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ORIGINAL ARTICLE

Sorption of fluoride using chemically modified *Moringa oleifera* leaves

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Abstract

Contamination of drinking water due to fluoride is a severe health hazard problem. Excess of fluoride (> 1.5 mg/L) in drinking water is harmful to human health. Various treatment technologies for removing fluoride from groundwater have been investigated. The present study showed that the leaves of *Moringa oleifera*, a herbal plant is an effective adsorbent for the removal of fluoride from aqueous solution. Acid treated *Moringa oleifera* leaves powder showed good adsorption capacity than alkali treated *Moringa oleifera* leaves powder. Batch sorptive defluoridation was conducted under the variable experimental condition such as pH, contact time, adsorbent dose and initial fluoride ion concentration. Maximum defluoridation was achieved at pH 1. The percentage of fluoride removal increases with adsorbent dose. The equilibrium sorption data were fitted into Langmuir, Freundlich and Temkin isotherms. Of the three adsorption isotherms, the R^2 value of Langmuir isotherm model was the highest. The maximum monolayer coverage (Q_{max}) from Langmuir isotherm model was determined to be 1.1441 mg/g, the separation factor indicating a favorable sorption experiment is 0.035. It was also discovered that the adsorption did not conform to the Freundlich adsorption isotherm. The heat of sorption process was estimated from Temkin Isotherm model to be − 0.042 J/mol which vividly proved that the adsorption experiment followed a physical process.

Keywords Adsorption · Fluoride · Freundlich isotherm · Langmuir isotherm · *Moringa oleifera* · Temkin isotherm

Introduction

Water is most abundant and is an essential component of our life supporting system. Near about 97% of earth's surface is covered by water. But from the last few decades, these water resources are getting polluted by various natural and anthropogenic contaminants such as heavy metals, fluoride, arsenic, lead and mercury (Abu Bakar et al. 2016; Bashir et al. 2012). Among all the contaminants, fluoride contamination of water has now become a major issue in most of the parts of the world because of its toxic effects. Fluoride is well recognized as an element of public health concern. Fluoride is present universally in almost every water (higher concentrations are found in ground water), earth crust, many minerals, rocks, etc. It is also present in most of our everyday needs, viz. toothpastes, drugs, cosmetics, chewing gums, mouthwashes, and so forth (Bashir et al. 2012; Rout et al. 2015). Though a small amount of it is beneficial for human health for preventing dental caries, it is very harmful when present in excess. Maximum permissible limit of fluoride in drinking water has been set as 1.5 mg/L by many regulatory authorities such as WHO, US EPA, CPCB and so forth (Bashir et al. 2015; Bell and Ludwig 1970; Kanaujia et al. 2015; Singh 2017). The high fluoride levels in drinking water and its impacts on human health have increased the importance of defluoridation studies (Chidambaram et al. 2004; Singh 2017). The magnitude of the problem is sinking in, and efforts are being made towards defluoridation of drinking water, combating the debilating fluorosis and taking steps to prevent and control the disease (Karthikeyan and Ilango 2007). Chemical coagulants like Aluminum sulphate (alum), $FeCl_2$ are used in the Municipal drinking water treatment plant for the purification process. This excess use of an amount of chemical coagulants can affect human health, e.g., Aluminum has also been indicated to be a causative agent in neurological diseases such as pre-senile dementia (Muyibi and Evison 1995). The conventional method of fluoride removal includes: ion-exchange, reverse osmosis, and adsorption (Popat et al. 1994). Adsorption processes using natural adsorbents or agricultural waste products are becoming the new alternatives for the removal of fluoride from aqueous solution as they are

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cheap, simple, sludge-free, regenerable, environment friendly, involve small initial cost, and minimal chemical use (Saka and Sahin 2011).

The use of *Moringa oleifera* has an added advantage over the chemical treatment of water because it is biological and has been reported as edible.

Experimental methods

Collection and preparation of adsorbent and adsorbate

Moringa oleifera leaves were used as adsorbent and were collected from local trees and were washed with water many times to remove dirt and then sun dried for 3 days. The dried sample was then ground to powder using a pestle and mortar, the dried sample powder was then sieved to select the particle size of 350 µm and was then used as an adsorbent. 40 g of the powder sample was added to 400 mL of 1N HNO_3 for acid treatment, and 40 g of the powder sample was added to 0.5N NaOH for alkali treatment. This modified procedure is in accordance with the reported work of Parlikar and Mokashi (2013). The mixture was boiled for about 20 min on a sand bath. Washing of the powder sample was carried out using distilled water until the maximum color was removed and clear water was obtained. Finally, it was dried again in an oven at 50 °C for 6 h.

The preparation of adsorbate was carried out by preparing a standard solution of 2 ppm fluoride. It was prepared by dissolving 2 mg of anhydrous sodium fluoride in 1000 mL of distilled water.

Preparation of the reagent

The SPADNS solution, 0.003721 M was prepared by dissolving 0.4750 g of SPADNS in 250 mL deionized water. The Zirconyl chloride acid solution, 0.0375 M was by prepared by dissolving 0.0665 g of $ZrOCl_2.8H_2O$ in 25 mL of deionized water. Then 25 mL of HCl was added, and deionized water was added until the total volume of the solution was 250 mL. The concentration of zirconyl acid-SPADNS reagent was prepared by mixing the two solutions in the ratio of 1:1. This reagent was further diluted.

Sorption experiment

Synthetic fluoride bearing water sample having initial fluoride ion concentration of 2 mg/L was used. This fluoride solution was filtered using Whatman's filter paper no. 41 to this filtrate, SPADNS and zirconyl acid solution of 5 mL each was used. The sample was checked for fluoride detection using spectrophotometer at wavelength 570 nm.

The fluoride removal studies by adsorption were conducted in 250 mL conical flask using 100 mL of synthetic water sample. To these conical flasks acid and alkali treated (activated) adsorbent was added and after giving a required contact time of 150 min the contents of the flask were then filtered using Whatman's filter paper no. 41. The filtrate was used for fluoride ion estimation using the SPADNS method. The fluoride content in the filtrate was determined by UV–visible spectrophotometer. The values of percent fluoride removal by adsorbent were calculated using the following relation (Bashir et al. 2015).

$$\text{Removal\%} = \frac{C_0 - C_i}{C_0} \times 100$$

where, C_0 is initial fluoride ion concentration, and C_i is the final fluoride ion concentration.

Langmuir isotherm

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface (Foo and Hameed 2010). The linear form of Langmuir isotherm model is described as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max K_L}} + \frac{1}{q_{\max}} c_e$$

where,

$q_{\max}$ = The monolayer adsorption capacity of the adsorbent (mg/g).

K_L = The Langmuir adsorption constant (L/mg).

C_e = Equilibrium concentration of the solution in (mg/L).

q_e = Amount adsorbed per unit weight of adsorbent (mg/g).

Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor, R_L, which is defined by the following equation,

$$R_L = \left[1/\left(1 + bC_i\right)\right].$$

where C_i is the initial concentration of the fluoride solution and b is the Langmuir constant related to the energy of adsorption (L mg^{-1}). R_L value indicates the adsorption nature to be either unfavorable if $R_\mathrm{L} > 1$), linear if $R_\mathrm{L} = 1$, favorable if $0 < R_\mathrm{L} < 1$ and irreversible if $R_\mathrm{L} = 0$ (Foo and Hameed 2010).

Freundlich isotherm

It is applicable to both monolayer and multilayer adsorption and is based on assumption that adsorbate adsorbs onto heterogeneous surfaces of an adsorbent (Bashir et al. 2017; Foo and Hameed 2010). The linear form of Freundlich equation is expressed as:

$$q_e = K_f C_e^{1/n}$$

where,

q_e = Amount adsorbed per unit weight of adsorbent (mg/g).

C_e = Equilibrium concentration of the solution in (mg/L).

K_f and n are Freundlich Isotherms constants which is a measure of adsorption capacity or fundamental effectiveness of the adsorbent. K_F and n can be determined from the linear plot of log q_e verses log C_e as shown in the equation. The adsorption process is said to be favorable when the value of 'n' satisfies the condition $1 < n < 10$ which indicated favorability of adsorption and the degree of heterogeneity, otherwise it is unfavorable (Foo and Hameed 2010).

Temkin isotherm

This isotherm contains a factor that explicitly takes into account of adsorbent–adsorbate interactions. The model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed q_e against ln C_e and the constants were determined from the slope and intercept (Foo and Hameed 2010). The model is given by the following equation:

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

A_T = Temkin isotherm equilibrium binding constant (L/g).

b_T = Temkin isotherm constant.

R = universal gas constant (8.314 J/mol/K).

T = Temperature.

B = Constant related to heat of sorption (J/mol).

Chemical kinetics

The experimental data are analyzed to observe the appropriate kinetic model followed by adsorption process including mass transfer and chemical reactions (Bashir et al. 2017). Pseudo-first-order and pseudo-second-order kinetic models are used to describe the kinetics of adsorption. The integrated form of Lagergren first-order kinetic model is represented by the equation given below:

$$\log q_e - q_t = \log q_e - \frac{k1}{2.303} t$$

where k_1 is the rate constant of first-order adsorption (1/min); q_e is the amount of dye adsorbed in mg/g at equilibrium; and q_t is the amount of dye adsorbed in mg/g at any time t.

The linear form of pseudo-second-order kinetic model rate equation is expressed as:

$$t/qt = 1/k_2 q_e^2 + \left(1/q_e\right) t$$

where k_2 is the rate constant of second-order adsorption (g/mg-min) depends on the sorption capacity of the solid phase. The initial sorption rate, h (mg/g-min), is also calculated with the help of second-order kinetic model by the following expression:

$$h = k_2 q_e^2.$$

Results and discussions

Understanding of adsorption technique is possible with knowledge of the optimal conditions, which would herald a better design and modeling process. Thus, the effect of some major parameters such as pH, contact time, dose of adsorbent and initial concentration of fluoride ions uptake on adsorbent materials were investigated from a kinetic viewpoint. Adsorption studies were performed by batch technique to obtain the equilibrium data. The experimental data from batch experiment were analyzed using adsorption isotherm equations (Langmuir, Freundlich, and Temkin), in which linear regression analysis was used to evaluate whether the theoretical models have better or worse fit for the experimental data.

Effect of pH on defluoridation

The pH of the aqueous solution is a controlling factor in the adsorption process (Bashir et al. 2015). The experiments were carried out for acid treated and alkali treated *Moringa oleifera* leaves powder for determining optimum pH. The pH was varied from 1 to 10 for acid treated *Moringa oleifera* leaves powder and 2–10 for alkali treated *Moringa oleifera* leaves powder. The adsorbent having 350 µm size, acid treated as well as alkali treated, was used to determine optimal pH at which the adsorption was maximum. For these experiments, initial fluoride ion concentration was 2 mg/L, with an adsorbent dose of 2.5 g/L and contact time of 150 min. As shown in Table 1, the acid treated adsorbent showed the maximum removal efficiency 83% at pH 1. Whereas in case of alkali treated adsorbent the maximum removal efficiency was 85% at pH 10. Similar observations have been reported by (Parlikar and Mokashi 2013).

Table 1 Effect of pH on sorption of fluoride

S. no	pH	Acid treated powder		Alkali treated powder	
		Absorbance (*A*)	% Removal	Absorbance (*A*)	% Removal
1.	1	0.020	83		
2.	2	0.023	81	0.055	54
3.	4	0.031	74	0.040	67
4.	6	0.044	63	0.030	75
5.	8	0.057	53	0.021	82
6.	10	0.059	51	0.018	85

Effect of contact time on defluoridation

The adsorbent dose of 2.5 g/L was taken and kept constant throughout the experimental work. The contact time was varied from 0.5 to 2.5 h for acid treated as well as alkali treated *Moringa oleifera* leaves powder of particle size 350 µm. The experimental study was carried out to determine optimal contact time using acid and alkali treated adsorbents with same particle size. The pH was 8 and dose was 2.5 g/L for the study. As depicted in Table 2 in case of alkali treated adsorbent it is found that the removal fluoride ion increased with increase in contact time but after sometime it approaches a constant value, denoting attainment of equilibrium. Whereas, in case of acid treated adsorbent the amount of percentage removal of fluoride ion increased with increase in time, as well as the maximum percentage removal (98%) was obtained at 150 min. Similar results were reported by Kosari and Sepehrian (2017).

Effect of adsorbent dose on defluoridation

The response of adsorbent dose on the removal of fluoride is presented in Table 3. In case of alkali treated powder, the observations reveal that an increase in the adsorption occurs with the corresponding increase in the amount of adsorbent. The increase in the removal efficiency with simultaneous increase in adsorbent dose is due to the increase in quantity, and hence more active sites were available for the adsorption of fluoride. The results showed that the alkali treated *Moringa oleifera* leaves powder was efficient for 95% removal of fluoride ions at the lowest dose of 100 mg/L and 98% at a maximum dose of 400 mg/L, respectively, at room temperature. This finding is supported by (Tembhurkar and Dongre 2009).

Table 2 Effect of contact time on defluoridation

S. no	Time (min)	Acid treated powder		Alkali treated powder	
		Absorbance (*A*)	% Removal	Absorbance (*A*)	% Removal
1.	30	0.015	87	0.015	87
2.	60	0.013	89	0.011	90
3.	90	0.012	90	0.010	91
4.	120	0.006	95	0.006	95
5.	150	0.002	98	0.005	95

Table 3 Effect of adsorbent dose on defluoridation

S. no	Adsorbent dose (mg)	Acid treated powder		Alkali treated powder	
		Absorbance (*A*)	% Removal	Absorbance (*A*)	% Removal
1.	100	0.003	97	0.006	95
2.	200	0.006	95	0.004	96
3.	300	0.008	93	0.003	97
4.	400	0.010	91	0.002	98

Table 4 Effect of fluoride ion concentration on defluoridation

S. no	Fluoride ion concentration (mg)	Acid treated powder		Alkali treated powder	
		Absorbance (*A*)	% Removal	Absorbance (*A*)	% Removal
1.	0.5	0.017	86	0.023	81
2.	1	0.010	91	0.020	83
3.	1.5	0.007	94	0.013	89
4.	2	0.002	98	0.009	92

Effect of initial fluoride ion concentration

Studies on the effect of initial fluoride concentration were conducted by varying it from 0.5 to 2 mg/L keeping adsorbent dose of 2.5 g/L, pH of 8, and contact time of 150 min.

The response of different fluoride ion concentration on the removal of fluoride is presented in Table 4. For alkali as well as acid treated powder, the observations reveal that with the increase in fluoride ion concentration the % removal of fluoride also increases. With increase in initial concentration of fluoride the driving force for transport of fluoride from the bulk to the surface of adsorbent increases, which results more adsorption of fluoride per unit mass of adsorbent. This finding is supported by (Dwivedi et al. 2014).

Adsorption isotherms

In this study, adsorption isotherm study was carried out on three isotherm models: Langmuir, Freundlich and Temkin. The applicability of isotherm models to the adsorption study done was compared by observing the correlation coefficients, R^2 value. Adsorption isotherm helps in determining the feasibility of acid and alkali treated *Moringa oleifera* leaves powder for treating fluoride ion in water. Langmuir, Freundlich and Temkin isotherms were plotted to provide deep insight to the adsorption of fluoride ion on *Moringa oleifera* leaves powder.

From Table 5, it is clear that acid and alkali treated adsorbent responded good behavior with all three types of isotherm models but Langmuir's isotherm fitted best with them which is also well explained and depicted in Fig. 1a and b by the good regression coefficient of 0.97 and 0.88, respectively. The Langmuir's model described the monolayer sorption nature of the adsorbent.

Table 5 shows adsorption of fluoride on the adsorbents having a range of values of linear regression coefficient, R^2 (0.885–0.993) as illustrated in Fig. 2a and b, demonstrating that the experimental data fitted well with the Freundlich isotherm equation. Moreover, it was reported that the Freundlich isotherm constant can be used to explore the favorability of adsorption process (Foo and Hameed 2010). As observed in Table 5, the value of n for the adsorption of fluoride on acid treated *Moringa oleifera* leaves is situated outside the range of 1–10 indicating unfavorable adsorption process. Whereas, the value of n for the adsorption of fluoride on alkali treated *Moringa oleifera* leaves is situated in the range of 1–10 indicating favorable adsorption process.

It is well defined from the Table 5 and so is shown in Fig. 3a and b, that Temkin isotherm data fitted quite well. The values of R^2 are positioned within 0.983–0.986, which gave a close fit to the adsorption of fluoride on acid and alkali treated *Moringa oleifera* leaves powder. Furthermore, it can also be observed in Table 5, that the heat of adsorption of fluoride on *Moringa oleifera* leaves was restricted within −59,979 to 26,241 kJ/mol.

In the present study, the value of R_L is greater than 0–1 for acid and alkali treated adsorbent indicating that Langmuir isotherm is favorable (Bashir et al. 2015; Foo and Hameed 2010). While the value of n is greater than 10 for acid treated adsorbent indicating unfavorable adsorption process whereas for alkali treated adsorbent it is favorable.

Through the adsorption equilibrium study employing Langmuir, Freundlich and Temkin isotherms models, the

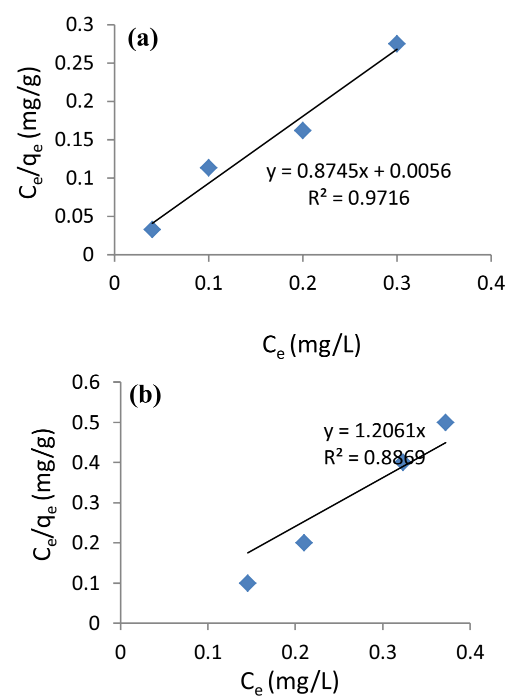

Fig. 1 **a** Langmuir Isotherm for effect of initial fluoride ion concentration on defluoridation (Acid treated *Moringa oleifera* leaves powder). **b** Langmuir Isotherm for effect of initial fluoride ion concentration on defluoridation (Alkali treated *Moringa oleifera* leaves powder)

Table 5 Langmuir, Freundlich and Temkin equation values for adsorption of fluoride with respect to initial fluoride ion concentration

Adsorbents	Langmuir				Freundlich			Temkin		
	Q_{max} (mg/g)	R_L	K_L (L/mg)	R^2	K_f (mg/g)	Value of 'n'	R^2	B (J/mol)	A_T (L/g)	R^2
Acid treated	1.1441	0.003589	138.79	0.971	0.6546	17.543	0.885	−0.042	1.951×10^{-7}	0.897
Alkali treated	0.8340	0.000833	0.002	0.884	0.5727	7.2463	0.983	−0.096	0.0029	0.986

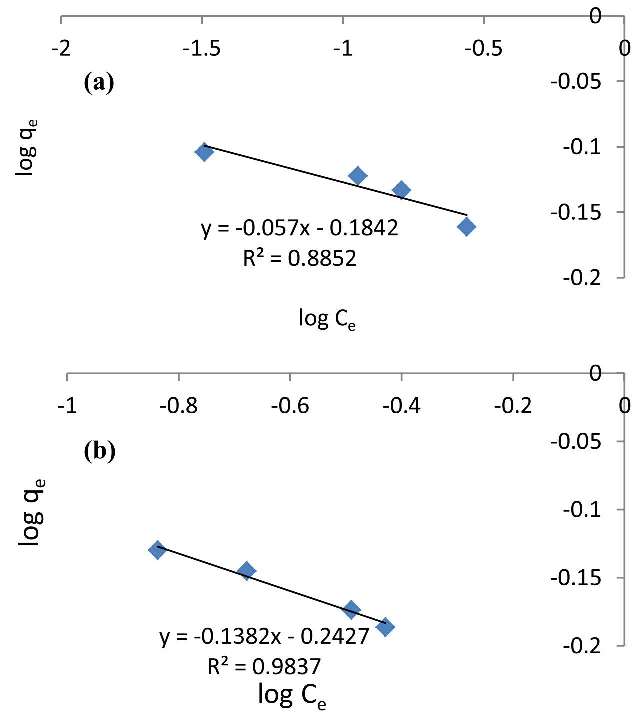

Fig. 2 **a** Freundlich Isotherm for effect of initial fluoride ion concentration on defluoridation (Acid treated *Moringa oleifera* leaves powder). **b** Freundlich Isotherm for effect of initial fluoride ion concentration on defluoridation (Alkali treated *Moringa oleifera* leaves powder)

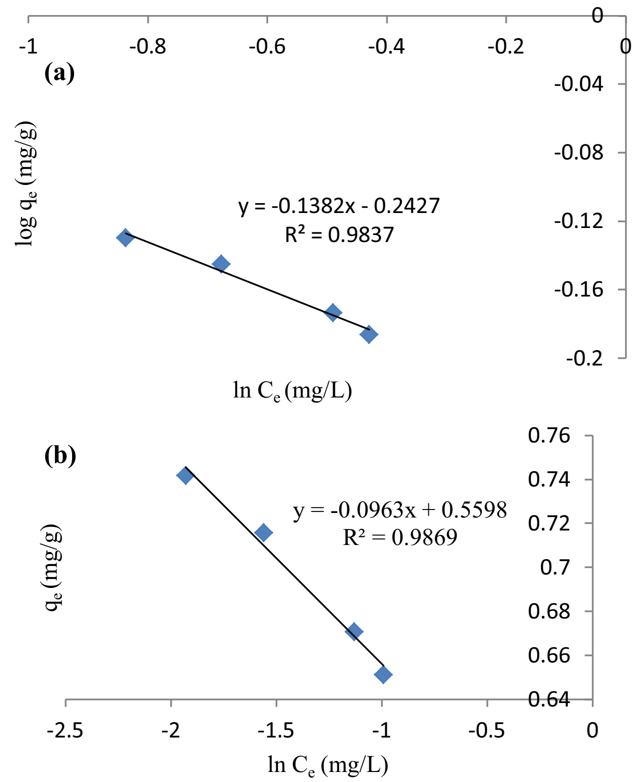

Fig. 3 **a** Temkin Isotherm for effect of initial fluoride ion concentration on defluoridation (Acid treated *Moringa oleifera* leaves powder). **b** Temkin Isotherm for effect of initial fluoride ion concentration on defluoridation (Alkali treated *Moringa oleifera* leaves powder)

maximum adsorption capacity was determined where the adsorption of fluoride with acid treated *Moringa oleifera* leaves powder was 1.1441 mg/g and with alkali treated *Moringa oleifera* leaves powder was 0.8340 mg/g. It is concluded by referring to the data obtained that the acid treated *Moringa oleifera* leaves powder was more efficient in removing fluoride than alkali treated *Moringa oleifera* leaves powder.

Mechanism of adsorption

The acid treated adsorbent contains the functional groups such as –OH, C=O and secondary amine group that is involved in adsorption process (Abu Bakar et al. 2016; Bello et al. 2015). Whereas, in case of alkali treated adsorbent functional groups that are involved in the process of adsorption are –OH and C=O (Bello et al. 2015). Protonation of heteroatoms took place due to lone pairs of electrons. Thus, heteroatoms such as O and N developed the positive charge. These positive charges on heteroatoms are responsible for the adsorption of fluoride ions from aqueous solution.

$$\text{S–OH} + \text{H}^+ \rightarrow \text{S–OH}_2^+ \ (\text{protonation}) \quad [+\ \text{F}^- \ (\text{Electrostatic attraction})]$$

$$\text{S–C=O} + \text{H}^+ \rightarrow \text{S–C=OH}^+ \ (\text{protonation}) \quad [+\ \text{F}^- \ (\text{Electrostatic attraction})]$$

$$\text{S–HN–R}_2 + \text{H}^+ \rightarrow \text{S –H}_2\text{N}^+\text{–R}_2 \ (\text{protonation}) \quad [+\ \text{F}^- \ (\text{Electrostatic attraction})]$$

Electrostatic physisorption between ions and dipole (second strongest among the physical bonds). Here, Electrostatic attraction between positive poles of partial polar bonds of OH, NH and CO groups of adsorbent and anionic fluoride ion took place.

Table 6 Kinetics of pseudo-first-order and pseudo second order of the two adsorbents studied

Adsorbents	Pseudo first order			Pseudo second order				Q_e (exp) (mg/g)
	$Q_{e(cal)}$ (mg/g)	K_1 (L/min)	R^2	$Q_{e(cal)}$ (mg/g)	K_2 (g/mg-min)	R^2	H	
Acid treated	4.89	0.88	0.835	1.23	0.093	0.996	0.142	1.20
Alkali treated	1.65	1.70	0.867	1.27	0.135	0.999	0.219	1.20

$$S—O^{-\delta}—H^{+\delta} + F^{-} \rightarrow S—O^{-\delta}—H^{+\delta}\ldots\ldots F^{-}$$

$$S—N^{-\delta}—H^{+\delta} + F- \rightarrow S—N^{-\delta}—H^{+\delta}\ldots. F^{-}$$

$$\underset{\underset{O^{-\delta}}{\|}}{S—C^{+\delta}} + F^{-} \rightarrow \underset{\underset{O^{-\delta}}{\|}}{S—C^{+\delta}}\ldots..F^{-}$$

Chemical kinetics

A larger adsorption rate constant k_1 usually represents a quicker adsorption rate. Larger the k_2 values slower the rate of adsorption. The correlation coefficients of pseudo first order are less than those of pseudo-second-order reaction (Tables 6). This indicates that kinetic data for adsorption of fluoride by the acid and alkali treated adsorbents prepared from *Moringa oleifera* leaves are better fitted to pseudo-second-order rate equation than to pseudo first-order rate equation. The values of the pseudo first-order rate constant (k_1) for both the adsorbent are not close to each other compared to those of pseudo-second-order rate constant (k_2). Moreover, the calculated values of qe for both the adsorbents from second-order kinetic equation are found to be agreed well with the experimental values of q_e. Therefore, it is concluded that the adsorption of fluoride by these adsorbents follows the pseudo-second-order reaction kinetics. This result is in agreement with the results obtained for the defluoridation using banana peel and coffee husk (Getachew et al. 2014).

Conclusion

The correlation coefficient, R^2 value for both the adsorbents indicated that all three Isotherms (Langmuir, Freundlich and Temkin) showed a good fit to the experimental data. The Langmuir Isotherm was slightly better than Freundlich and Temkin Isotherm. The process of adsorption also follows pseudo-second-order rate equation in both cases. It is concluded by referring to the data obtained that the acid treated *Moringa oleifera* leaves powder was more efficient in removing fluoride than alkali treated *Moringa oleifera* leaves powder.

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