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Removal of fluoride from aqueous solution using *Psidium guajava* leaves

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ABSTRACT

A novel, inexpensive, easily available and eco-friendly biosorbent, *Psidium guajava* leaves (L), has been evaluated for its capability to remove fluoride from water. Batch experiments were carried out to study the effect of various parameters affecting the biosorption such as pH (2–10), biosorbent dose (1–7 mg/50 mL), contact time (30–210 min) and initial fluoride concentration (5–12 mg L^{-1}) for the adsorption of fluoride at room temperature. The maximum removal of fluoride was found to be 88% at pH 6.5, biosorbent dose 5 mg/50 mL and contact time 180 min. Freundlich isotherm was best fitted to explain the multilayer adsorption of fluoride on treated *Psidium guajava* L. The maximum biosorption capacity was found 62.50 mg g^{-1}. The kinetic data of biosorption of fluoride on treated *Psidium guajava* L followed the pseudo-first-order rate equation. The present study demonstrates the treated *Psidium guajava* L that can effectively remediate fluoride contaminated water.

Keywords: Biosorbent; Defluoridation capacity; *Psidium guajava* leaves; Isotherms; Kinetics

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1. Introduction

Fluoride may be beneficial or detrimental for human body depending on its concentration in drinking water. Fluoride concentrations in the range of 1.5–4.0 mg L^{-1} may result in dental fluorosis, and prolonged exposure at still higher concentrations (4 to 10 mg L^{-1}) may cause skeletal fluorosis [1], and any concentration beyond 10 mg L^{-1} causes highest incidence of skeletal fluorosis and crippling skeletal fluorosis [2]. According to World Health Organization (WHO), permissible fluoride concentration in drinking water is 0.5–1.5 mg L^{-1} [3]. High fluoride concentrations in ground water have been found widely in many parts of the world including India, Pakistan, China, Sri Lanka, West Indies, Spain, Holland, Poland, Italy, Iraq, Iran, Sudan, Uganda, Kenya, United Republic of Tanzania, Mexico, Thailand, Serbia, Ethiopia, West Africa, Southern Africa, and North and South American countries [4–9]. Excessive fluoride concentrations have been reported in ground water (used for drinking purpose) of more than 19 states in India alone where people are facing acute fluorosis problems [10]. The most seriously affected states are Andhra Pradesh, Assam, Chhattisgarh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh [11]. The highest fluoride concentration of 48 mg L^{-1} has been reported in Rewari district of Haryana state in India [12].

There are several defluoridation techniques for removal of fluoride that include membrane separation [13,14], precipitation-coagulation [15], nanofiltration [16,17], reverse osmosis [17,18], electrolytic coagulation [19], electrolytic defluoridation [20,21], Donnan dialysis [22], ion exchange [23], electrodialysis [24], integrated physiochemical and biological

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adsorption [25] process and so on. Among all the ion exchanges, electrodialysis and membrane separation have been found to be effective and can remove the fluoride to appropriate level [23,24]. Due to lack of frequent regeneration capability of ion exchange beds or expensive cleaning of the scaling and fouling on the membrane required an alternative approach for effective removal of fluoride from water resources.

The adsorption process has been found comparatively cost-effective, flexible and easily available technique for removal of various analytes by physical or chemical interaction on a variety of adsorbents. Several conventional and synthesized adsorbents are widely accepted for removal of impurities present in water. Activated charcoal, clay materials, fly ash, activated dolomite and zeolite are well-reported robust adsorbent. However, abominable regeneration, economic factor and persisting of impurities on adsorbent sites ceased their application. Nowadays, low-cost biosorbents based on natural product such as eggshell powder [26], rice husk ash [27], algal biosorbent [28], lemon leaf [9], limestone [29], chitosan beads [4], tea ash [30], waste fungus [31], wheat straw [32], bagasse [33], barley straw [34], orange waste gel [35], biochar [36] and tamarind fruit shell [37] are being used to replace conventional adsorbents. Biosorption is a property of certain types of biomass to adsorb cations and anions from even very dilute aqueous solutions. Chitosan is deacetylation product of naturally occurring chitin, and their adsorption potential is varied by degree of deacetylation that required skilled technique in particular area [38,39]. Likewise, biosorbents based on fungus and algae are affected by culture conditions. Guava or *Psidium guajava* is tropical and semitropical plant belonging to Myrtaceae family and abundantly distributed in India. Raw leaves of *Psidium guajava* plant having a number of beneficial compounds such as vitamin C, quercetin with fixed oil 6.0%, and volatile oil 0.37%, resin 3.15%, and tannin 8.50% possess antibacterial, anticough, antioxidant and antidiabetic properties to treat a number of human ailments. Moreover, the *Psidium guajava* leaves (L) powder is low-cost, biodegradable and biocompatible adsorbent, and has shown excellent adsorption of methylene blue and auramine dyes. The present study has been conducted to assess the viability of fluoride removal from fluoride spike water using acid and alkali treated *Psidium guajava* L powder. A batch adsorption study for removal of fluoride using *Psidium guajava* L as biosorbent was carried out at variable pH, biosorbent dose, initial fluoride concentration and contact time followed by isotherms, kinetic studies and desorption studies.

2. Materials and methods

2.1. Chemicals, reagents and preparation of stock solution

Stock solution (100 mg L^{-1}) of fluoride was prepared by dissolving 221.01 mg of anhydrous sodium fluoride (NaF) in 1 L deionized water. Fluoride standards of smaller concentrations were prepared from stock solution.

2.2. Preparation of biosorbent material

Psidium guajava L were collected locally from the trees planted in IIT BHU campus. The collected leaves were washed twice with tap water followed by deionized water and finally oven dried (York Scientific Industries, New Delhi, Model: YSI 431) at 100°C ± 5°C. The dried sample was grounded and sieved through sieve size 150 μm. The sieved *Psidium guajava* L powder was treated with acid and alkali before being used as biosorbent. For acid treatment, *Psidium guajava* L powder was taken in a conical flask, and 1 M HCl was added to it. The mixture was heated for 15 min, and then *Psidium guajava* L was filtered out and washed with deionized water till a clear solution having neutral pH is obtained. The acid treated *Psidium guajava* L was then subjected to alkali treatment with 0.5 M NaOH [8]. The mixture was again heated for 15 min and washed with deionized water till a clear solution having neutral pH is obtained. The acid and alkali treated *Psidium guajava* L (biosorbent material) was dried in an oven at 100°C ± 5°C to remove moisture, and powder was stored in desiccator for further study.

2.3. Adsorption study

Batch experiments were conducted to study the adsorption process for fluoride removal. Experiments were carried out by taking different biosorbent dose (1 to 7 mg) in 250 mL conical flasks containing 50 mL of fluoride solution (5 to 12 mg L^{-1}) and agitated at 120 rpm on incubator shaker (Stuart incubator shaker, UK, Model: S1500). pH of the solution was maintained by adding 0.1 N, H_2SO_4/0.1 N, NaOH. The contact time was varied from 30 to 210 min at room temperature having pH 2–10. Ion selective electrode (Thermo Electronic Corporation, USA, Model: Orion 4 Star) was used to detect the concentration of fluoride. Total ionic strength adjustment buffer (TISAB) solution for the determination of fluoride concentration was used. In order to optimize the parameters (such as pH, contact time, adsorbent dose and initial fluoride concentration), trial runs were initially conducted by keeping three parameters constant at a time and varying the forth one. The optimum values of the parameters were thus determined from the trial setup and applied for the final studies.

2.4. Quality control

Analytical (AR) grade chemicals and reagent blanks were used in all analyses to check impurities. Before analysis of samples, instruments were calibrated and validated as per standard guidelines to evade changeable readings. Triplicate samples were used to verify the precision of the analytical method and instrument. Necessary measures were taken to minimize the uncertainty, which was <5% of the observed value with respect to true value.

3. Results and discussion

The fluoride removal efficiency of biosorbent was checked by varying the various factors including pH, contact time, biosorbent dose and initial fluoride concentration.

3.1. Effect of pH

The effect of pH was studied by varying the pH of the solution as 2.0, 3.0, 4.0, 5.0, 6.0, 6.5, 7.0, 7.5, 8.0, 9.0 and 10.0. Fluoride solution (50 mL) having 5 mg L^{-1} of fluoride concentration (from trial run) was taken in conical flasks. pH of solutions was adjusted to obtain desired pH values, and 5 mg of powder *Psidium guajava* L (from trial run) was added to each flask. Solution was agitated (120 rpm; from trial run) on incubator shaker. Thereafter, flasks were placed into shaker for 180 min (from trial run).

As shown in Fig. 1, the removal of fluoride was very less initially at low pH. As pH of the solution increases, the percentage removal of fluoride was increased, and the maximum removal of fluoride was observed at pH 6.5. Further increase in pH beyond 6.5, removal percentage of fluoride decreased. From these observations, it can be concluded that the removal of fluoride was more in acidic medium as compared with alkaline one. It might be due to the gradual increase in attractive force between positive charge of surface and negative charge of fluoride ions. Tomar et al. [40] also studied fluoride removal onto Zr–Mn composite and found that the maximum removal of fluoride occurs under acidic condition. Solution pH of 6.5 was selected as optimum pH for further experiments.

3.2. Effect of contact time

The effect of the contact time on the defluoridation capacity of powdered *Psidium guajava* L was studied by varying contact time from 30, 60, 90, 120, 150, 180 to 210 min at pH 6.5 (from Section 3.1), biosorbent dose of 5 mg/50 mL and initial fluoride concentration 5 mg L^{-1}.

It was found that the removal of fluoride increased with the increase in contact time. Initially in first 120 min, the rate of fluoride removal was seen rapid, and maximum fluoride removal took place at 180 min (Fig. 2). Further increase in contact time did not increase the fluoride uptake due to excess deposition of fluoride ions on the adsorption sites of biosorbent material. Viswanathan et al. [41] investigated for the removal of fluoride onto protonates chitosan beads and observed that removal was more in first 120 min. Jaikumar et al. [42] also found the maximum fluoride removal efficiency after 120 min was found, and rate of removal was more in first 120 min, which is the similar finding of present study.

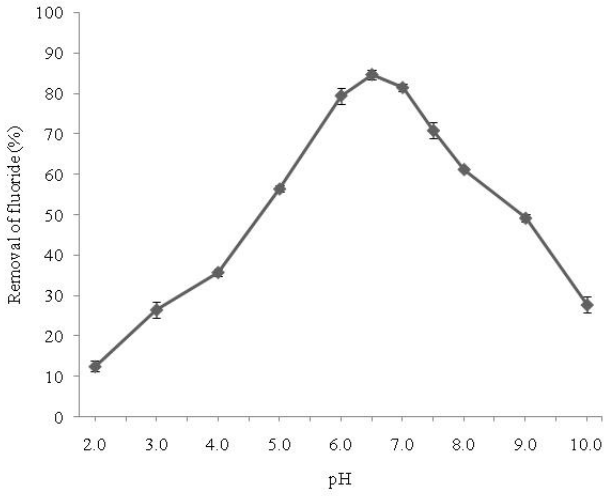

Fig. 1. Removal of fluoride with variation in pH (at dose 5 mg, contact time 180 min, fluoride concentration 5 mg L^{-1} and agitation speed 120 rpm).

3.3. Effect of biosorbent dose

To study the effect of biosorbent dose on the percentage removal of fluoride, the amount of biosorbent was varied from 1, 2, 3, 4, 5, 6 to 7 mg 50 mL^{-1}. The pH of the solution was maintained at 6.5 (from Section 3.1), while contact time was kept 180 min (from Section 3.2), and initial fluoride concentration was set at 5 mg L^{-1}. Fig. 3 shows that the removal percentage of fluoride was increased from 39% to 88% when biosorbent dose was increased from 1 to 5 mg L^{-1}. On further increasing the biosorbent dose, the rate of fluoride removal became stagnant. The result shows that 88% fluoride removal efficiency took place at biosorbent dose of 5 mg L^{-1}, which is a very good defluoridation efficiency provided by low-cost biosorbent material. The increase in removal efficiency with increase in biosorbent dose can be attributed to greater surface area and the availability of more adsorption sites [42]. Mane et al. [43] have also reported that the fluoride removal efficiency increased with an increase in biosorbent dose. For further experiments, 5 mg L^{-1} of the adsorbent was selected as optimum dose.

3.4. Effect of initial fluoride concentration

The effect of the defluoridation capacity of treated *Psidium guajava* L was studied at different initial fluoride

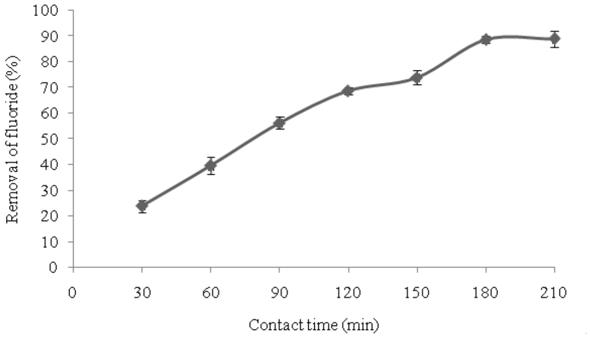

Fig. 2. Removal of fluoride with variation in contact time (at dose 5 mg, pH 6.5 agitation speed 120 rpm and fluoride concentration 5 mg L^{-1}).

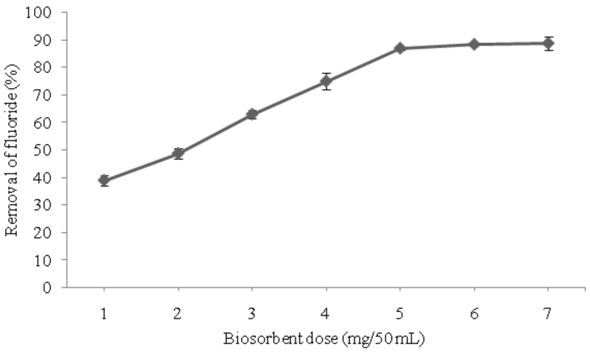

Fig. 3. Removal of fluoride with increase in biosorbent dose (at pH 6.5, fluoride concentration 5 mg L^{-1}, contact time 180 min and agitation speed 120 rpm).

concentrations in the range of 5–12 mg L^{-1} at pH 6.5 (from Section 3.1), contact time 180 min (from Section 3.2) and biosorbent dose 5 mg L^{-1} (from Section 3.3).

It was observed that the fluoride removal capacity was more at lower initial fluoride concentration but less at higher concentration, which indicates that the capacity of the biosorbent materials gets exhausted penetratingly with increase in initial fluoride concentration (Fig. 4). At 5 mg L^{-1} fluoride concentration, percentage removal of fluoride was maximum (88%). Therefore, when fluoride concentration increases, removal of fluoride decreases. Similar result has been reported in recent study as well as by other researcher [44]. Tomar et al. [9] also investigated for the removal of fluoride onto Citrus limonene R. (lemon) leaf and observed that removal was more at lower initial fluoride ion concentration.

3.5. Adsorption isotherm

Langmuir isotherm [45–47] is based on the monolayer coverage of sorbent. It can be expressed in linear form as shown in Eq. (1):

$$\frac{1}{Q_e} = \frac{1}{Q} + \frac{1}{bQC_e} \tag{1}$$

where Q_e and C_e, respectively, are the equilibrium adsorption capacity (mg g^{-1}) and the equilibrium adsorbate concentration (mg L^{-1}); Q is the monolayer surface coverage (mg g^{-1}) and b is the equilibrium adsorption constant (L mg^{-1}).

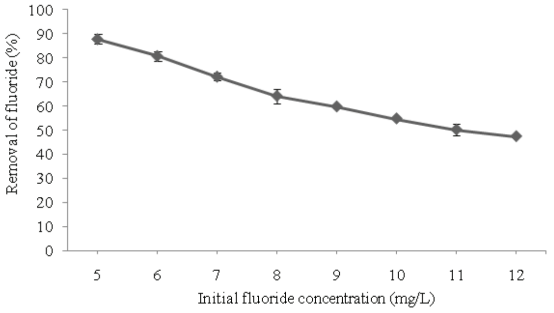

Fig. 4. Removal of fluoride with increase in initial fluoride concentration (at dose 5 mg/50 mL, pH 6.5, contact time 180 min and agitation speed 120 rpm).

For Langmuir, plot of 1/Q_e vs. C_e was plotted (Fig. 5). The constant values b and Q can be determined from its slope and intercept as shown in Table 1.

Freundlich isotherm is based on the multilayer adsorption of an adsorbate onto the heterogeneous surface of biosorbent. The linear form of the Freundlich isotherm [45–47], commonly used to describe adsorption isotherm data, is shown in Eq. (2):

$$\log Q_e = \log K_f + \frac{1}{n \log C_e} \tag{2}$$

where Q_e and C_e are the equilibrium adsorption capacity (mg g^{-1}) and the equilibrium adsorbate concentration (mg L^{-1}), respectively; K_f and n are empirical constants that are dependent on several environmental factors.

Plot of logQ_e vs. logC_e (Fig. 6) facilitates to determine the empirical constant K_f and 1/n from the intercept and slope of the linear regression as represented in Table 1.

Temkin isotherm [46] can be expressed as shown in Eq. (3):

$$Q_e = \frac{RT}{B_T}\text{In}(A_T C_e) \tag{3}$$

where A_T is the equilibrium constant corresponding to maximum binding energy; B_T is the Temkin isotherm constant; T is the temperature (K) and R is the ideal gas constant (8.3145 J mol^{-1} K).

Table 1
Langmuir, Freundlich and Temkin adsorption isotherm constants (Biosorbent dose 5 mg/50 mL, pH 6.5, contact time 180 min, agitation speed 120 rpm and fluoride concentration varying from 5 to 12 mg L^{-1})

Langmuir constants		Freundlich constants		Temkin constants	
b	0.096	K_f	0.975	A_T	0.020
Q	62.500	n	1.016	B_T	0.565
R^2	0.9852	R^2	0.9954	R^2	0.9951

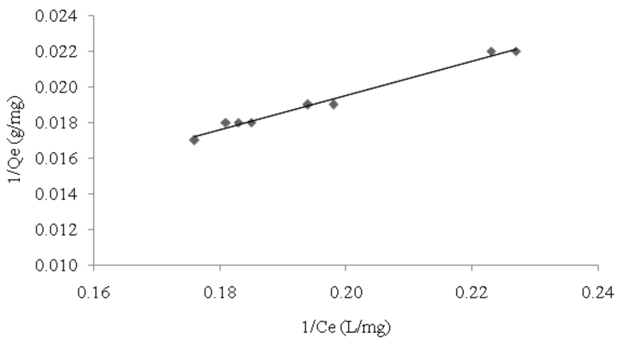

Fig. 5. Langmuir isotherm for removal of fluoride removal using *Psidium guajava* L.

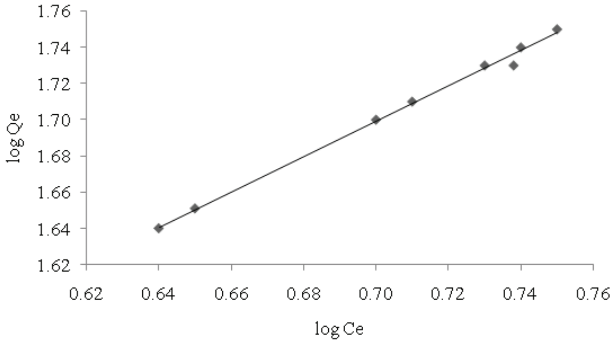

Fig. 6. Freundlich isotherm for removal of fluoride using *Psidium guajava* L.

A plot of Q_e vs. $\ln C_e$ (Fig. 7) enables to determine the empirical constant A_T and B_T from the intercept and slope of the linear regression as shown in Table 1.

Among the Langmuir and Freundlich isotherms, it was observed that isotherm data fitted well with Freundlich isotherm, which indicated that multilayer adsorption occurred at the surface of treated *Psidium guajava* L. Relatively lower value of b (0.096 L mg^{-1}) in this study indicates a weak interaction between fluoride and *Psidium guajava* L surface. Low values of B_T (0.565 J mol^{-1} K) in this study indicate a weak interaction between biosorbent and fluoride adsorption mechanism of ion exchange. The maximum defluoridation capacity of biosorbent was calculated using Eq. (1) (Q = 62.50 mg g^{-1}). Tomar et al. [40] studied on fluoride removal and found that Freundlich isotherm better explain the absorption experiment, which is the similar to present finding. Table 2 shows the comparison of maximum adsorption capacity of different adsorbents with their general characteristics of methods. The present proposed procedure uses the most inexpensive, easily available and eco-friendly biosorbent for the fluoride removal. Moreover, the present method removes the fluoride having concentration 4 mg L^{-1}. Thus, we can say that present method is quite sensitive, effective and rapid for the removal of fluoride as compared with literature reported methods and found to be more effective than others.

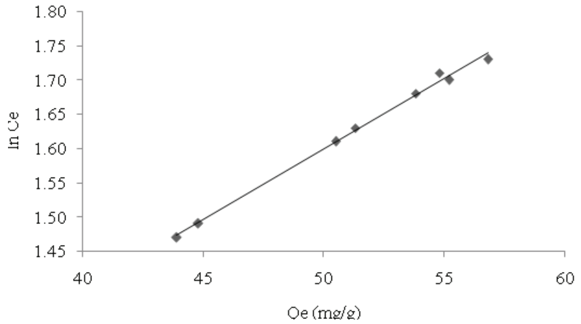

Fig. 7. Temkin isotherm for removal of fluoride using *Psidium guajava* L.

3.6. Adsorption kinetics

Adsorption kinetics is one of the most important characteristics to signify the adsorption efficiency [53,54]. The integrated form of pseudo-first-order kinetic can be expressed as shown in Eq. (4):

$$\mathrm{In}(Q_e - Q_t) = \mathrm{In}\, Q_e - k_1\, t \qquad (4)$$

where Q_e (mg L^{-1}) is the solid phase concentration of the fluoride at equilibrium; Q_t (mg g^{-1}) is the average solid phase concentration of fluoride at time t (min) and k_1 (min^{-1}) is the pseudo-first-order rate constant.

Table 2
Comparison of maximum adsorption capacity of different adsorbents

Material	pH	Contact time (min)	Adsorbent dose (g L^{-1})	Fluoride Conc (mg L^{-1})	Isotherm	Kinetics	Removal capacity (mg g^{-1})	Reference
Powdered biomass Tinospora cordifolia	7.0	120	7.0	5.0	Langmuir and Freundlich	Pseudo-first-order	25.00	Pandey et al. [47]
Activated carbon derived from rice straw	2.0	180	1.5	20	Langmuir and Freundlich	Pseudo-second-order	15.90	Daifullah et al. [48]
Sawdust	6.0	60	4.0	5.0	Freundlich	Pseudo-second-order	1.73	Yadav et al. [32]
Wheat straw raw	6.0	60	4.0	5.0	Freundlich	Pseudo-second-order	1.93	Yadav et al. [32]
Activated bagasse carbon	6.0	60	4.0	5.0	Freundlich	Pseudo-second-order	1.15	Yadav et al. [32]
Cynodon dactylon based activated carbon	7.0	105	1.25	3.0	Langmuir	Pseudo-second-order	4.61	Alagumuthu et al. [49]
Granular zirconium–iron oxide (GZI)	7.0	180	5.0	10.0	Langmuir	Pseudo-second -order	9.80	Dou et al. [50]
Nanosized hydroxyapatite in presence of low molecular weight organic acids	7.0	120	8.0	50.0	Freundlich	Pseudo-second-order	7.60	Wang et al. [51]
Iron–zirconium hybrid oxide	6.8	45	—	5.0	Redlich–Peterson	Pseudo-first-order	8.21	Biswas et al. [52]
Psidium guajava leaves	6.5	180	0.1	5.0	Freundlich	Pseudo-first-order	62.50	Present study

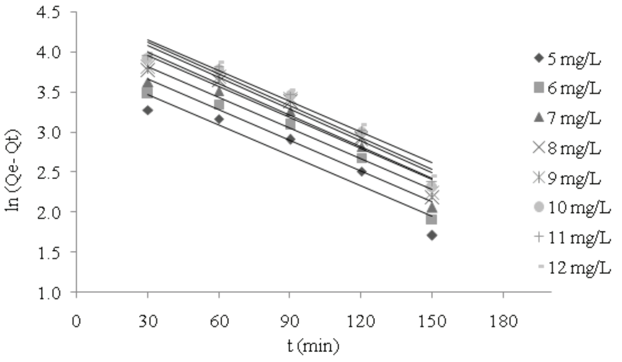

Fig. 8. Pseudo-first-order plot of fluoride sorption using *Psidium guajava* L as biosorbent.

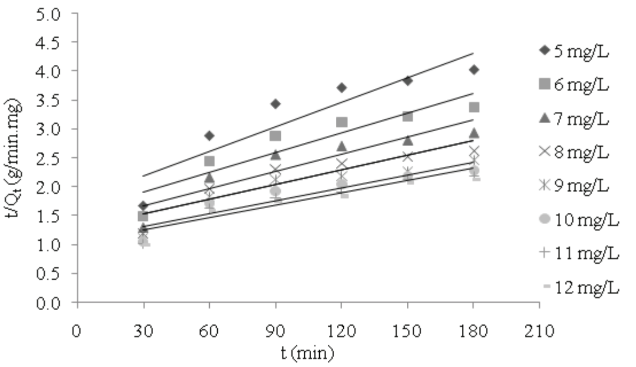

Fig. 9. Pseudo-second-order plot of fluoride biosorption using *Psidium guajava* L.

In order to obtain the rate constants, the straight line plot of ln(Q_e − Q_t) vs. t for different treatment conditions were plotted (Fig. 8).

The adsorption kinetics may also be described by a pseudo-second-order kinetic equation [53,55,56]. On integrating and applying the boundary conditions, the pseudo-second-order kinetic equation is converted to the form as shown in Eq. (5):

$$\frac{t}{Q_t}=\frac{1}{k_2Q_e^2}+\frac{1}{Q_e}\times t \qquad (5)$$

where k_2 is the rate constant of adsorption (mg g^{-1} min); Q_t is the amount of fluoride adsorbed by biosorbent (mg g^{-1}) at time t; Q_e is equilibrium adsorption capacity (mg g^{-1}).

Pseudo-second-order plot of fluoride adsorption using *Psidium guajava* L is shown in Fig. 9. In order to obtain the rate constant, the straight line plot of t/Q_t vs. t for different treatment conditions were analyzed (Fig. 9).

The values of pseudo-first-order and pseudo-second-order constants k_1 and k_2 have been calculated by plots shown in Figs. 8 and 9 and are tabulated in Table 3.

R^2 values were ranging from 0.8928 to 0.9462 in pseudo-first-order kinetic model, whereas in case of pseudo-second-order kinetic model, R^2 values were in the range of 0.8087–0.8684 with corresponding to ascending order of initial concentration of fluoride. R^2 values, in case of pseudo-first-order kinetic model, better correlated as compared with pseudo-second-order kinetic model. Hence, it is concluded that the fluoride biosorption using *Psidium guajava* L as biosorbent follows pseudo-first-order kinetic (Table 3). Kumar et al. [57] studied on fluoride removal and found that pseudo-first-order kinetic better explain the adsorption experiment, which is the similar to present finding.

Table 3
Pseudo-first-order and pseudo-second-order adsorption kinetics constants (biosorbent dose 5 mg/50 mL, pH 6.5, contact time varying from 30 to 180 min, agitation speed 120 rpm and fluoride concentration varying from 5 to 12 mg L^{-1})

Fluoride concentration (mg L^{-1})	Pseudo-first-order		Pseudo-second-order	
	$k_1 \times 10^{-3}$	$q_{e\,\mathrm{cal}}$	k_2	$q_{e\,\mathrm{cal}}$
5	6.6	0.893	1.59	0.831
6	6.6	0.905	1.34	0.818
7	6.6	0.902	1.81	0.838
8	6.6	0.912	1.82	0.809
9	7.2	0.925	1.82	0.868
10	7.2	0.936	1.74	0.846
11	7.2	0.946	1.69	0.810
12	7.2	0.943	1.74	0.817

3.7. Reusability study

Reusability study of biosorbent is necessary parameter to influence their cost. 0.1 g L^{-1} fluoride exposed *Psidium guajava* L was used to carry out regeneration study in mild acidic and alkaline media. It was observed that leaching of adsorbed fluoride is quite small in acidic pH, whereas in alkaline pH efficient leaching of the fluoride occurred. The exhausted material was regenerated with the help of 2.5% of 10 mL NaOH solution. At this concentration, almost 89.7% of the fluoride was desorbed by biosorbent. Reuse potential of the regenerated biosorbent was tested by means of biosorption–desorption studies up to the six cycles of repetition under the same conditions. During sixth cycle of repetition, the biosorption capacity reduced to almost 29.2% demonstrating that biosorbent can be reused up to six times with considerable efficiency and generation of sludge will be reduced. Banerjee et al. [58] also concluded that after reusing of adsorbent the amount of sludge generation was less.

4. Conclusions

Acid and alkali treated, powdered, locally available, low-cost *Psidium guajava* L has been found to be effective biosorbent for removal of fluoride with maximum adsorption capacity of 62.50 mg g^{-1}. The removal of fluoride was found to be maximum (88%) at pH 6.5 and increased with the increase in biosorbent dose as well as contact time, whereas increase in initial fluoride concentration resulted in decreased fluoride removal. Data obtained from biosorption studies confirmed that Freundlich isotherm is the better fitted as compared with Langmuir suggesting that multilayer biosorption on the surface of *Psidium guajava* L. The biosorption kinetics suggests that the pseudo-first-order rate expression will describe well the dynamic behavior of *Psidium guajava* L. This study suggests that *Psidium guajava* L can be used as an alternative and effective resource material for the removal of fluoride.

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