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# Kinetic and thermodynamic studies for fluoride removal using a novel bio-adsorbent from possotia (*Vitex negundo*) leaf

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## Abstract

**Background:** Possotia leaf powder (PLP), a novel biosorbent obtained from a locally available wild plant with environment friendly and low cost nature, has found to be effective to remove fluoride from fluoride contaminated drinking water.

**Methods:** The kinetic and thermodynamic parameters for the adsorption have been studied. Its fluoride adsorption efficiency is found to be nearly 75% at natural pH range and is affected by the parameters like contact time, adsorbent dose, solution temperature and initial fluoride concentration.

**Results:** The optimum contact time and adsorbent dose were found to be 120 min and 3gm/L, respectively. Langmuir, Freundlich and Temkin isotherm are studied through this experimental data and found to be well followed. The adsorption kinetics data were fitted to pseudo first order, pseudo second order, and intraparticle diffusion models and was best fitted for pseudo second order model.

**Conclusions:** The thermodynamic study points out the efficiency of this bio-adsorbent at low temperature indicating the physical nature of adsorption with weak adsorbent-adsorbate force of attraction. By studying enthalpy, entropy and Gibb's free energy via van't Hoff plot, it was observed that the adsorption process was favorable and exothermic in nature.

**Keywords:** *Vitex negundo*, Possotia leaf powder, Kinetics, Isotherm, Bio-adsorbent

## Background

Water is life, but we are still unable to make healthy drinking water available and affordable to all. Waste or contaminated water from any source must ultimately return to the natural water reservoir. A large number of people depend heavily on underground water due to lack of other water resources. People in the world are suffering as 80% of the diseases come from ill or deteriorated water, which is threatening for human life (Mamba et al., n.d.). Fluoride is one such life-threatening water contaminant. Its gaseous form is a very powerful oxidizing agent. Naturally, fluoride exists as a very reactive fluoride ion, and its natural abundance by weight in the Earth's crust ranges from 0.065–0.09% (Mondal et al., n.d.-a). The World

Health Organization (WHO) announced the acceptable range of fluoride in drinking water as 1–1.5 mg/L (Swain et al., n.d.; Mohan et al., n.d.).

Intake of fluoride from drinking water at the level of 1 mg/L enhances bone development and prevents dental carries. Exceeding the limit of fluoride intake may lead to dental and skeletal fluorosis. The main constituent of teeth and bone is hydroxyl apatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) and fluoride can substitute the hydroxide ion within the hydroxyl apatite crystal structure to form fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ), which makes teeth and bones denser, harder, and more brittle (Yu et al., n.d.). Young children are the most susceptible as dental enamel and skeletal formation is most active during early childhood (Levin et al., n.d.). Moreover, excessive fluoride intake may interfere in DNA synthesis (Bhatnagar et al., n.d.).

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Therefore, researchers are trying to focus on various defluoridation processes. The most commonly used methods for defluoridation of drinking water are reverse osmosis, precipitation, membrane filtration, ion-exchange, etc. (Yadav et al., n.d.). Among these, adsorption is considered as the best method for its low maintenance cost and effectiveness towards fluoride removal even at low concentrations (Gandhi et al., n.d.). Hence, researchers have focused on locally available bio-adsorbents like *Moringa oleifera* (drum stick), tulsī, tamarind seed, tea ash (Mondal et al., n.d.-b), babool bark (Mamilwar et al., n.d.), banana peel (Bhaumik & Mandal, 2016), neem leaf, kīkar leaf (Kumar et al., n.d.), papal leaf (Ramanjaneyulu et al., n.d.), red mud, fly ash, rice husk ash, and maize ash (Waghmare & Arfin, n.d.).

*Vitex negundo*, popularly known as possotia trees in the North Eastern Region of India, belong to the family *Lamiaceae* which are easily available in Assam, India, and are known for their medicinal properties. Studies have shown that chemicals isolated from the plant have potential anti-inflammatory, antibacterial, antifungal, and analgesic activities (Dharamasiri et al., n.d.; Gupta & Tandon, n.d.). Moreover, local people use it as vegetable leaf for treatment of rheumatism and deworming. Use of its bark for defluoridation was already reported (Suneetha et al., n.d.). But as it is a herb-like plant, many plants will be required for the preparation of the bio-adsorbent. Therefore, it is imperative to study if this particular leaf could be used for the wastewater treatment. With this background, this study was undertaken and a detailed kinetic and thermodynamic interpretation of the process involved has been presented in this manuscript.

## Methods

### Preparation of required solutions

Stock solution of the adsorbate NaF of concentration 100 mg/L is prepared by dissolving 0.22 g of NaF in 1.0 L of distilled water. SPADNS solution is prepared by dissolving 958 mg SPADNS [sodium 2-(parasulfo-phenylazo)-1,8 dihydroxy-3,6 naphthalene disulfonate] in 500 mL of distilled water. The zirconium-oxychloride solution is prepared by first dissolving 133 mg of zirconium-oxychloride octahydrate ( $ZrOCl_2 \cdot 8H_2O$ ) in 25 mL of distilled water, then adding 350 mL of concentrated HCl and making the total volume of the solution up to 500 mL with distilled water. By mixing equal volume of SPADNS and zirconium-oxychloride solution, the SPADNS reagent is prepared which is used in the experiments.

A stock solution of 0.05 M copper (II) bisethylenediamine complex is prepared by mixing 50 mL of 0.1 M  $CuCl_2$  solution with 102 mL of 1.0 M ethylene diamine solution and is used to determine the cation exchange capacity of the bio-adsorbent.

### Preparation of possotia leaf powder

The bio-adsorbent possotia leaf powder is prepared from the matured leaves of the possotia tree. The leaves are collected, cleaned thoroughly, and dried for 3–4 days. The dried leaves are crushed into fine powder by using a mechanical grinder. The resultant powder is sieved and fractionated using a series of sieves with different sizes. The powder is then again dried in an air oven at 60–70 °C for 12 h and washed with distilled water to remove all the color pigments so that it will not interfere in spectroscopic studies. Then the sample is kept at room temperature and used for further experiments.

### Adsorption experiments

In a 100-mL conical flask, the required amount of possotia leaf powder (PLP) is taken and 50 mL of NaF solution of a particular concentration is added. It is then agitated in a shaker at a constant speed for some time. As soon as the adsorption is over, the mixture is filtered off and the amount of un-adsorbed fluoride is estimated spectrophotometrically by SPADNS method at  $\lambda_{max} = 570$  nm (Bharali & Bhattacharyya, n.d.). Effects of pH on fluoride sorption is studied in the pH range of 4.0 to 11.0 with a bio-adsorbent amount of 3.0 g/L, fluoride concentration of 3.0 mg/L, and contact time of 120 min at 30 °C. The pH of the fluoride solutions are adjusted by adding 0.1 M ( $M = \text{mol/dm}^3$ ) HCl and 0.1 M NaOH solutions. The effect of contact time (in minutes) is studied by taking a constant amount of adsorbent (3 g/L) at 30 °C at time intervals of 5, 10, 15, 30, 60, 90, 120, and 180 min. The effect of adsorbent doses for fluoride removal is studied by taking adsorbent doses as 1, 2, 3, 4, and 5 g/L at the contact time of 120 min at 30 °C. Also, the effect of fluoride concentration on the defluoridation process of the adsorbent is studied taking the fluoride concentration as 3, 6, 9, 12, and 15 mg/L. The amount of fluoride adsorbed per unit mass of the adsorbent ( $q_t$ ) at a time  $t$  is calculated using the following equations.

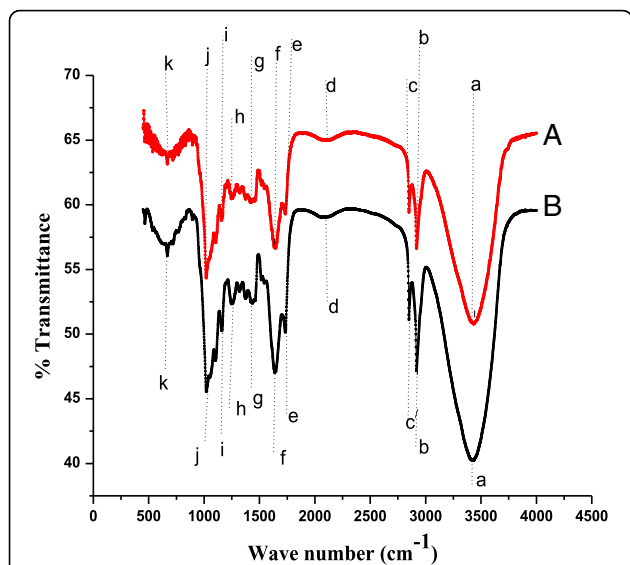
$$q_t(\text{mg/g}) = (C_o - C_t)/m$$

$$\text{Extent of adsorption (\%)} = [(C_o - C_t)/C_o] \times 100$$

where  $C_o$  and  $C_t$  are initial ( $t = 0$ ) and final ( $t = t$ ) fluoride concentrations in milligrams per liter when the adsorption was carried out for a time interval of  $t$  minutes, with an adsorbent amount of milligrams per liter.

### Cation exchange capacity

Cation exchange capacity of PLP is determined by copper (II) bisethylenediamine complex method. In this method, 0.5 g of PLP is added in 25 mL of each of the solution of 0.05, 0.03, 0.02, and 0.01 M of  $[Cu(en)_2]^{+2}$  and centrifuged for 30 min. After adsorption is over, the mixture is filtered off and the used  $[Cu(en)_2]^{+2}$  is

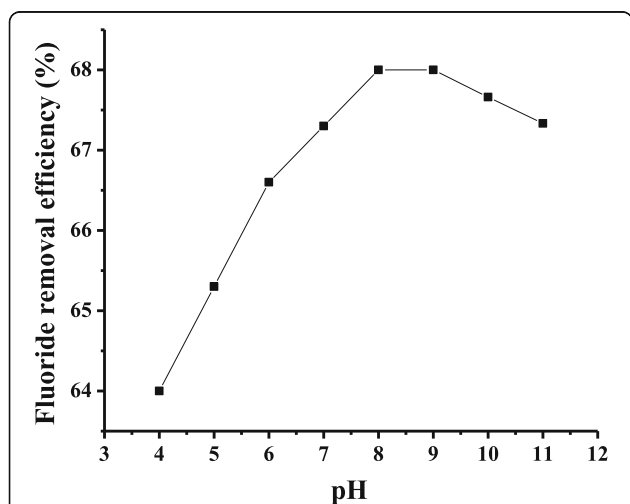


**Fig. 1** FTIR spectrum of PLP before (B) and after (A) fluoride adsorption. [In "A"—a=3442 cm<sup>-1</sup>, b=2936 cm<sup>-1</sup>, c=2876 cm<sup>-1</sup>, d=2122.13 cm<sup>-1</sup>, e=1739 cm<sup>-1</sup>, f=1662.23 cm<sup>-1</sup>, g=1439 cm<sup>-1</sup>, h=1297 cm<sup>-1</sup>, i=1192 cm<sup>-1</sup>, j=1039.4 cm<sup>-1</sup>, k=684.6 cm<sup>-1</sup>. In "B"—a=3431.7 cm<sup>-1</sup>, b=2899.4 cm<sup>-1</sup>, c=2854.26 cm<sup>-1</sup>, d=2111.8 cm<sup>-1</sup>, e=1744.7 cm<sup>-1</sup>, f=1639.5 cm<sup>-1</sup>, g=1437.1 cm<sup>-1</sup>, h=1249 cm<sup>-1</sup>, i=1167.2 cm<sup>-1</sup>, j=1027 cm<sup>-1</sup>, k=672.3 cm<sup>-1</sup>]

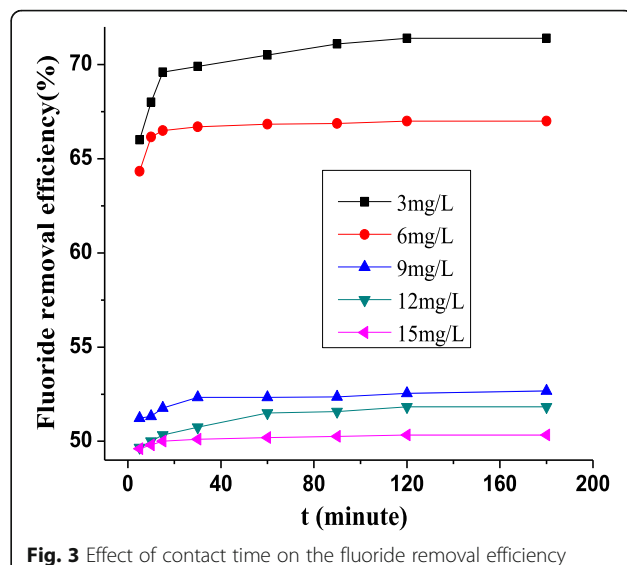
estimated spectrophotometrically using UV spectrometer at λ<sub>max</sub> = 550 nm. The cation exchange capacity (CEC) of PLP is calculated using the equation:

$$(\text{meq/g}) = (M-S)/m$$

where *M* is the initial concentration of the solution, *S* is the concentration of the solution after adsorption, and *m* is the amount of the bio-adsorbent.



**Fig. 2** Effect of pH on the removal efficiency of fluoride



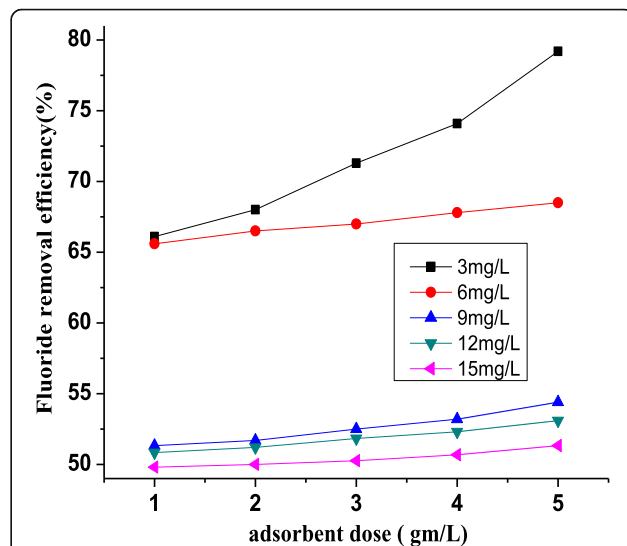
**Fig. 3** Effect of contact time on the fluoride removal efficiency

**Anion exchange capacity**

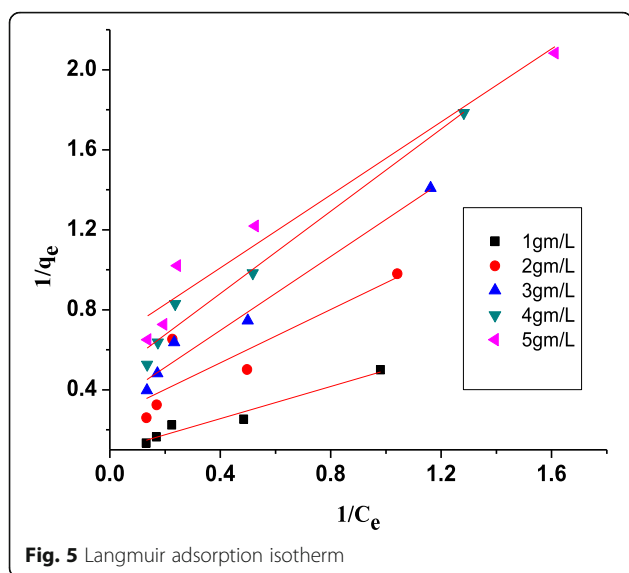
To determine the anion exchange capacity (AEC), 0.1 M AgNO<sub>3</sub> and 0.01 M NaCl were prepared and titrated conductometrically. Again 0.1 M AgNO<sub>3</sub> is titrated with the adsorbent solution containing 0.2 g adsorbent in 50 mL distilled water. Then using the following equation, AEC of PLP is calculated.

$$(\text{meq/g}) = NV/m$$

where *N* is the normality of AgNO<sub>3</sub>, *V* is the volume difference of AgNO<sub>3</sub> in two sets of titration, and *m* is the amount of the bio-adsorbent (anion exchanger).



**Fig. 4** Effect of adsorbent dose on the fluoride removal efficiency



**Results and discussion**

**Identification of surface functional groups with IR spectroscopy**

FTIR spectra of PLP before (B) and after (A) fluoride adsorption are presented in Fig. 1. The functional groups identified from the spectra are -OH (3431.7 cm<sup>-1</sup>), -CH<sub>3</sub> (2899.4 and 2854.26 cm<sup>-1</sup>), C-C, C-N<, C-O- (1027 and 1249.7 cm<sup>-1</sup>), >C=O (1639.5 cm<sup>-1</sup>), >C=S (1167.2 cm<sup>-1</sup>), -C≡C- (2111.8 cm<sup>-1</sup>), -CH<sub>2</sub> (1427.1 cm<sup>-1</sup>), C=C (1744.7 cm<sup>-1</sup>), and C-X (672.2 cm<sup>-1</sup>). Comparing the FTIR spectra of PLP before (B) and after (A) fluoride adsorption, it is seen that the respective groups are shifted towards the higher value after fluoride adsorption. The chief cause of these shifts may be the interaction with fluoride.

**The effect of pH**

Figure 2 represents the effect of pH on removal efficiency of fluoride of adsorbent dose 3 g/L in 3 ppm fluoride solution. The test solution is found to be slightly acidic (having pH = 6.38) which was changed during the experiment from pH 4 to 11. It is observed

that adsorption efficiency increases as the pH increases and gets the maximum at a pH of 8 and then starts decreasing. The relatively lower adsorption of fluoride in the acidic range indicates the possibility of formation of weakly ionized hydrofluoric acid. The quick reduction of the amount of fluoride adsorption in the alkaline pH range (after attaining pH 8) may be due to competition of hydroxyl ions with fluoride for adsorption sites of PLP (Swain et al., n.d.).

**The effect of contact time**

Figure 3 reflects that on increasing contact time, fluoride removal efficiency of the adsorbent increases up to 120 min and remains constant afterwards. This may be due to the fluoride ion deposition on the available adsorption site of the PLP. The initial fast adsorption could be the result of participation of specific functional groups and active surface sites of PLP which decreases towards the end of the experiments. The monolayer formation of fluoride ion on the PLP outer surface and diffusion into the inner surface plays a crucial role in this case (Jamode et al., n.d.).

**The effect of adsorbent dose**

During the experiment, the amount of adsorbent dose is varied from 1 to 5 g/L for various concentrations of fluoride solutions (3, 6, 9, 12, and 15 mg/L) at a constant shaking time of 120 min. It is seen from Fig. 4 that for each of the concentration of the fluoride solution, the adsorption efficiency of the adsorbent increases with increase of the adsorbent dose. This is due to increasing adsorbent site (Swain et al., n.d.).

**Adsorption isotherm**

The adsorption isotherm is nothing but a mathematical relationship between the amount adsorbed on the adsorbent surface and the pressure (in case of gaseous adsorbate) or the concentration (in case of liquid) of the adsorbate in equilibrium at a constant temperature. To describe the adsorbate-adsorbent interactions quantitatively and to study the effectiveness

**Table 1** Equilibrium isotherm parameters of the defluoridation process

PLP dose (g/L)	Langmuir isotherm						Freundlich isotherm		Temkin isotherm		
	a (mol/g)	b (L/mg)	R <sub>L</sub>					1/n	K (L/g)	B (J/mol)	A <sub>T</sub> (L/g)
			3 mg/L	6 mg/L	9 mg/L	12 mg/L	15 mg/L				
1	10.75269	26.41938	0.01246	0.006269	0.004188	0.003144	0.002517	0.598	2.118361	5.583	1.395779
2	3.703704	5.577867	0.05639	0.029013	0.019531	0.01472	0.011811	0.532	1.08893	2.536	1.465255
3	3.067485	3.319789	0.091246	0.047804	0.032385	0.024487	0.019686	0.54	0.810961	1.734	1.562499
4	2.12766	2.067696	0.138829	0.074592	0.050996	0.038741	0.031235	0.504	0.656145	1.242	1.682087
5	1.550388	1.701852	0.163785	0.089197	0.061287	0.04668	0.037696	0.462	0.594292	0.948	1.902833

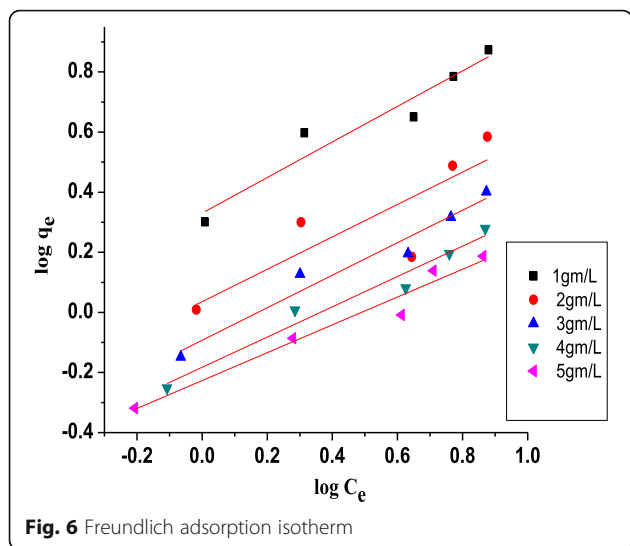


Fig. 6 Freundlich adsorption isotherm

of the absorbent for the particular adsorbate, the following adsorption isotherms have been evaluated.

**Langmuir isotherm**

For monolayer adsorption at specific homogeneous sites of adsorbent surface, the Langmuir isotherm is usually used. The Langmuir isotherm expression is:

$$1/q_e = (1/a) + (1/abC_e)$$

where,  $C_e$  is the equilibrium concentration of the adsorbate in liquid phase,  $a$  is the number of moles of solute adsorbed per unit weight of the adsorbent in forming a monolayer on the surface (Langmuir monolayer coverage), and  $b$  is the constant related to the equilibrium

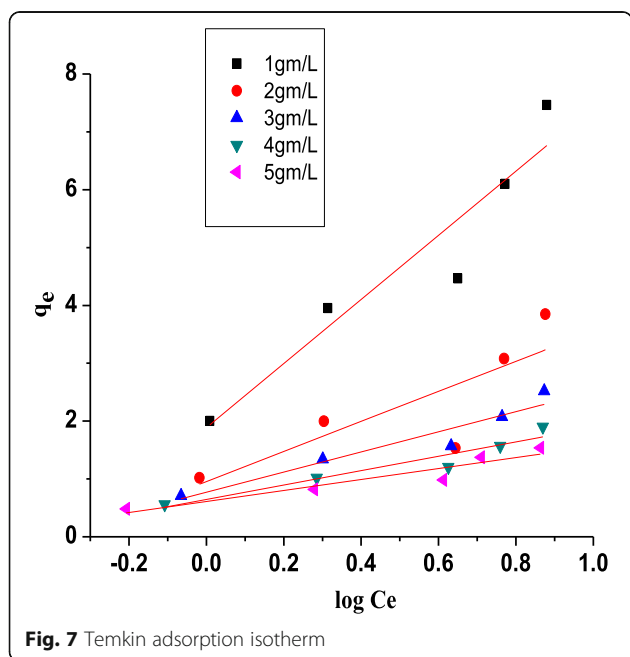


Fig. 7 Temkin adsorption isotherm

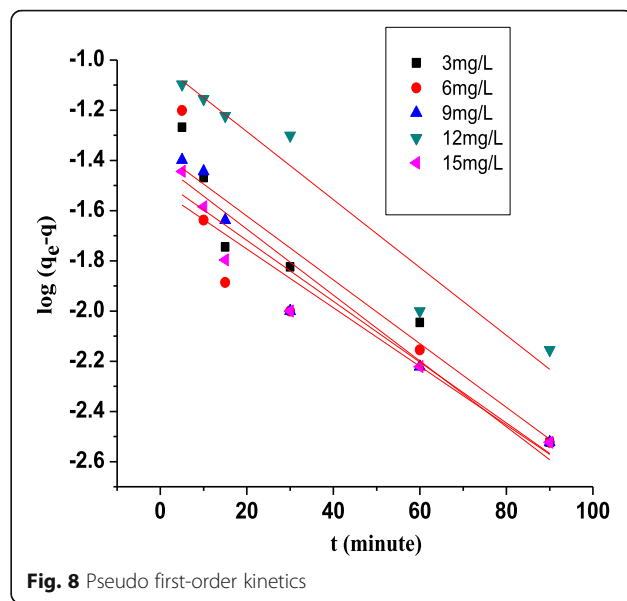


Fig. 8 Pseudo first-order kinetics

constant of adsorbate-adsorbent equilibrium. As shown in Fig. 5, a plot of  $1/q_e$  versus  $1/C_e$  yields “a” and “b” as the slope and intercept, respectively (Table 1), which is comparable to the previously reported values of various bio-adsorbents (Bharali et al., n.d.). To know whether the Langmuir-type adsorption is favorable or not, the separation factor  $R_L$  is calculated using the equation:

$$R_L = 1/(1 + bC_0)$$

where  $b$  is the Langmuir coefficient (L/mg) and  $C_0$  is the adsorbate initial concentration. For favorable adsorption,

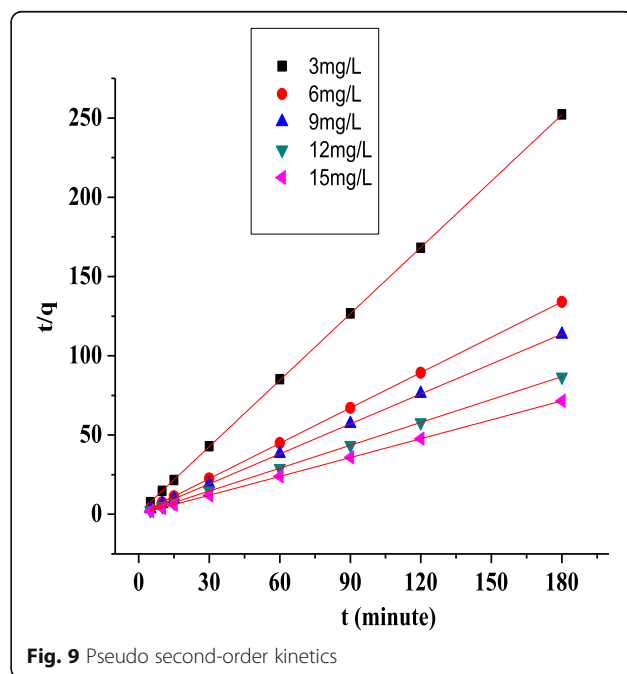


Fig. 9 Pseudo second-order kinetics

**Table 2** Kinetic parameters of the pseudo first- and second-order kinetics

Initial con (mg/L)	Pseudo 1st-order parameters			Pseudo 2nd-order parameters		
	$q_e$ (mg/g)	$q_e$ (mg/g) from plot	$k_1$ (min <sup>-1</sup> )	$q_e$ (mg/g)	$q_e$ (mg/g) from plot	$k_2$ (L/mol/min)
3	0.714	0.042954	0.027636	0.714	0.716332	2.388256
6	1.343	0.033497	0.027636	1.343	1.345895	3.049995
9	1.576	0.038815	0.029939	1.576	1.587302	1.593975
12	2.07	0.096828	0.029939	2.07	2.079002	0.929161
15	2.516	0.030269	0.025333	2.516	2.518892	3.353383

the value of  $R_L$  lies between 0 and 1. While  $R_L > 1$  indicates unfavorable adsorption,  $R_L = 1$  indicates linear adsorption and  $R_L = 0$  indicates irreversible adsorption (Erhayem et al., n.d.-a). In this case, the value of  $R_L$  (Table 1) indicates that the adsorption of fluoride on the PLP surface is favorable for the Langmuir model.

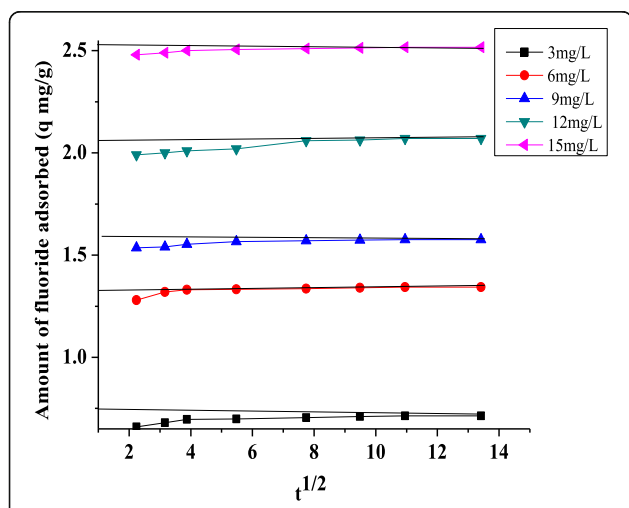
**Freundlich isotherm**

The Freundlich isotherm is generally applicable to physico-chemical adsorption on heterogeneous surface energy systems (non-uniform distribution of adsorption heat) (Erhayem et al., n.d.-a; Oladoja et al., n.d.). The linear form of the Freundlich adsorption isotherm is represented as:

$$\log q_e = (1/n) \log C_e + \log K_f$$

where  $K_f$  is the adsorption capacity,  $n$  is the adsorption intensity (both  $K_f$  and  $n$  are known as the Freundlich constant),  $q_e$  is the amount of solute adsorbed per unit mass of the adsorbent (mg/g), and  $C_e$  is the equilibrium concentration of the adsorbate (mg/L).

A plot of  $\log q_e$  versus  $\log C_e$  (Fig. 6) gives a straight line in which the slope gives the value of  $1/n$  and the intercept gives the value of  $K_f$  (Table 1) which is comparable to the previous reported values of various bio-



**Fig. 10** Intra-particle diffusion

adsorbents (Bharali et al., n.d.). The numerical value of  $1/n$  varies between 0 and 1 and is a measure of adsorption intensity or surface heterogeneity. The closer to zero value of  $1/n$  indicates surface heterogeneity. A value of  $1/n < 1$  implies a chemisorption process whereas  $1/n > 1$  is indicative of cooperative adsorption.

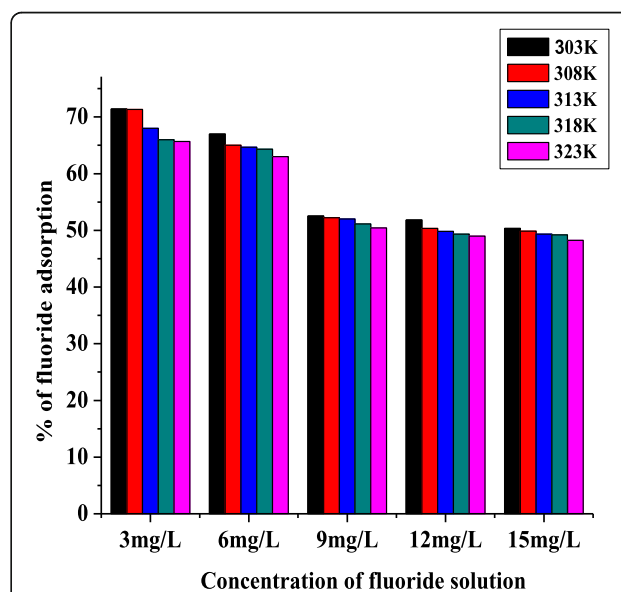
In the present case, the  $1/n$  values lies between 0 and 1 (Table 1), and hence, fluoride adsorption on a PLP surface at a low concentration is favorable. The same magnitude of “ $n$ ” values suggests that the retention of fluoride from the solution takes place by ionic interactions.

**Temkin isotherm**

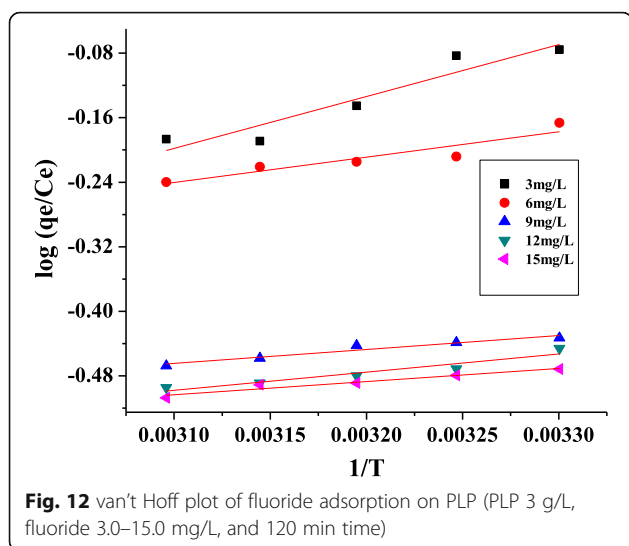
For heterogeneous surface energy systems (non-uniform distribution of adsorption heat), the Temkin isotherm is usually used. It helps in evaluating the adsorption potential of the adsorbent and adsorbed solution. The linearized form of the Temkin isotherm is:

$$q_e = B \ln A_T + B \ln C_e$$

where  $A_T$  is the equilibrium binding constant (L/g),  $b$  is



**Fig. 11** Effect of temperature on extent of fluoride adsorption by PLP (PLP 3 g/L, fluoride 3.0–15.0 mg/L, and 120 min time)



**Fig. 12** van't Hoff plot of fluoride adsorption on PLP (PLP 3 g/L, fluoride 3.0–15.0 mg/L, and 120 min time)

the adsorption constant (J/mol K),  $R$  is universal gas constant (8.314 J/K mol),  $q_e$  is the amount of solute adsorbed per unit mass of the adsorbent (mg/g),  $T$  is absolute temperature, and  $B = (RT/b)$  is a constant related to the heat of adsorption (J/mol). As shown in Fig. 7, the slope of the linear plot of  $q_e$  versus  $\ln C_e$  gives the value of  $B$  and the intercept gives the value of  $A_T$ . The result shows small value of  $B$  (Table 1) which indicates weak interaction between adsorbent and adsorbate supporting a mechanism of ion exchange (Erhayem et al., n.d.-a; Oladoja et al., n.d.; Nechifore et al., n.d.).

**Adsorption kinetics**

Kinetic study on adsorption process is significant as it provides valuable information about the reaction pathways and the mechanism of sorption interactions. Besides, it describes the solute uptake rate which controls the residence time of the adsorbate at the solid–solution interface. Therefore, it is important to predict the rate at which a pollutant is removed from aqueous solutions for designing appropriate water treatment processes.

To fit the experimental data, Lagergren pseudo first-order and pseudo second-order kinetic models are used. The pseudo first-order kinetic model is represented as

$$\log (q_e - q_t) = \log q_e - (k_1/2.303).t$$

and the expression for the pseudo second-order kinetic model is

$$t/q = 1/h + (1/q_e).t, \text{ here } h = k_2q_e^2$$

where  $q_t$  is the amount of fluoride adsorbed (mg/g) at time  $t$ ,  $q_e$  is the amount of fluoride adsorbed (mg/g) at equilibrium time,  $k_1$  is the rate constant of the pseudo first-order kinetics, and  $k_2$  is the rate constant of the pseudo second-order kinetics. In the plot of  $\log (q_e - q_t)$  versus  $t$ , the intercept gives the value of “ $q_e$ ” in the pseudo first-order kinetics (Fig. 8).

In the plot of  $t/q$  versus  $t$ , the slope gives the value of “ $q_e$ ” and the intercept  $h$  (Fig. 9). The test of validity can be done by comparing the experimental  $q_e$  value to the  $q_e$  value obtained from the plot. The result (Table 2) reveals that the adsorption mechanism proceeds through pseudo second-order kinetics (Erhayem et al., n.d.-a).

**Intra-particle diffusion**

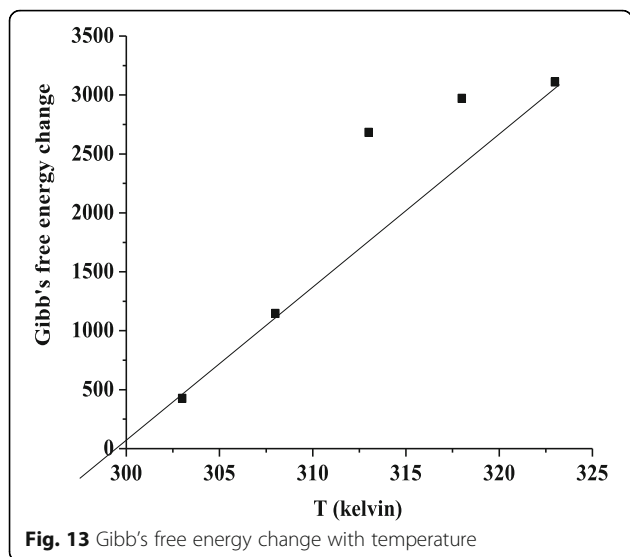
Adsorption is a multi-step process which involves the transport of the solute molecules from the aqueous phase to the surface of the adsorbent particles and then diffusion of the solute molecules into the interior of the pores which is likely to be a slow process and is therefore considered as a rate-determining step. The possibility of existence of intra-particle diffusion is tested by plotting a graph (Fig. 10) between amount of fluoride adsorbed ( $q_t$ ) and the square root of time from the following equation:

$$q_t = X + K.t^{1/2}$$

The slope of linear portion of the plot gives the value of rate constant  $K$ . As could be observed from the figure, the linear portion of the plot does not pass through the origin indicating that the mechanism of fluoride adsorption is complex and both the surface adsorption and the intra-particle diffusion contribute to the rate-determining step (Bharali & Bhattacharyya, n.d.).

**Table 3** Values of thermodynamic parameters for fluoride adsorption on PLP

$C_e$ (mg/L)	$\Delta H$ (J/mol)	$\Delta S$ (J/mol)	$\Delta G$ (J/mol)				
			303 K	308 K	313 K	318 K	323 K
3	-12,307.998	-41.9467	401.8521	611.585	821.3191	1031.053	1240.786
6	-6001.4435	-23.2063	1030.065	1146.097	1262.128	1378.16	1494.191
9	-3310.2682	-19.2352	2517.997	2614.173	2710.349	2806.525	2902.701
12	-4312.0418	-22.8999	2626.628	2741.127	2855.627	2970.126	3084.626
15	-3111.2314	-19.262	2725.155	2821.465	2917.775	3014.085	3110.395



**Adsorption thermodynamics**

Temperature plays a significant role in adsorption. In the present case, the effect of temperature is studied in five different temperatures of 303, 308, 313, 318, and 323 K. Results reveal that on increasing temperature, the extent of fluoride adsorption on PLP decreases (Fig. 11). This may be due to decreasing adsorptive force between PLP and fluoride ions.

Thermodynamic parameters were calculated using the van't Hoff equation:

$$\log(q_e/C_e) = \Delta S/(2.303R) - \Delta H/(2.303RT)$$

where  $\Delta S$  is the entropy change,  $\Delta H$  is the enthalpy change, and  $(q_e/C_e)$  is the adsorption affinity. From the intercept and slope of the plot of  $\log(q_e/C_e)$  vs  $1/T$

(Fig. 12),  $\Delta S$  and  $\Delta H$  could be determined. Gibb's free energy change was calculated using the fundamental equation:

$$\Delta G = \Delta H - T \Delta S$$

where  $\Delta G$  is Gibb's free energy change and  $T$  is the respective absolute temperature.

From the result (Table 3), the negative values of  $\Delta H$  indicate the exothermic nature of the adsorption process, the negative values of  $\Delta S$  indicate a decrease in randomness at the PLP surface during the adsorption process, and the  $\Delta G$  values point out the feasibility of adsorption in a low temperature (Fig. 13) which indicates the usefulness of this bio-adsorbent at room temperature (Islam & Patel, 2007).

**Cation exchange capacity**

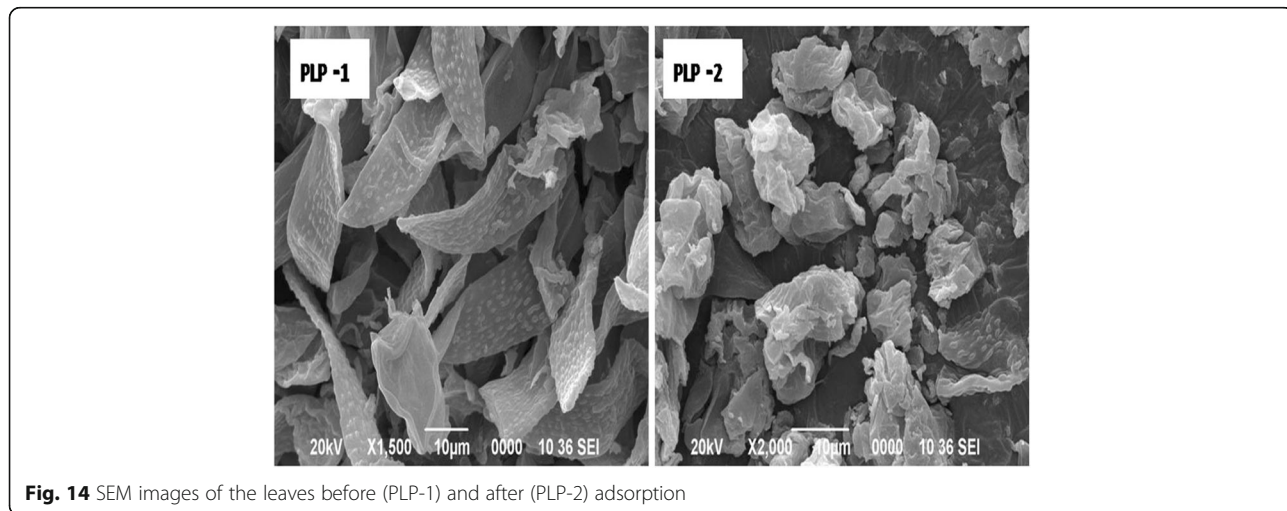
The ability to react with positively charged molecules is called the cation exchange capacity (CEC) of that substance. Higher CEC indicates the higher negative charge of the substance and hence can bind more cations. The cation exchange capacity of PLP is estimated to be 0.0074 (meq/g).

**Anion exchange capacity**

The anion exchange capacity (AEC) of a substance indicates the degree to which it can adsorb and exchange anions. The anion exchange capacity of PLP is estimated to be 1.25 meq/g.

**SEM analysis**

The SEM micrographs of PLP samples before and after fluoride sorption are shown in Fig. 14 (PLP 1 and PLP 2 respectively). As could be seen in the micrographs, the surfaces of the particles of PLP are irregular and have





broken edges. This may be the indication of higher surface area and higher adsorption capacity of PLP. After fluoride adsorption, surface morphologies of the PLP samples are somewhat swollen and there changes in the size of the particles. The change in the surface morphologies reveals that the process of fluoride adsorption on PLP is predominantly a surface phenomenon.

## Conclusions

From the systematic study, the following conclusions could be drawn:

1. The PLP can remove more than 70% of fluoride from a 3-ppm aqueous solution on its own at a normal pH range, at a contact time of 120 min and 3 g/L of its dose.
2. Adsorption of fluoride by PLP follows a pseudo second-order mechanism, and the mechanism of fluoride removal is found to be complex. The surface adsorption as well as the intra-particle diffusion contributes to the rate-determining step.
3. Significant amount of fluoride can be removed in the pH range 7–8 by using PLP, which makes it suitable to utilize in defluoridation of drinking water especially in rural areas where sophisticated facilities are not available.
4. It is a cost affordable, easily available, and environment-friendly bio-adsorbent.
5. Further studies need to be carried out for evaluation of the bio-adsorbent for reusability.

## Authors' contributions

PS conceived of the study and contributed in design and organization of the manuscript. HKB carried out the adsorption and kinetic experiments. RKB helped in analysing the data. All authors read and approved the final manuscript.

## Competing interests

The authors declare that they have no competing interests.

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