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Fluoride Removal from Aqueous Solutions by Mechanically Modified Guava Seeds

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Abstract

Removal of fluoride ions by mechanically modified guava seeds (MGS) from aqueous solutions in batch systems was investigated. The kinetic parameters as well as the sorption capacity of MGS were evaluated. The effect of different parameters such as particle size, initial fluoride concentration and contact time was studied on the sorption process. The rate of sorption for fluoride was rapid in the first 150 minutes and reached a maximum in 300 minutes. It was observed that particle size plays an important role in the kinetics of fluoride removal by this biosorbent since biosorption rate increased as particle size decreased. Sorption kinetic data were fitted to Lagergren, pseudo-second order and Elovich models. It was found that the pseudo second-order kinetic model describes the sorption kinetic experimental data and the Langmuir-Freundlich model describes biosorption isotherm, indicating that this system presents chemisorption on heterogeneous surfaces. It was also found that. Fluoride removal was evidenced by FTIR and SEM. Guava seeds showed a high affinity for fluoride ions compared with conventional adsorbents; therefore, it can be considered as a good low-cost biosorbent for defluoridation of water.

Keywords: Fluoride; Removal; Water; Guava seeds; Biosorption.

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1. Introduction

Fluoride is present in groundwater in many areas of the world in concentrations ranging from 0.1 to 10 mg/L. Fluoride concentration levels between 0.5 and 1 mg/L are beneficial to health, providing substantial protection against dental caries, but higher concentrations of fluoride (1.5-2 mg/L) may lead to dental fluorosis. At 3-6 mg/L, skeletal fluorosis may be observed, and crippling skeletal fluorosis can develop with fluoride concentrations in drinking water that are higher than 10 mg/L [1, 2]. The dental and skeletal fluorosis is irreversible and no treatment exists. People living in places where water has high concentrations of fluoride ions may develop fluorosis, this is one of the most frequently occurring endemic diseases and currently affecting millions of people worldwide. The only remedy is prevention by keeping fluoride intake within the safe limits [3, 4, 5].

Fluoride is a persistent and non-degradable poison that accumulates in soil, plants, wild life and in humans. Fluoride can be enriched in natural waters by geological processes. Besides, there can also be contributions from industries. High fluoride containing wastewaters are generated by thermal power plants, rubber, fertilizer and semiconductor manufacturing, glass and ceramic production and electroplating industries. According to the World Health Organization guidelines and recommendations in the areas with a warm climate, the optimal fluoride concentration in drinking water should remain below 1 mg/L, while in cooler climates it could go up to 1.2 mg/L [1]. The differentiation derives from the fact that people perspire more in hot weather and consequently drink more water. The problem is more acute in rural and small urban communities particularly in the third world countries [3]. In Mexico, the prevalence and incidence of fluorosis have increased during the past years, as a result of ingestion of fluorine during dental formation by means of water, food prepared with fluorinated salt, and inadvertent ingestion of this element during dental brushing with fluorinated tooth paste, as well as hidden fluorine in beverages [6], [7]. Fluoride concentrations above drinking water standards have been detected in various Mexican aquifers. The geological characteristics of the Mexican territory indicate that fluoride may be above drinking water standards in many areas of the country. The exposed population may be larger than that already identified [8].

Defluoridation of water is normally carried out by adsorption, chemical treatment, electro-chemical methods, dialysis and ion exchange processes. Among various processes, adsorption process is found to be effective, environmental friendly and economical [9]. Many studies have reported the possible utilization of conventional adsorbents for fluoride removal, like modified activated carbon, zeolites, clays, activated alumina, etc., with different degrees of success [10-13]. It has also been reported that removal of fluoride can be achieved by different types of biomass, such as algae [9, 14], Tamarind fruit shell [15], rice husk, *Moringa oleifera* seeds extract [16], protonated chitosan beads [17], and zirconium-loaded garlic peel [18], among others.

Guava (*Psidium guajava*) seeds are considered as a solid waste produced at great quantities by agricultural and industrial activities in Mexico, particularly on the State of Michoacán. Guava seeds have structural properties, like high content of cellulose, lignin and protein that make them suitable for their use as a biosorbent, particularly for anionic contaminants present in water. It has been reported the use of guava seeds as biosorbent for the removal of Cr (VI) from aqueous solutions with acceptable sorption capacity [19]. The aim of this work was to evaluate the guava seeds for the removal of fluoride from aqueous solutions, including their modification by mechanical procedures, by obtaining the kinetic and equilibrium parameters of the system, as well as to determine some variable effects over these parameters and to elucidate the main functional groups involved on fluoride biosorption.

2. Materials and Methods

2.1. Biosorbent preparation

The guava seeds (GS) were obtained from a local food industry as a solid residue produced by its manufacturing process. The material was washed and rinsed several times with distilled water to remove fruit pulp traces and impurities. The seeds were dried at room temperature to eliminate water content. GS were mechanically crushed with mill and then they were sieved to obtain different size fractions for later use in biosorption experiments. The seeds mechanically modified by grinding were identified as modified Guava seeds (MGS).

2.2. Fourier transform infrared spectroscopy (FTIR)

FTIR was performed on the mechanically modified Guava seeds (MGS) both before and after sorption contact with fluoride ions. For the measurement, 0.3 g of dry KBr were mixed with 0.02 g of the dry MGS sample and then compressed with a 3-ton force for 1 min. The samples were analyzed in a Bruker Tensor 27 FTIR spectrophotometer. The frequency range used was between 200 and 4000 cm^{-1}.

2.3. Scanning electron microscopy (SEM)

Samples of GS and MGS were covered with copper and analyzed using a JEOL JMS-6400 scanning electron microscope/Bruker X FLASH 4010 SEM microanalysis detector, in order to observe surface morphology of the samples and to obtain semi-quantitative elemental analysis.

2.4 Chemical characterization of biosorbent

Moisture, ash, and protein levels of the lemon residues were determined by AACC (2000) methods [20]. Total carbohydrates were determined using the Clegg (1956) method [21], and the Van Soest (1963) method [22] was used for cellulose, hemicellulose, and lignin analysis.

2.5. Effect of contact time on fluoride biosorption

In order to obtain kinetic parameters and the equilibrium sorption time, batch type biosorption kinetic experiments were carried out. 0.8 g of modified guava seeds (MGS) were weighed and placed in a plastic flask. Then 100 mL of sodium fluoride (NaF) solution at 100 mg/L were added. This solution was stirred at room temperature (25 °C) at different contact times, which ranged from 5 to 180 min. After the contact time was achieved, the supernatants were separated by filtration and the residual fluoride concentration was analyzed by a potentiometric method using a selective electrode (Hanna HI 98402 fluorometer). The same procedure was used with different particle sizes of 1 and 2 mm at the same temperature, in order to determine the effect of this parameter on the kinetics of biosorption. The experiments were performed in triplicate to determine reproducibility. Blank experiments showed no detectable fluoride ions adsorbed on the walls of the flask or by filtration of supernatants.

The quantities of fluoride adsorbed onto MGS were calculated from the initial concentration of the solution (Eq. 1):

$$q=\frac{V(C_0\text{-}C_e)}{M} \tag{1}$$

Where q is the measured sorption per unit weight of solid, V is the volume of solution, C_0 and C_e are the initial and equilibrium concentrations of fluoride, respectively, and M is the dry weight of biosorbent.

2.6. Effect of biosorbent dose

The effect of MGS dose on biosorption was studied by contacting a fixed particle size (1 mm) at a range of MGS dosages from 0.05 to 3 g with 25 mL of fluoride solution of a fixed initial concentration (200 mg/L) using an orbital shaker at a fixed temperature (25 °C).The experiments were performed in triplicate to determine reproducibility.

2.7. Biosorption isotherms

Biosorption, batch-type experiments were carried out with 1 mm particle size MGS and aqueous solutions of fluoride at concentrations from 0.001 N to 0.5 N to determine maximum biosorption capacities of MGS for this ion. In centrifuge tubes, 0.5 g of MGS samples were put into contact with 5 mL of fluoride aqueous solutions at different concentrations. The tubes were placed in a thermostat-adjusted water bath agitator at 25 °C for the equilibrium time determined by the biosorption kinetics experiments. At the end of the contact time, the solution was filtered, and the supernatant was placed in vials for metal analysis by a potentiometric method, as mentioned above. The experiments were performed in triplicate, as in the previous cases.

3. Results and discussion

3.1 Chemical characterization of biosorbent.

Because biosorbents show potential in several detoxification processes, it is essential to know their chemical composition to infer how they are effective in retaining these compounds [23, 24]. Chemical analysis of the MGS (Table 1) showed that the main components of the dietary fiber were lignin (69.78%), hemicellulose (12.96%), cellulose (11.04%), and pectin(1.32%).The probable sites involved in the MGS biosorption of fluoride ions are pectin (D-galacturonic acid), lignin (hydroxycinnamyl alcohol monomers), and cellulose. In addition, the various functional groups found in both carbohydrates and proteins are potential F^- binding sites.

Table 1. Chemical characterization of MGS

Component	Percent
Ash	0.3907
Ether extract	3.7774
N_2 free extract	0.4327
Fiber components	
Pectin	1.3295
Hemicellulose	12.96
Cellulose	11.04
Lignin	69.7863
Protein	0.0192
Other components	0.2642

3.2 Scanning electron microscopy (SEM).

The surface morphology of MGS was observed with SEM, to infer the possible adhesion sites of fluoride ions (Figure 1). We found that MGS have a heterogeneous surface, consisting of both smooth areas and rough areas. Besides, it can be observed that the mechanical milling of guava seeds infer to the material a range of pore sizes that went up to the micron level, clearly present at the rough areas but absent at the unmodified guava seeds (GS) (Figures 1A, 1B). These sites are important because the pores increase surface area and thus increase fluoride adsorption capacity [24]. Further, an elemental analysis of the adsorbent was carried out indicating the percentage chemical composition of the adsorbent used. The elemental analysis of the adsorbent showed the presence of Carbon, Nitrogen and Hydrogen. The presence of fluoride was detected on this semi-quantitative analysis.

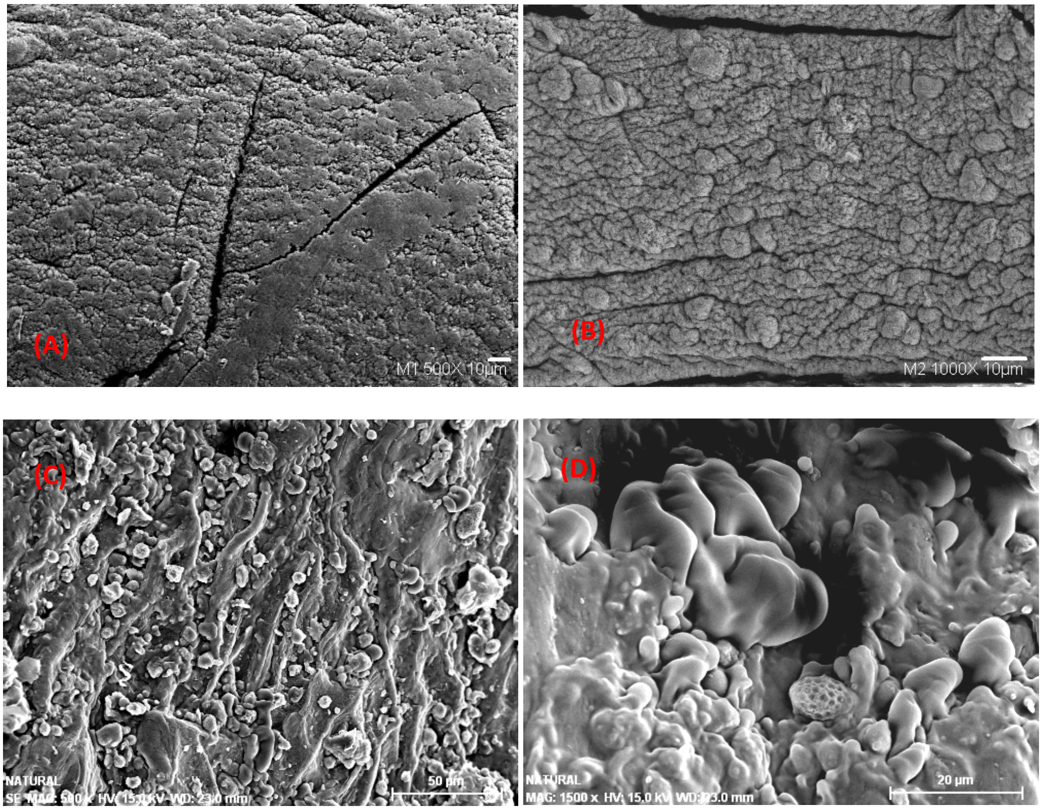

Figure 1. Unmodified guava seeds (A and B) observed at 500x and 1000x, respectively; and mechanically modified guava seeds (C and D) observed at 500x and 1500x, respectively.

3.3 Fourier transform infrared spectroscopy (FTIR).

The FTIR results for the MGS, before and after biosorption of fluoride ions, are shown in Figure 2 and the resulting surface functional groups before and after fluoride biosorption were depicted in Table 2. The intensity of and shifts in the transmittance bands in the FTIR spectrum were directly related to changes in the molecules of the various MGS samples. The sample spectrum is complex and contains different bands from functional groups of proteins, sugars, and complex carbohydrates (dietary fiber components). Differences in the 3950 to 2800 cm^{-1} region were associated with amines (NH) and hydroxyl groups (OH). In this study, high intensity broad absorption bands were observed at 3382 and 3370 cm^{-1}, and were caused by the bonded OH stretch contained in lignin, cellulose, hemicelluloses, pectin, and sugars. Differences in transmittance before and after treatment with fluoride solutions suggest that these groups could be involved on fluoride (F$^-$) biosorption. In addition, bands found at 2926, 2924, 2856, 2857, 1382 and 1377 cm^{-1} are associated with CH stretch related with alkanes groups from cellulose, hemicelluloses and lignin. Carbonyl (C=O) group was also observed in this study at 1745 and 1742 cm^{-1} bands before and after F$^-$ biosorption, respectively. These bands are associated with aldehydes and ketones from simple and complex carbohydrates, as well as from esterified carboxylic acids from pectin, hemicelluloses and lignin [25]. The bands appeared in the region of 1540 and 1400 cm^{-1} might be attributed to the presence of quinine and OH bonds. Moreover, the band observed at 1165 cm^{-1} before biosorption was attributed to C-O asymmetrical stretching of hydroxyl groups from primary alcohols related to phenolic compounds present in lignin. This band is not longer in MGS sample after F$^-$ biosorption. The bands appearing after biosorption in the region 1377, 1249 and 1052 cm^{-1} indicated the presence of C-H, C-N and C-F stretch groups, respectively. The latter group (C-F) is an important indicator of fluoride biosorption by MGS since only occurs in MGS samples after contact with fluoride solutions. Furthermore, FTIR results indicated that mainly hydrogen atoms in the carboxylic groups were involved in fluoride ion sorption. Similar results were also observed in fluoride removal onto algal biosorbent [26].

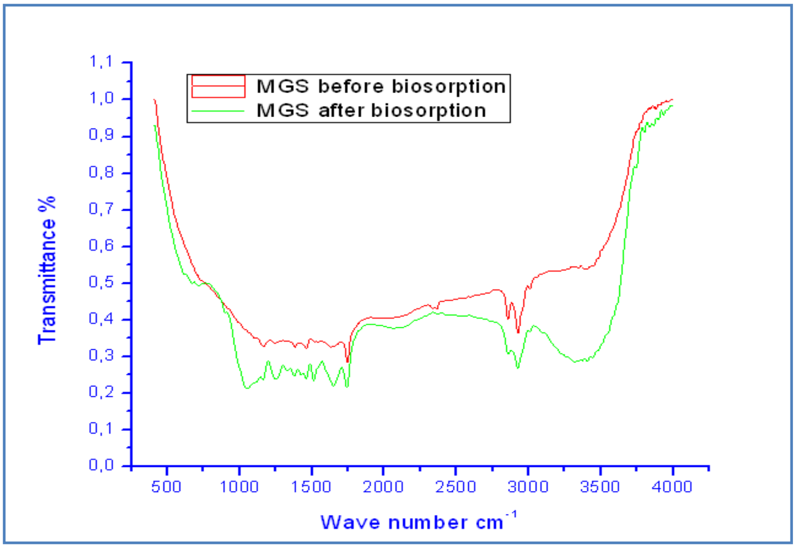

Figure 2. FTIR spectra from MGS before and after fluoride biosorption.

Table 2. Main surface functional groups involved in fluoride biosorption by MGS observed by FTIR spectroscopy.

Wavenumber (cm^{-1})		Functional group
Before biosorption	After biosorption	
3382	3370	OH
2926	2924	C-H
2856	2857	C-H
1382	1377	C-H
1745	1742	C=O
--	1249	C-N
1165	--	C-O
--	1052	C-F

3.4 Effect of contact time on fluoride biosorption.

Figure 3 shows the results obtained from the tests of fluoride removal by MGS at different particle sizes and as a function of time. The curves of fluoride removal are characterized by a relatively fast sorption in the first 150 minutes of contact time, especially at 1mm particle size (Figure 3). During the first five hours of contact time, almost all of fluoride sorption occurred, and the equilibrium was reached. A total fluoride removal from the aqueous solution, near 100%, was observed at 1mm particle size, and near 60% was observed at 2 mm particle size. Control experiment showed no significant F^- removal. From these data, it can be observed that particle size plays an important role in the kinetics of fluoride removal by this biosorbent. It can be noticed that equilibrium time is not affected at larger particle size, but percent removal is affected negatively. This behavior suggests that available adsorption sites increase as particle size decreases, due to the appearance of small pores on the surface of this biosorbent. However, these pores are not deep enough to have a negative impact on intraparticle diffusion and, therefore, over the time to reach equilibrium. Moreover, this behavior might be explained by the fact that for a small particle a large external surface area is presented to the solute molecules and as a result lowering the driving force per unit surface area for mass transfer than for larger particles [22, 27].

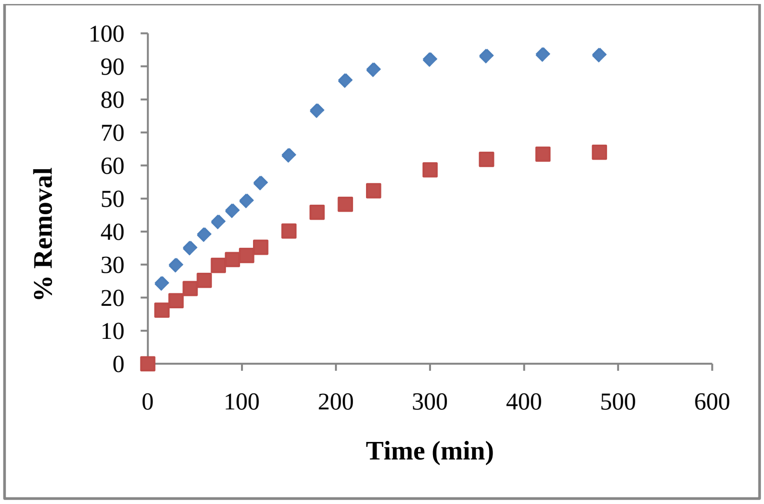

Figure 3. Fluoride biosorption by MGS as a function of contact time at different particle sizes: (♦) 1mm, (■) 2mm.

Experimental data were fit to empirical kinetic models by linear regression analyses to obtain the kinetic parameters for each of the systems studied at different particle sizes. Lagergren's pseudo-first order model, a pseudo-second order model and the Elovich equation were used to fit the data. Pseudo-first order and pseudo-second order equations can be used while assuming that the measured concentrations are equal to surface concentrations. These models are expressed as in Eq. 2-4:

Lagergren's pseudo-first order model (Eq. 2) [28]:

$$q_t = q_e(1-e^{-K_L t}) \tag{2}$$

Pseudo-second order model (Eq. 3) [29]:

$$q_t = \frac{K_2 q_e^2 t}{1+2K_2 q_e t} \tag{3}$$

Elovich equation (Eq. 4) [30, 31]:

$$q_t = \frac{1}{b} Ln(1+abt) \tag{4}$$

Where q_t is the solute (fluoride ions) concentration at time, t, per weight of adsorbent (mg/g), q_e is the concentration of solute removed at equilibrium per weight of adsorbent (mg/g), K_L is the pseudo-first order kinetic constant (min^{-1}), K_2 is the pseudo-second order rate constant of sorption (g/mg.min), a and b are Elovich constants related to the initial adsorption rate (mg/g.min) and the desorption rate (g/mg), respectively. In general, the experimental data for the sorption of fluoride on MGS, as a function of time, were best fitted to the linearized form of pseudo-second order model [29] (Figures 4 and 5), with a correlation coefficient R=0.9908 for 1 mm particle size and R=0.9850 for 2 mm particle size (Table 3).

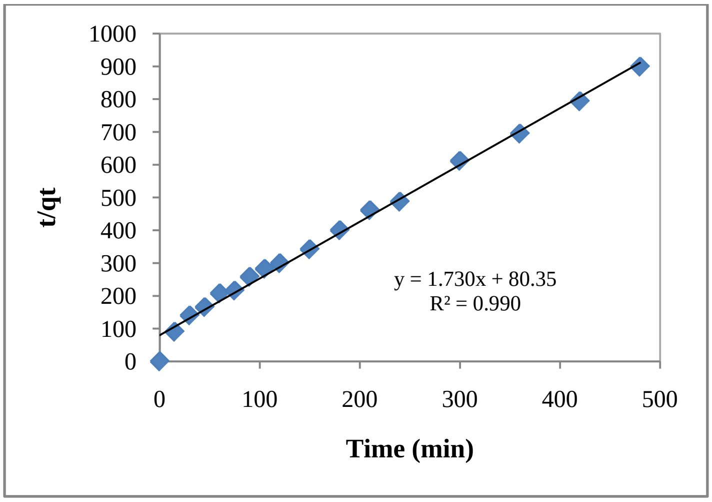

Figure 4. Pseudo-second order model plot for fluoride removal as a function of time by MGS (1mm particle size).

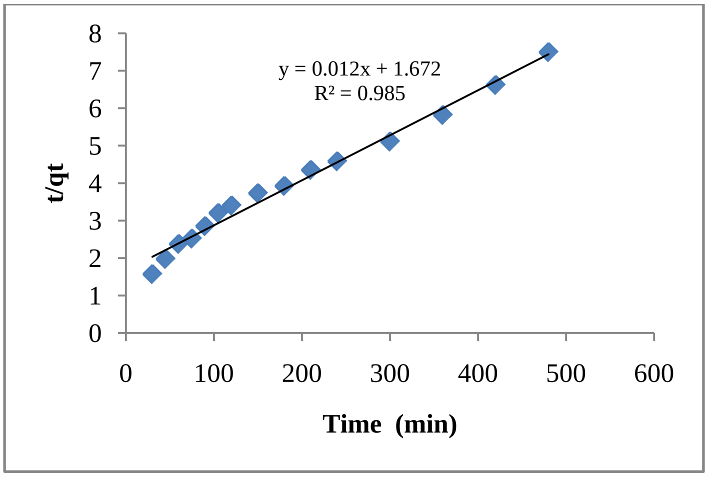

Figure 5. Pseudo-second order model plot for fluoride removal as a function of time by MGS (2mm particle size).

The kinetic parameters of the models are shown in Table 3. The low correlation coefficient values obtained for the pseudo-first order model indicate that sorption is not occurring exclusively onto one site per ion [32]. In accordance with the pseudo second-order reaction mechanism, the overall rate of F^- sorption processes appears to be controlled by chemical processes, through sharing of electrons between biosorbent and sorbate, or covalent forces, through the exchange of electrons between the particles involved [33, 34]. For the pseudo-second order constant (K_2), it can be observed that this parameter increases as particle size decreases for F^- sorption kinetics, thereby implying that the biosorption system reached equilibrium faster at lower particle sizes. Generally, the smaller the adsorbent particles, the greater the amount of ions could be adsorbed. Comparatively higher adsorption with smaller adsorbate particles may be due to the fact that smaller particles give a larger external surface area, indicating that mechanical modification of guava seeds could provide a higher surface area, which enhance fluoride sorption kinetics. Also, for a large particle size some of the few interior pores of unmodified guava seeds could be unapproachable by the F^- ions. Access to all pores is facilitated through small size particles [35].

Table 3. Kinetic parameters of fluoride biosorption by MGS at different particles sizes.

Model	Parameters		R^2	
	1 mm	2mm	1mm	2mm
Pseudo first order	$K_L = 0.0042$	$K_L = 0.0034$	0.9664	0.9836
Pseudo-second order	$K_2 = 0.0372$	$K_2 = 1.9\text{x}10^{-5}$	0.9908	0.9860
Elovich	$a = 2.6233$ $b = 0.8115$	$a = 2.2224$ $b = 2.9411$	0.9726	0.9662

3.5 Effect of biosorbent dose

Adsorbent dose is also an important parameter owing to its effect on efficiency (% removal) and on the amount of fluoride adsorbed per unit weight of biomass (q_t) [36]. Figure 6 shows the biosorbent dose effect over fluoride removal by MGS. It was observed that percentage of fluoride removal increased with increasing of adsorbent dose (Figure 6), as expected. Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more active adsorption sites [36]. Figure 6 also shows a slight decrease of percent removal with increase of adsorbent dose, this behavior might be due to the formation of aggregates between the MGS particles and overlapping of active sites at high adsorbent doses, reducing the effective active site area. Similar observation has been reported for sorption of fluoride onto Ca-pretreated biomass [37, 38]. The optimum MGS dosage was fixed as 2 g/25 mL and used in further experiments.

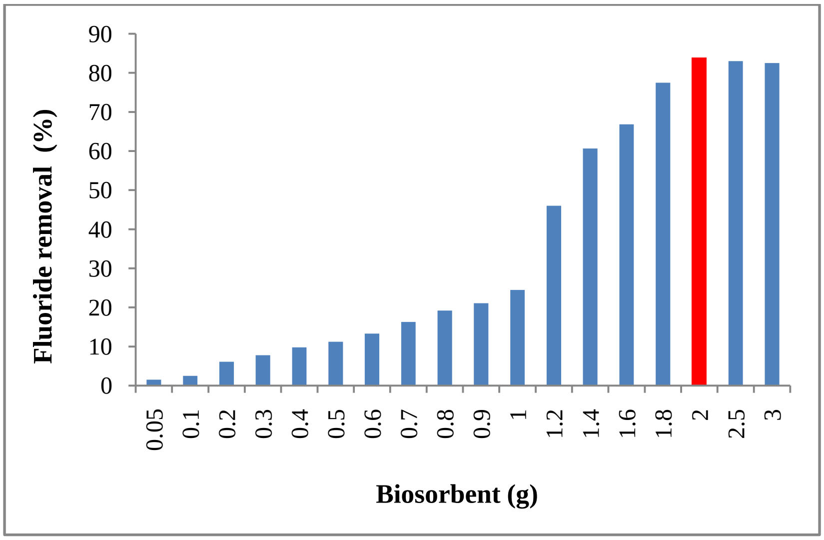

Figure 6. Effect of adsorbent dose on the biosorption of fluoride by MGS (experimental conditions: Initial fluoride concentration: 100 mg/L, pH: 6.0, agitation speed: 120 rpm, Contact time: 300 minutes, Temperature: 25 °C).

3.6 Biosorption isotherms

The biosorption isotherm of fluoride ions using MGS is shown in Figure 7. The gradual decrease in adsorption rate of F^- with an increasing initial concentration of these ions in the solution shows the continued saturation of the available binding sites. According to the results shown in Figure 7, it can be observed that the amount of F^- adsorbed by MGS increased by raising the initial ion concentration, and it followed a nonlinear-type isotherm.

Experimental data from these plots were fitted to the following isotherm models by nonlinear regression analysis (Eq. 5-7):

Freundlich: $$q_e = K_F C_e^{1/n_F} \qquad (5)$$

Where q_e is the amount of solute per unit weight of adsorbent (mg/g), C_e is the solute concentration in the solution at equilibrium (mg/L), K_F is the equilibrium constant indicative of adsorption capacity, and n_F is the adsorption equilibrium constant whose reciprocal is indicative of adsorption intensity,

Langmuir: $$q_e = \frac{q_0 a_L C_e}{1+a_L C_e} = \frac{K_L C_e}{1+a_L C_e} \qquad (6)$$

Where q_e is the amount of solute per unit weight of adsorbent (mg/g), C_e is the solute concentration in the solution at equilibrium (mg/L), q_o is the amount of solute retained per unit weight of adsorbent in forming a complete monolayer on the surface (mg/g), a_L is the constant related to the energy or net enthalpy of adsorption, and K_L is the Langmuir constant, (L/g), and

Langmuir-Freundlich: $$q_e = \frac{K_{LF} C_e^n}{1+ a_{LF} C_e^n} \qquad (7)$$

Where q_e is the amount of solute per unit weight of adsorbent (mg/g), C_e is the solute concentration in the solution at equilibrium (mg/L).

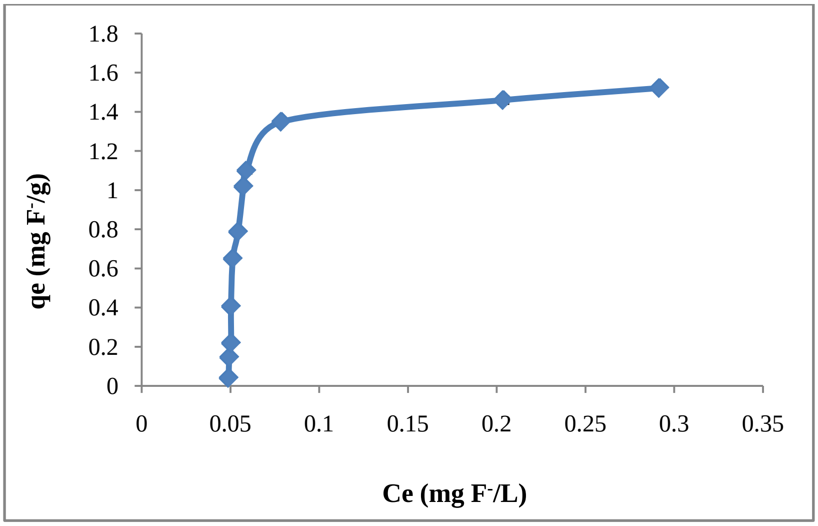

Figure 7. Fluoride biosorption isotherm by MGS.

The isothermal biosorption parameters for these models are shown in Table 4. The experimental data were best fit by the Langmuir-Freundlich isotherm model (Eq. 7), as shown in Figure 8. The Freundlich and Langmuir models tested to fit the equilibrium experimental data showed significantly lower *R*-values in all cases (Table 4), as it can be observed in Figure 8. At low adsorbate concentrations, the Langmuir-Freundlich isotherm (Eq. 7) effectively reduces to the Freundlich isotherm, and thus, it does not obey Henry's Law. At high sorbate concentrations, this isotherm predicts a monolayer sorption capacity characteristic of the Langmuir isotherm [39]. The Langmuir-Freundlich model (L-F) has been widely used to describe data from the equilibrium of adsorption onto heterogeneous surfaces. Thus, the fact that the fluoride equilibrium data fits well within this model suggests that F^- biosorption onto MGS is of a heterogeneous nature. Maximum fluoride biosorption capacity q_0=15.6 mg/g was calculated from L-F model. A comparison of maximum adsorption capacities of different adsorbents reported in literature is included in Table 5.

Table 4. Isotherm model parameters and correlation coefficients (*R*) for fluoride biosorption by MGS.

Model	Parameters		R
Freundlich	K_F = 36.76 (mg/g)(mg/L)$^{1/n}$	*n=1.7954*	0.7764
Langmuir	q_0 = 25.18 (mg/g)	a_L=7.55 (L/mg)	0.8640
Langmuir-Freundlich	K_{LF} = 8.13 (mg/g)(mg/L)$^{1/n}$ *n* = 6.97	a_{LF} = 17.88 (mg/L)	0.9777

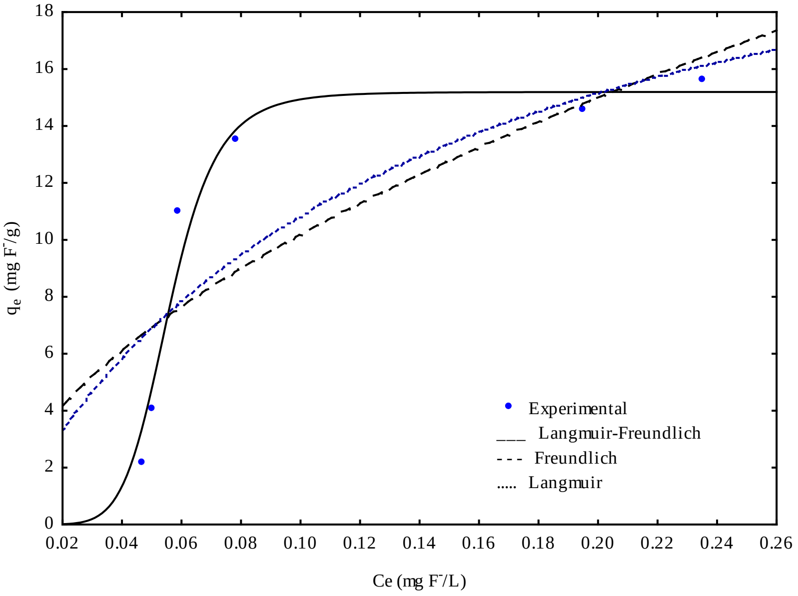

Figure 8. Isotherm models plots for fluoride biosorption by MGS.

Table 5. Comparison of sorption capacities of various adsorbents for fluoride removal.

Adsorbent	Sorption capacity, q_o (mg/g)	Reference
Guava seeds (MGS)	15.6	This work
boehmite	2.05	[2]
algal *Spirogyra* IO1	1.27	[9]
Mg- modified CHT	1.18	[12]
Zr-loaded garlic peel	20.9	[18]
Hydrous ferric oxide	16.5	[40]
Bone char	5.9	[41]
Activated alumina	8.27	[42]
Treated Tamarind fruit cover	6.11	[43]

Conclusions

In general, it can be concluded that mechanically modified guava seeds (MGS) have good properties for the sorption of fluoride ions from aqueous solutions. The pseudo-second order model describes the fluoride biosorption kinetics using MGS at different particle sizes. The Langmuir-Freundlich model best describes the isotherm's experimental data, which indicates that fluoride biosorption onto MGS is characterized by chemisorption on heterogeneous surfaces. The particle size is an important parameter that affects the sorption for fluoride on MGS since the sorption of these ions increases as the particle size decreases. Finally, this low-cost material can be employed as an adsorbent for fluoride removal from drinking water, in particular in domestic systems where fluoride-related problems exist.

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