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Evaluation of Guava Seeds (Psidium Guajava) As a Low-Cost Biosorbent for the Removal of Fluoride from Aqueous Solutions

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Abstract: - The sorption of fluoride ions by guava seeds (GS) from aqueous solutions in batch systems was investigated. The kinetic parameters, as well as the sorption capacities, of GS at different temperatures were evaluated. It was found that the pseudo second-order kinetic model describes the sorption kinetic experimental data and that the Langmuir model describes the isotherms. It was also found that pH has an important effect on the adsorption of fluoride ions by GS, as more were removed at pH values between 5 and 8. Sorption capacities of fluoride increase as temperature rise; suggesting an endothermic nature of the process. GS 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, biosorption, guava seeds, kinetics, isotherms.

I. INTRODUCTION

Fluoride is present in ground water 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. The only remedy is prevention by keeping fluoride intake within the safe limits [3], [4]. 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 [5], [6]. 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 [7].

Defluoridation of water was 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 [8]. 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 [9]-[12]. It has also been reported that removal of fluoride can be achieved by different types of biomass, such as algae [8], [13], Tamarind fruit shell [14], rice husk, *Moringa oleifera* seeds extract [15], protonated chitosan beads [16], zirconium-loaded garlic peel [17], 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 [18].

The aim of this work was to evaluate the guava seeds for the removal of fluoride from aqueous solutions by obtaining the kinetic and equilibrium parameters of the system, as well as to determine some variable effects over these parameters.

II. MATERIALS AND METHODS

A. 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 and then they were sieved to obtain the 2 mm size fraction for later use in biosorption experiments.

B. Kinetics of fluoride biosorption

In order to obtain kinetic parameters and the equilibrium sorption time, batch type biosorption kinetic experiments were carried out. 0.5 g of guava seeds were weighed and placed in a plastic flask. Then 50 mL of sodium fluoride (NaF) solution at 5 mg/L were added. This solution was stirred at room temperature. A fluorometer (Hanna HI 98402) was immersed on the flask to obtain fluoride concentrations at different contact times, which ranged from 5 to 180 min. The same procedure was used with different agitation speeds of 60 rpm and 100 rpm 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.

C. Effect of pH

In order to establish the pH value at which GS have a higher fluoride removal and to determine the influence of this parameter on the biosorbent material, batch type adsorption experiments with GS and 5 mg/L aqueous solutions of sodium fluoride were performed. Different pH values of solutions (between 2 and 9) were established to determine their influence on the biosorption process and set this as a parameter to carry out further experiments. These values were adjusted by adding small amounts of 0.1 M solutions of HCl or NaOH, as appropriate. Biosorption experiments were performed as mentioned above, at different pH values of the NaF solution. Fluoride solutions were stirred at 60 rpm and at room temperature. Fluoride concentrations with a fluorometer were determined as mentioned before.

D. Biosorption isotherms

Biosorption isotherms were obtained using a batch equilibrium method. Samples (400 mg) of GS were placed in contact, in centrifuge tubes, with 50 mL of different concentrations of fluoride solutions (from 10 to 1800 mg/L), and at different temperatures (25, 35 and 50 °C), to determine the effect of this parameter on biosorption maximum capacities of GS. Tubes were placed in thermostat adjusted water bath shaker, during the equilibrium time determined by the biosorption kinetics experiments. At the end of the contact time the solution was decanted and the supernatant was placed in plastic flask to determine fluoride concentration. The experiments were performed in triplicate as the previous cases.

III. RESULTS AND DISCUSSION

A. Kinetics of fluoride biosorption

Fig. 1 shows the results obtained of fluoride removal by guava seeds (GS) at different agitation speeds and as a function of time. It can be noticed that fluoride biosorption curves are characterized by a relatively fast sorption in the first 30 minutes of contact time. Approximately 25 and 30% fluoride removal occurred during the first two hours of contact time at 100 and 60 rpm of agitation, respectively, and the equilibrium was reached. From this data, it can be observed that agitation speed is not a significant parameter on kinetics of fluoride removal by this biosorbent.

Experimental data were fitted to empirical kinetic models by nonlinear regression analysis to obtain the kinetic parameters for the system at a temperature of 25 °C and different agitation speeds. Lagergren's pseudo-first order model, pseudo-second order model and Elovich equation were the equations 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 follows:

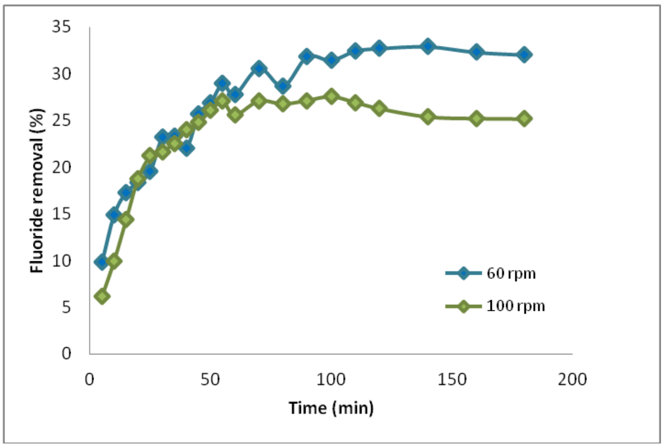

Fig. 1 Biosorption capacity of fluoride by GS at different agitation speeds vs. time.

Lagergren's pseudo-first order model [19]:

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

$$q_t = q_e(1 - e^{-K_L t}) \quad \ldots\ldots. \ (1)$$

Pseudo-second order model [20]:

$$\frac{t}{q_t} = \frac{1}{(K_2 q_e^2)} + \frac{t}{q_e}$$

$$\frac{t}{q_t} = \frac{t}{(K_2 q_e^2)} + \frac{t}{q_e} \quad \ldots\ldots. \ (2)$$

Elovich equation [21]:

$$q_t = \frac{1}{b} \ln(1+abt)$$

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln t \quad \ldots\ldots. \ (3)$$

Where q_t is the adsorbate concentration at time, t, per weight of adsorbent (mg/g) and it was calculated as in [22]; q_e is the concentration of adsorbate 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.h); a and b are Elovich constants related to initial adsorption rate (mg/g.h) and desorption rate (g/mg), respectively. In general, the experimental data for the sorption of fluoride on GS, as a function of time, at 60 and 100 rpm (Fig. 2 and Fig. 3, respectively) were best fitted to the pseudo-second order model with correlation coefficients (R) between 0.9825 and 0.9837.

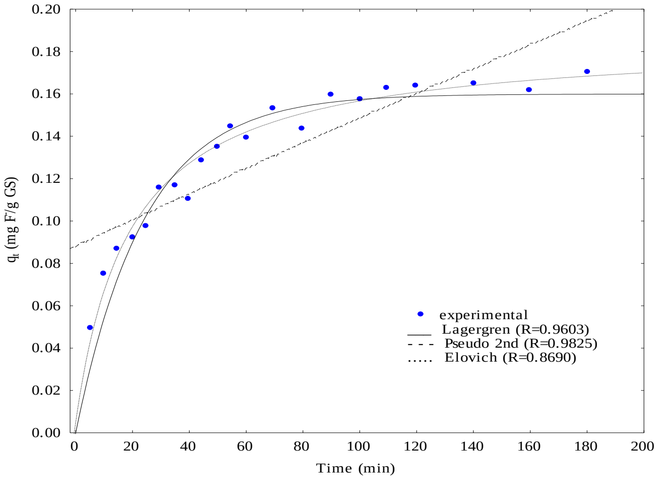

Fig. 2 Biosorption capacity of fluoride by GS vs. time, at 60 rpm agitation speed, adjusted to kinetic empirical models.

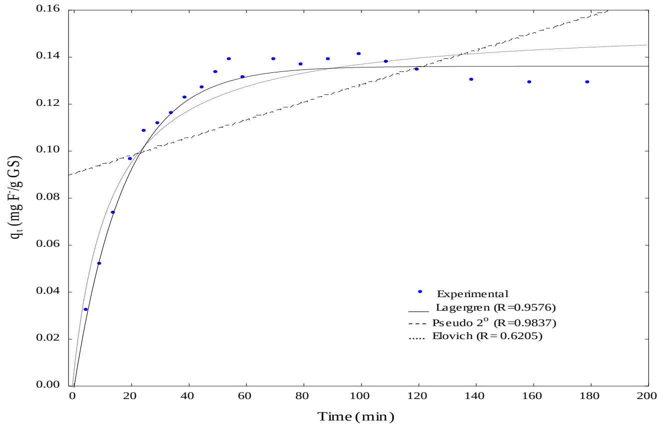

Fig. 3 Biosorption capacity of fluoride by GS vs. time, at 100 rpm agitation speed, adjusted to kinetic empirical models.

The kinetic parameters of the models are shown in Table I. The low correlation coefficient values obtained for the pseudo first-order model indicate that sorption is not occurring exclusively onto one site per ion. In accordance with the pseudo second-order reaction mechanism, the overall rate of fluoride ions (F^-) sorption processes appear to be controlled by the chemical processes, through sharing of electrons between biosorbent and sorbate, or covalent forces, through the exchange of electrons between the particles involved. For the pseudo second order constant (K_2) it can be observed that this parameter increases as agitation speed rises, implying that biosorption system reached equilibrium relatively faster at higher agitation and that the sorption processes could be enhanced by an increment in this parameter, suggesting also that diffusion could play an important paper on fluoride biosorption kinetics by GS. The correlation coefficients obtained greater than 0.98 and the adequate fitting of theoretical and experimental q_e values for all temperatures suggest the applicability of this models based on the assumption that the rate limiting step may be chemisorption in explaining the kinetics of biosorption for the entire sorption period. This indicated that the pseudo second order kinetic model describes fluoride biosorption kinetics adequately.

Table I: Kinetic parameters of fluoride biosorption by guava seeds at different agitation speeds.

Agitation speed (rpm)	**Pseudo first order (Lagergren)**			**Pseudo 2nd order**			**Elovich**		
	K_L (min^{-1})	**q_e (mg/g)**	**R**	**K_2 (min^{-1})**	**q_e (mg/g)**	**R**	**a (min^{-1})**	**b (mg/g)**	**R**
60	0.0412	0.1599	0.9603	0.2891	0.1852	0.9825	0.0006	1.0472	0.8690
100	0.0567	0.1361	0.9576	0.5043	0.1539	0.9837	0.0004	1.0486	0.6205

B. Effect of pH

The pH is an important parameter to be considered in sorption processes because it may affect both the properties of the adsorbent and the composition of the solution. It is also important due to the ionization of surface functional groups and composition of solutions. Fig. 4 shows pH effect over fluoride biosorption by GS. It can be noticed that fluoride removal by biosorption is observed only in a pH range between 5 and 8, since below this pH value there is formation of HF and, as a result, an increase in fluoride removal is observed in Fig. 4. pH affects directly the surface chemistry of the biosorbent. When active sites of the material are weakly acidic or basic, free sites availability depends on this parameter. Acidic groups tend to liberate protons, particularly in basic media, while basic groups tend to capture protons on acid media. Therefore, positive or negative charges appear on the surface of the adsorbent under these conditions. According to numerous authors, the pH can influence both ionic forms of adsorbate found in solution and the functional groups responsible for the binding of the adsorbate to the solid surface. At low pH values, the H^+ ions bind to functional groups which are positively charged and prevent, therefore, binding of metal cations, this fact favors the binding of fluoride ions from the solution, as shown in Fig. 4, but at lower pH values the joining with H^+ ions forms hydrofluoric acid (below pH 4) which implies a decrease in the concentration of fluoride ions in solution reducing fluoride biosorption on GS but showing higher removal efficiencies which should not be confused as removal by biosorption. As solution pH rises, the functional groups become negatively charged, inhibiting fluoride biosorption by this material, this behavior may me explained because when the pH of the solution increases to 8, the number of positively charged sorbent sites decreased and the number of –OH groups increased. Therefore, the positive sites of the sorbent and the presence of –OH groups are likely responsible for the low sorption at pH values higher than 8 [2]. Based on these facts, it can be deemed that the optimum pH values for fluoride biosorption by GS was between 5 and 8, as it is observed in Fig. 4.

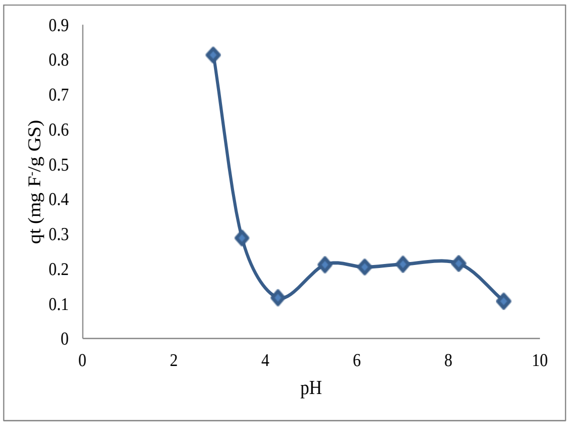

Fig. 4 Influence of pH on the biosorption of fluoride by guava seeds.

C. Biosorption isotherms

The biosorption isotherms of fluoride using GS at different temperatures are shown in Fig. 5. The gradual decrease in adsorption rate of F^- with increasing initial concentration of this adsorbate in the solution shows the continued saturation of the available binding sites. According to the results showed on Fig. 5, it can be observed that the amount of F^- adsorbed by GS increased by raising the initial adsorbate concentration, following a nonlinear type isotherm. The maximum amount F^- adsorbed by GS increased slightly with increasing temperature. This behavior could be due to the surface binding reactions that occur simultaneously with changes in temperature, and it indicates that Guava seeds have a greater affinity for F^- when the temperature increases (Fig. 5). It was reported that fluoride sorption by different types of adsorbents was positively affected by temperature in the test range of 10°C to 50°C [23]. This may be attributed to the fact that at higher temperature the rate of adsorption gets accelerated which in turn indicated the endothermic nature of reaction.

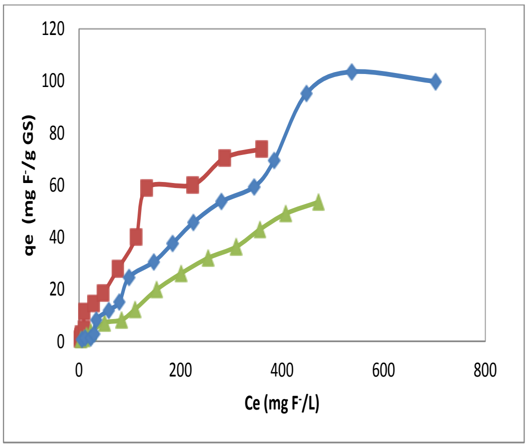

Fig. 5 Isotherms of fluoride biosorption by GS at 25 °C (▲), 35 °C (■), and 50 °C(♦).

Experimental data from these plots were fitted to the following isotherm models by nonlinear regression analysis:

Freundlich: $q_e = K_F C_e^{1/n_F}$ ……. (4)

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: $$q_e = \frac{q_o a_L C_e}{1 + a_L C_e} = \frac{K_L C_e}{1 + a_L C_e} \quad \ldots\ldots\ (5)$$

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), 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: $$q_e = \frac{K_{LF} {C_e}^n}{1 + a_{LF} {C_e}^n} \quad \ldots\ldots\ (6)$$

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), and K_{LF} and a_{LF} are empirical constants.

The isothermal biosorption parameters for these models are shown in Table II for fluoride removal. It can be observed that the experimental data were best fit by the Langmuir isotherm model since the correlation coefficients (R) obtained by nonlinear regression analyses ranged from 0.996 to 0.999. Langmuir model is often considered an empirical model and it is widely accepted that this model considers that the sorption energy of each molecule is the same, independently of the surface of the material; the sorption takes place only on some sites and there are no interactions between the molecules [4]. Therefore, it is assumed that homogeneous biosorption plays an important role in the removal of fluoride by GS. It can also be observed that maximum biosorption capacities (q_o) increase at higher temperatures, suggesting an endothermic nature of the fluoride sorption process. Moreover, the magnitude of the Langmuir constant a_L has small values (0.0003 to 0.0051 L/mg), which indicates a low heat of adsorption. According to Freundlich model the parameter n_F should have values lying in the range of 1 to10 for classification as favorable adsorption [3]. A smaller value of n_F indicates a weaker bond between adsorbate and adsorbent and also it indicates the adsorbent surface to be of heterogeneous nature.

Table I: Kinetic parameters of fluoride biosorption by guava seeds at different agitation speeds.

Temperature (°C)	**Langmuir**			**Freundlich**			**Langmuir-Freundlich**			
	q_0	**a_L**	**R**	**K_F**	**n_F**	**R**	**K_{LF}**	**a_{LF}**	**n**	**R**
25	116.50	0.0051	0.997	2.2488	1.6493	0.980	0.3599	0.0066	1.1288	0.987
35	316.53	0.0003	0.998	0.1663	1.0607	0.987	1.4377	0.0007	0.5736	0.955
50	413.83	0.0007	0.996	0.5092	1.2091	0.982	0.0113	0.0029	1.6115	0.986

The maximum adsorption capacity of GS was compared with the adsorption capacities of different adsorbents of previous literature reports at similar pH and temperature conditions and it was found that GS had better adsorption capacity for fluoride in comparison to other adsorbents as shown in Table III.

Table III: Comparison of the adsorption capacities of different adsorbents for defluoridation

Adsorbent	**q_o (mg g^{-1})**	**Reference**
Guava seeds	116.50	This work
boehmite	2.05	[2]
algal *Spirogyra* IO1	1.27	[8]
Mg- modified CHT	1.18	[11]
Zr-loaded garlic peel	20.9	[17]
Carbon nanotubes	33.7	[24]
Hydrous ferric oxide	16.5	[25]
Bone char	5.9	[26]
Activated alumina	8.27	[27]

CHT= calcined hydrotalcite

IV. CONCLUSIONS

In general, it can be concluded that guava seeds (GS) have good properties for the sorption of fluoride from aqueous solutions. The pseudo-second order model describes the fluoride sorption kinetics using GS at different temperature. The Langmuir model best describes the isotherm's experimental data, which may indicate that the sorption mechanism of fluoride ions on GS is chemisorption on a homogeneous material. pH affected fluoride biosorption at highly acidic and alkaline values. The sorption temperature is an important parameter that affects the sorption for fluoride on GS, and the sorption of this ion increases as the temperature increases, which indicate that the sorption process is endothermic. 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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