to be $0.562 \text{ mg}\cdot\text{g}^{-1}$.

In the present study in order to better express the adsorption of fluoride onto *C. nucifera* Linn. root activated adsorbent, the sorption kinetic models mainly pseudo-first, pseudo-second, Weber and Morris diffusion model, and Elovich model are discussed and the kinetic parameters are determined.

Table 3
Comparative isotherm constants for fluoride adsorption onto various adsorbents

No.	Adsorbent	Freundlich isotherm		Langmuir isotherm			Temkin isotherm	D-R isotherm	Author
		$k_f/\text{mg}\cdot\text{g}^{-1}$	n	$a/\text{mg}\cdot\text{g}^{-1}$	$b/\text{L}\cdot\text{mg}^{-1}$	R_L	$B/\text{J}\cdot\text{mol}^{-1}$	$E/\text{kJ}\cdot\text{mol}^{-1}$	
1	<i>Cocos nucifera</i> root adsorbent	0.657	1.61	2.037	0.823	0.195	0.507	9.13	Present study
2	Activated carbon								
	Banana peel	0.177	3.954	0.395	0.426	0.086	–	–	[1]
	Coffee husk	0.225	4.601	0.415	0.789	0.048	–	–	[1]
3	Activated carbon (from rice husk)	1.993	1.101	0.05	0.375	–	–	–	[19]
4	Activated carbon (bark of <i>Vitex negundo</i> plant)	1.119	4.01	1.15	0.154	0.029	0.196	7.07	[20]
5	Activated charcoal	0.312	1.917	1.076	0.429	–	–	–	[21]
6	Carbonaceous material								
	CG600	5.90	2.38	26.8	0.17	–	–	–	[22]
	CG800	6.84	2.70	18.2	7.45	–	–	–	[22]
	CG1000	6.46	7.14	11.4	0.45	–	–	–	[22]
7	Activated carbon (from rice straw)	4.54	2.63	15.9	0.27	–	–	10.46	[9]
		1.3	1.46	18.9	0.05	–	–	10.46	[9]
		0.6	1.2	16.7	0.03	–	–	10.46	[9]
8	Activated carbon (inexpensive adsorbents)	0.004	1.29	0.122	0.484	–	–	–	[23]

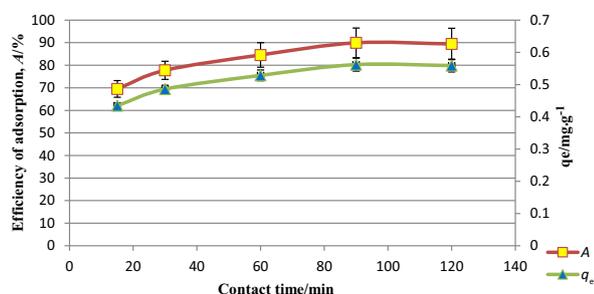


Fig. 8. Influence of contact time on the percentage sorption (A) and the equilibrium uptake (q_e) on *Cocos nucifera* Linn. adsorbent. Adsorbent dose – $8 \text{ g} \cdot \text{L}^{-1}$, stirring speed – $80 \text{ r} \cdot \text{min}^{-1}$, pH – 7; room temperature (26 ± 1) °C.

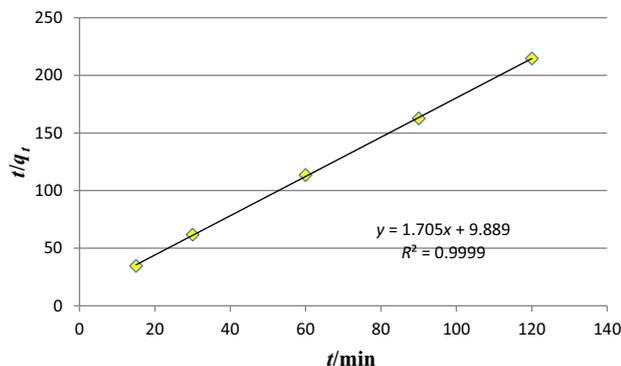


Fig. 9. Pseudo-second order sorption kinetics.

The adsorption data has been analyzed with various rate models of kinetics namely pseudo-first rate, pseudo-second rate, Weber and Morris model and Elovich model when compared, the correlation coefficient obtained in the case of the pseudo-second-order kinetic model ($R^2 = 0.9999$) is comparatively higher than all the other sorption kinetic models, which in turn clearly suggests the best fit model for the fluoride adsorption onto thermally activated adsorbent developed from *C. nucifera* Linn. root is the pseudo-second-order kinetic model (Fig. 9). Some of the earlier researches on the adsorption of fluoride also reported the suitability of the pseudo-second-order kinetics for the adsorption of fluoride on tea ash [26], chitosan coated silica [27], eggshell powder as an adsorbent [18], and rice straw activated carbon [9]. Following, the first order kinetic model with a correlation coefficient ($R^2 = 0.9775$), Weber and Morris intra-particle diffusion model ($R^2 = 0.8857$), and Elovich kinetic model with a correlation coefficient ($R^2 = 0.9697$) indicates that the adsorption of fluoride with thermally activated carbon from *C. nucifera* Linn. root as adsorbent follows Elovich kinetics and propound mainly diffusion as an adsorption rate-determining step. Table 4 shows the comparative adsorption kinetic parameters with different adsorbents.

Table 4
Comparison of adsorption kinetic parameters with various adsorbents

No.	Adsorbent	Pseudo-first order		Pseudo-second order		Intra-particle diffusion model $K_p/\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$	Elovich model		Ref.
		$K_1/\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$	$q_e/\text{mg} \cdot \text{g}^{-1}$	$K_2/\text{mg} \cdot \text{g}^{-1}$	$h/\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$		α	β	
1	<i>Cocos nucifera</i> root adsorbent	0.0515	4.81	0.2935	0.101	0.0148	0.44	5.05	Present study
2	Activated carbon (Bark of <i>Vitex negundo</i> plant)	0.027	0.55	0.082	1.28	0.066	0.688	4.83	[20]
3	Activated carbon	0.046	2.142	0.011	0.240	0.299	0.236	1.184	[6]
4	Activated carbon (From <i>Acacia farnesiana</i>)	–0.037	–	0.524	–	0.163	–	–	[10]
5	Activated carbon ANC AKC	–0.133 –0.126	–	–	–	3.02 3.3	–	–	[3]
6	Activated carbon	0.017	1.233	0.049	0.236	–	0.693	3.105	[28]

3.5. Thermodynamic study

Thermodynamic study of the adsorption of fluoride onto thermally activated carbon developed from *C. nucifera* Linn. root was conducted in the range of 20–50 °C keeping the initial fluoride concentration of $5 \text{ mg} \cdot \text{L}^{-1}$, dose of adsorbent of $8 \text{ g} \cdot \text{L}^{-1}$, period of contact of 90 min, and agitation speed of $80 \text{ r} \cdot \text{min}^{-1}$. Fig. 10 shows the sorption efficiency (A) as well as sorption capacity versus temperature. It is evident from the figure that the efficiency of sorption and sorption capacity increases with an increase in temperature. The most probable reason for this is the enlargement of pore size [16] that means with the increase in temperature, the surface thickness of *C. nucifera* Linn. root adsorbent reduces and thereby the kinetic energy of adsorbate ion rapidly increases, which in turn increases the diffusion rate of adsorbate ions along the exterior border layer and intramural pores of *C. nucifera* Linn. root adsorbent [20].

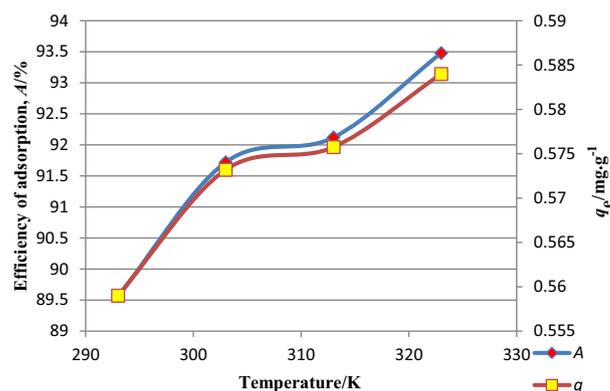


Fig. 10. Effect of temperature on fluoride adsorption. Adsorbent dose: $8 \text{ g} \cdot \text{L}^{-1}$, contact time: 90 min, stirring rate: $80 \text{ r} \cdot \text{min}^{-1}$, pH: 7.

The principal thermodynamic variables incorporated with the sorption studies are mainly the change in enthalpy (ΔH^\ominus), change in free energy (ΔG^\ominus), and change in entropy (ΔS^\ominus) and are reckoned by using the formulas discussed:

$$\Delta G = -RT \ln(K_d) \quad (3)$$

$$\ln K_d = \Delta S/R - \Delta H/RT \quad (4)$$

$$K_d = q_e/C_e \quad (5)$$

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

where, K_d indicates the sorption distribution coefficient, q_e is the adsorption capacity that means the amount of adsorbate adsorbed on

C. nucifera Linn. root adsorbent ($\text{mg} \cdot \text{g}^{-1}$), C_e indicates adsorbate equilibrium concentration, T indicates absolute temperature and R implies gas constant. Van't Hoff's plot for the adsorption of fluoride ($\ln K_d$ versus $1/T$) onto activated carbon adsorbent is shown in Fig. 11. Intercept and slope of $\ln K_d$ versus $1/T$ graph will give the value of ΔS and ΔH . The ΔG values are found out from the equation $\Delta G = \Delta H - T\Delta S$ [29,30]. The variation of ΔG versus temperature is shown in Fig. 12. The estimated thermodynamic parameters for fluoride adsorption onto

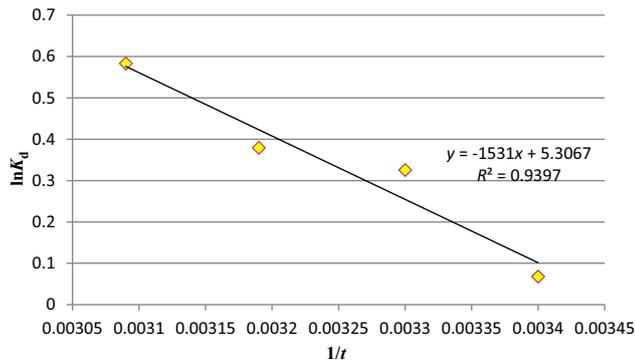


Fig. 11. Evaluation of thermodynamic parameters for sorption of fluoride on *Cocos nucifera* Linn. adsorbent.

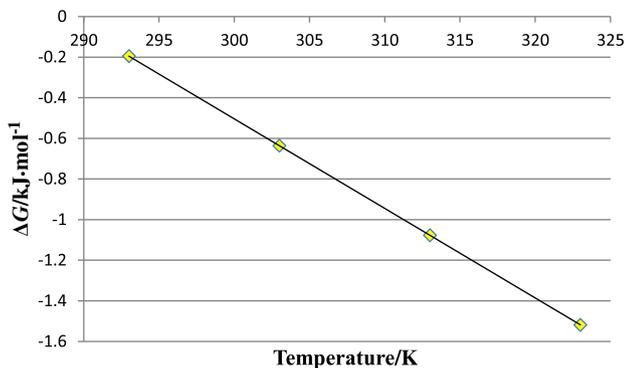


Fig. 12. Effect of temperature on Gibbs free energy.

C. nucifera Linn. root adsorbent is elucidated in Table 5.

The negative value of ΔG^\ominus with respect to different temperatures points out the suitability of sorption phenomenon and the spontaneous nature of the fluoride sorption onto *C. nucifera* Linn. root adsorbent. The more negative values of ΔG^\ominus with the rise in temperature indicates higher temperatures make the sorption favorable. The positive value of ΔH^\ominus ($12.728 \text{ kJ} \cdot \text{mol}^{-1}$) indicates that the adsorption phenomenon is endothermic in nature [24]. The positive value of entropy change (ΔS) suggests an increase in randomness with an increase of temperature. Similar observations were obtained previously on thermodynamic study for fluoride adsorption by *P. emblica* activated carbon [6], activated carbon developed from *Ficus racemosa* plant [31], activated biochar from domestic food waste [32], and pumice stone adsorbent [33].

Table 5

Estimated thermodynamic parameters (ΔH , ΔG , and ΔS) for fluoride adsorption onto activated adsorbent developed from *Cocos nucifera* Linn. root

Parameter	$\Delta H^\ominus/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta S/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$\Delta G/\text{kJ} \cdot \text{mol}^{-1}$				R^2
Temperature/K			293	303	313	323	
<i>Cocos nucifera</i> Linn. root	12.728	44.11	−.196	−.637	−1.078	−1.519	0.9397

3.6. Practical application

Six groundwater samples were collected from fluoride contaminated locations of Palakkad district in Kerala and initial concentration of fluoride present is analyzed. A batch adsorption studies were conducted using activated adsorbent developed from *C. nucifera* Linn. root and the removal efficiencies in each case are determined which is presented in Table 6. It clearly indicates that the % removal of fluoride

Table 6

Fluoride removal from ground water samples from the field using activated adsorbent developed from *Cocos nucifera* Linn. root

No.	Source of sample	$C_i/\text{mg} \cdot \text{L}^{-1}$	$C_e/\text{mg} \cdot \text{L}^{-1}$	Removal/%
1	Sample 1 (Athikodu)	1.71	0.11	93.56
2	Sample 2 (Kodumthirapalli)	2.8	0.246	91.21
3	Sample 3 (Vattalakkki)	2.02	0.156	92.27
4	Sample 4 (Chinnamoolathara)	3.12	0.308	90.128
5	Sample 5 (Anakatti)	1.84	0.128	93.04
6	Sample 6 (Kulukkur)	2.64	0.262	90.07

from all samples is more than 90%.

3.7. Comparative study for fluoride sorption capacity of *C. nucifera* Linn. root bio-sorbent

A comparative study is made with the present adsorbent developed from *C. nucifera* Linn. root with different adsorbents available in the literature for defluoridation of water and is presented in Table 7. It is clear that the adsorbent developed in present work is efficient for fluoride removal from the contaminated water up to an extent of $2.037 \text{ mg} \cdot \text{g}^{-1}$.

Table 7

Fluoride uptake capacity comparison of *Cocos nucifera* Linn. root biosorbent with other bio-sorbents from literature

No.	Adsorbent	$q_e/\text{mg} \cdot \text{g}^{-1}$	Ref.
1	<i>Cocos nucifera</i> Linn. root biosorbent	2.037	Present study
2	Sweet lemon peel powder	0.744	[34]
3	<i>Acacia catechu</i> leaf powder	0.9	[23]
4	Groundnut shell powder	1.498	[34]
5	Activated carbon of <i>Vitex negundo</i> plant	1.150	[20]

4. Conclusions

Based on the study, the adsorbent developed from *C. nucifera* Linn. root showed greater potential for the adsorption of fluoride ions from water. Maximum fluoride removal 93.48% was attained for an adsorbent dose of $8 \text{ g} \cdot \text{L}^{-1}$, contact period: 90 min, stirring speed: $80 \text{ r} \cdot \text{min}^{-1}$, and temperature: 50°C when the initial adsorbate concentration was $5 \text{ mg} \cdot \text{L}^{-1}$. The fluoride adsorption on thermally activated carbon adsorbent from *C. nucifera* Linn. can be best described by the Langmuir isotherm model. The adsorption kinetic data fitted well with the pseudo-second-order kinetic model. The negative value of ΔG^\ominus with respect to various temperatures points out the suitability of sorption phenomenon and the spontaneous nature of the fluoride sorption onto *C. nucifera* Linn. root. The more negative values of ΔG^\ominus with the

rise in temperature points out that increased temperatures make the sorption favorable. The positive ΔH^\ominus points out that the phenomenon of adsorption of fluoride on *C. nucifera* Linn. root adsorbent is endothermic in nature. Experimental results obtained from the present study showed that biosorbent developed from *C. nucifera* Linn. root is an efficient and eco-friendly adsorbent for removal of fluoride.

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