

## **Arsenate removal from aqueous solutions by iron-modified guava seeds: batch and fixed bed studies**

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**ABSTRACT** Arsenate removal from aqueous solutions by guava seeds chemically modified with iron (FeGS) in batch and fixed-bed systems was investigated. The effect of different parameters, such as initial arsenate concentration, biosorbent dose, and contact time, was studied on the sorption process. Batch-type contact experiments were performed to evaluate the kinetics and equilibrium of arsenate [As(V)] sorption. The maximum adsorption capacity of FeGS was 1.18 mg/g. The physical characterization of the biosorbent after adsorption showed arsenate removal in different functional groups on the surface of the modified material. These results suggested that the sorption mechanism was chemisorption on a heterogeneous material. The fixed bed column was used to investigate the dynamic adsorption characteristics where the effects of inlet arsenate concentration (4 and 20 mg/L) and FeGS bed height (15 - 45 cm) on the adsorption breakthrough were also investigated. The column study's maximum removal capacity was 4.97 mg/L with an initial As(V) concentration and flow rate of 20 mg/L and 10 mL/min, respectively, according to Bed Depth Service Time (BDST) model. The iron-modified guava seeds showed a high affinity for arsenate ions compared with conventional adsorbents; therefore, they can be considered an excellent low-cost biosorbent for arsenate removal from water.

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### **I. INTRODUCTION**

Groundwater contamination due to arsenic (As) is an important problem to be addressed. The challenges are manifold, and it is essential to develop effective methodologies for their remediation [1]. Arsenic contamination of potable groundwater poses a significant threat to human health. The potable water supplied in many countries (including Bangladesh, India, Taiwan, Mongolia, Chile, Mexico, and the United States) contains dissolved arsenic levels above 10 mg/L, the maximum level recommended by the World Health Organization. Long-term exposure to arsenic can cause various skin, kidney, bladder, and lung cancers, as well as neurological and cardiovascular problems [2, 3]. In aquatic environments, arsenic is found as As(III) or As(V), depending on the oxide-reduction conditions. The arsenic (III) species is the most toxic, although the arsenic (V) species is the most movable [4]. Generally, As(V) predominates in surface water, while As(III) is the main species in groundwater. However, both forms of arsenic can be found in groundwater due to changes in redox conditions and biological activity [5].

Different methods, including chemical treatment, electrochemical methods, membrane technologies, and ion exchange processes, can remove arsenic from water. However, implementing these technologies is usually restricted by the high cost, complex operation, and the high pollutant concentration of the water to be treated [6]. Adsorption is sometimes preferred concerning As removal in small-scale systems owing to its benefits of being easy to handle, high efficiency, and low cost. Moreover, the adsorption process is environmentally friendly, economical, and suitable for single families and small communities. Many studies have reported the possible utilization of conventional adsorbents for arsenic removal, like modified activated carbon, zeolites, clays, activated alumina, and titanium dioxide, with different degrees of success [7, 8]. Recently, more focus has been given by scientists to using various naturally occurring biosorbents in the adsorption process since these types of adsorbents offer advantages of low cost, minimization of the quantity of

chemical or biological sludge to be disposed of, high efficacy in dilute effluents, environmentally friendly properties, regeneration of biosorbent, and the possibility of metal recovery [9].

On the other hand, guava (*Psidium guajava*) seeds are considered a solid waste produced in significant quantities by agricultural and industrial activities in Mexico, particularly in the State of Michoacán. Recent increases in guava production and consumption have led to the production of large amounts of guava seed waste that requires disposal, which could be mitigated by developing uses for this waste as an inexpensive source of biomass. Guava seeds have structural properties like high cellulose, lignin, and protein content, making them suitable for their use as a biosorbent, particularly for anionic contaminants in water. These properties are due to the presence of various functional groups on its surface, such as amines, hydroxyl, carbonyl, carboxyl, and alkanes, which have been involved in fluoride sorption as well as in the formation of different types of interactions with metals [10, 11]. It has been reported that guava seeds are biosorbents to remove Cr(VI) from aqueous solutions with adequate sorption capacity. We also have reported elsewhere the use of natural and mechanically modified guava seeds to remove fluoride ions from aqueous solutions with different biosorption capacities [10, 12].

Sorption processes could be implemented in different ways, such as batch processes or fixed bed columns. Each of these implementations has characteristics that make them suitable for specific applications. The batch process could be used with organic or inorganic adsorbents, and they do not need sophisticated equipment; they could be carried out at different scales under normal temperature and pressure conditions. However, they are only used in small-scale operations, in occasional treatments. The most common use of adsorbents is as packed or fixed beds in columns, where the adsorbent or ion exchanger is placed inside a pressured vessel, provided with an input, output, and flow distribution systems that allow the solution to infiltrate through the bed adsorbent at a determined flow. Column operations are frequently used in cleaning primary coolers and their auxiliary systems, as well as in the treatment of water and wastewater. Thus, it is crucial to know the sorption behavior of ions related to arsenic in guava seed coming from local solid wastes, in batch processes as well as in continuous processes (columns), in order to have a good criterion for future applications in arsenate polluted groundwaters [13].

Therefore, this work aimed to evaluate the arsenate removal efficiency of iron-modified guava seeds from aqueous solutions in batch and fixed-bed systems by obtaining the kinetic, equilibrium, and dynamic parameters of the system, as well as to determine the influence of some variables over As(V) adsorption.

## II. MATERIAL AND METHODS

### 2.1. Adsorbent 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's were mechanically crushed with a mill and then sieved to obtain different-size fractions. After this treatment, the 1 mm fraction was used for biosorbent modification with iron to evaluate its arsenate sorption capacity. This modification of the biosorbent was carried out by the following procedure: 5 g of guava seeds were put in contact with 60 mL of FeCl<sub>3</sub> 0.3% (w/v) solution at 25 °C for 24 h, with an agitation speed of 90 rpm. Then, the modified guava seeds with FeCl<sub>3</sub> (FeGS) were filtered and washed with deionized water to eliminate any excess iron and chloride ions from the material. The FeGS was allowed to dry, and the modified material was stored in a desiccator for further experiments.

### 2.2. Scanning electron microscopy (SEM)

Samples of GS, FeGS, and arsenic-loaded FeGS (As-FeGS) were covered with copper and analyzed using a JSPM-5200 scanning electron microscope and a JEOL JSM-7600F FEG-SEM microanalysis detector in order to observe the surface morphology of the samples and obtain the semi-quantitative elemental analysis.

### 2.3. Fourier transform infrared spectroscopy (FTIR)

FTIR analyses were carried out on GS, FeGS, and As-FeGS. For the measurement, 0.3 g of dry KBr was mixed with 0.02 g of each biosorbent 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<sup>-1</sup>.

#### **2.4. Kinetic experiments**

Batch-type experiments were performed to determine the kinetics of arsenate removal with FeGS. 10 mL aliquots of a 2 mg/L Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O solution and 0.2 g of FeGS were placed in centrifuge tubes and shaken for different periods at a fixed temperature (25°C). Later, the samples were centrifuged and filtered to separate the aqueous phase, which was analyzed for total arsenic by an atomic absorption spectrometer with a hydride generation system (AAS). The quantity of arsenic adsorbed was deduced from the initial concentration using the following equation:

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

Where q is the measured sorption per unit weight of solid, V is the volume of solution, C<sub>0</sub> and C<sub>e</sub> are the initial and equilibrium concentrations of arsenic, respectively, and M is the dry weight of biosorbent. All sorption experiments were performed three times to ascertain the reproducibility of the results, and mean values were considered. Blank experiments showed no detectable As(V) adsorbed on the walls of the centrifuge tubes.

#### **2.5. Effect of adsorbent dose**

The effect of the FeGS dose on the equilibrium adsorption of arsenate ions was studied by contacting FeGS masses from 0.1 to 1 g with 10 mL of 2 mg/L Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O solution using an orbital shaker at a fixed temperature (25 °C). The flasks were shaken at 120 rpm until equilibrium was reached. The arsenate concentrations in the supernatants were determined as mentioned above. The experiments were performed in triplicate to determine reproducibility.

#### **2.6. Adsorption Isotherms**

Adsorption isotherms were obtained using a batch equilibrium method; 10 mL aliquots of different concentrations of Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O solutions (ranging from 20 to 500 mmol/L) were put in contact with 1 g of FeGS in centrifuge tubes. The tubes were placed in a shaker bath at a constant temperature until equilibrium was attained. Moreover, the samples were centrifuged and filtered. The supernatants were analyzed for arsenic by AAS, as described above.

#### **2.7. Fixed-bed experiments**

The arsenate uptake was conducted in three 15 cm long glass columns of 4 cm internal diameter. For each column system, 65 g of FeGS was carefully added to prevent air entrapment in the bed. The bed portion of the column was 15 cm high. Perforated polyethylene plates at the bottom and top of the columns helped to support the adsorbent and distribute the solutions uniformly. 4 and 20 mg/L Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O solutions (pH 7) were pumped through the columns in an upward flow mode by using peristaltic pump [13]. The studied flow rates entering the columns were 10 and 20 mL/min, and they were checked periodically by collecting samples at the outlet to ensure the system's proper operation. Liquid samples were withdrawn at the top of each column at different time intervals, from 5 min at the beginning of the operation (for the first column) to every 15 or 30 min at further stages of the sorption process. As mentioned above, arsenic was analyzed in the samples by atomic absorption spectroscopy. The breakthrough curves were obtained by plotting the ratio (C/C<sub>0</sub>) vs. time.

### **III. RESULTS AND DISCUSSION**

#### **3.1. Scanning electron microscopy (SEM)**

Surface characterization by SEM was performed in order to determine the morphology of GS, FeGS, and As-FeGs. SEM images were analyzed to determine the differences in their surface properties and structures due to the modification process with iron. For the case of GS (Figure 1), most of the sample has a smooth surface, small pores, and some particles adhering to the sample. In an elemental analysis of the samples, the main elements are those expected for this type of material, and also, a small amount of Fe is present in the sample. Rough surface morphology is observed in the FeGS sample (Figure 2). Small pores are also present in this type of biosorbent. These sites are essential because the pores increase the surface area and, thus, the arsenate adsorption capacity.

Furthermore, the clad of fibers due to chemical modification indicates the degradation of cells [14]. Moreover, an elemental microanalysis was performed on a small area of a FeGS sample, where the flat smooth surface (point 1) is located (Figure 2). The results showed that regardless of the morphological characteristics of the surface in the biosorbent, a certain percentage of iron adhered during the modification process. Some of

these areas have high or low concentrations of the analyzed elements due to the diversity of functional groups in the two types of surfaces.

An elementary analysis (mapping) consecutive to the experiments of adsorption of As(V) with the FeGS demonstrates that the arsenic is deposited homogeneously on the surface of the biosorbent (Figure 3). This fact suggests that As(V) ions are adsorbed by functional groups of GS and through adsorbate interactions with Fe species formed on the surface of the adsorbent.

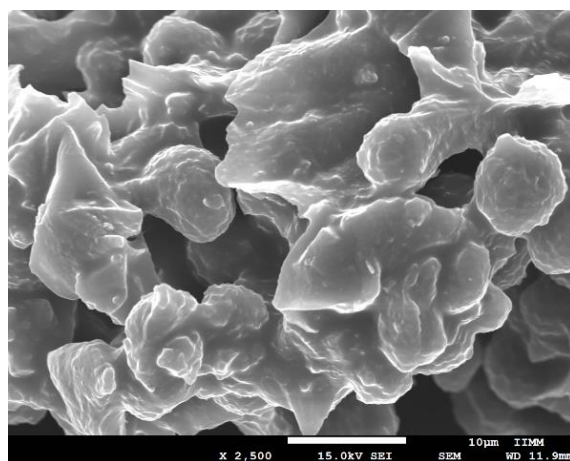


Figure 1. SEM analysis of GS observed at 2500x.

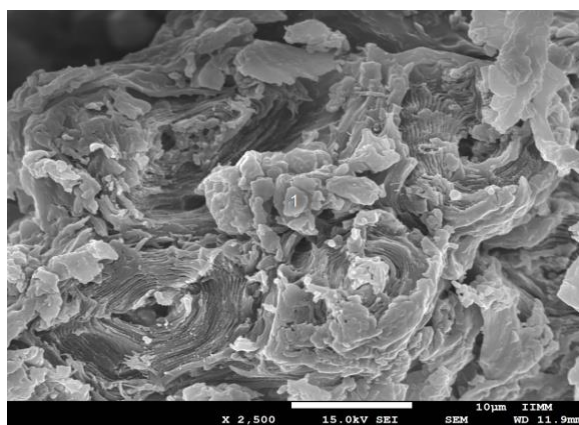


Figure 2. SEM analysis of FeGS samples observed at 2500x.

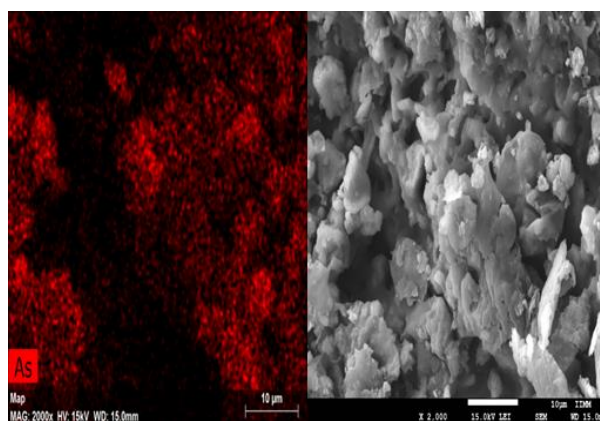


Figure 3. Elemental analysis (mapping) of As(V) adsorption with the FeGS.

### 3.2. Fourier transform infrared spectroscopy (FTIR)

The FTIR results for the GS, FeGS, and As-FeGS, before and after the adsorption of arsenate ions, are shown in Figure 4. The intensity of and shifts in the transmittance bands in the FTIR spectrum were directly

related to changes in the molecules of the various GS samples (Figure 4a). 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  $\text{cm}^{-1}$  region were associated with amines ( $\text{NH}_2$ ) and hydroxyl groups (OH). This study observed high-intensity broad absorption bands at 3382 and 3370  $\text{cm}^{-1}$  caused by the bonded OH stretch in lignin, cellulose, hemicelluloses, pectin, and sugars. Differences in transmittance before and after treatment with arsenate solutions (Figure 4b) suggest that these groups could be involved in Fe biosorption before  $\text{As(V)}$  removal. Also, bands found at 2926, 2924, 2856, 2857, 1382, and 1377  $\text{cm}^{-1}$  are associated with CH stretch related to alkanes groups from cellulose, hemicelluloses, and lignin. This study also observed the Carbonyl ( $\text{C=O}$ ) group at 1745 and 1742  $\text{cm}^{-1}$  bands before and after  $\text{As}$  adsorption, respectively (Figure 4b). These bands are associated with aldehydes and ketones from simple and complex carbohydrates and esterified carboxylic acids from pectin, hemicelluloses, and lignin [15]. The bands that appeared in the 1540 and 1400  $\text{cm}^{-1}$  region might be attributed to the presence of quinone and OH bonds. Moreover, the band observed at 1165  $\text{cm}^{-1}$  before adsorption was attributed to C-O asymmetrical stretching of hydroxyl groups from primary alcohols related to phenolic compounds present in lignin. Furthermore, FTIR results indicated that mainly hydrogen atoms in the carboxylic groups were involved in iron and subsequent arsenate adsorption (Figure 4b).

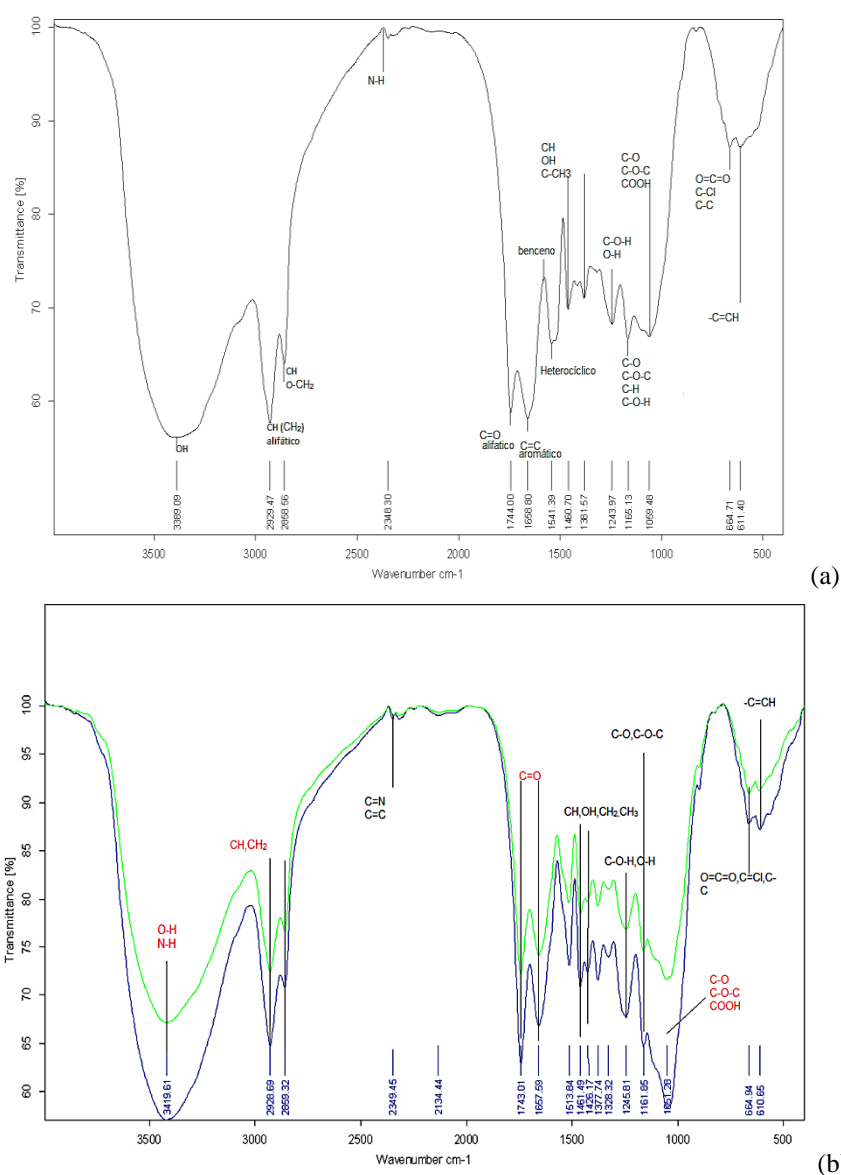


Figure 4. FTIR spectra from: a) GS samples; and b) FeGS samples (green line) and As-FeGS samples (blue line).

### 3.3. Kinetic experiments

As(V) adsorption onto GS and FeGS as a function of contact time was investigated. GS showed no significant arsenate removal (data not shown). Therefore, only FeGS kinetic adsorption data are discussed. Figure 5 shows the results obtained from adsorption kinetics experiments with FeGS. According to this plot, the arsenate removal by FeGS was characterized by a fast increase in arsenate adsorption in the first minutes of contact, where arsenate removal occurred almost instantly after the arsenate solution was in contact with the biosorbent. After this stage, the As(V) uptake rate was reduced as equilibrium approached.

Furthermore, it can be observed that the percentage of arsenate removed in the experiment with FeGS was approximately 90%. After 120 min of contact, significant changes were no longer observed in arsenic concentration, indicating that sorption equilibrium was reached; as a result, this time was chosen for further adsorption experiments. These results suggest that the modification with iron does not significantly affect the kinetics of arsenate removal by guava seeds; however, it does positively affect the quantity of arsenate removed, also suggesting that this modification could enhance arsenate adsorption onto iron-modified guava seeds.

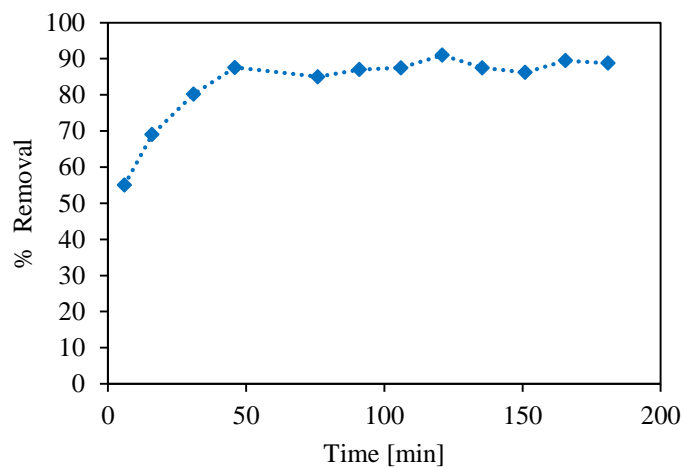


Figure 5. Arsenate adsorption from aqueous solution by FeGS as a function of time.

Arsenate adsorption kinetic data were fitted, by nonlinear regression analyses, to different empirical models such as the pseudo-first-order model, the pseudo-second-order model, and the Elovich equation to study the effect of contact time of As(V) adsorption and to determine kinetic constants from this models. The following equations can express these models:

Lagergren [16] proposed a first-order rate equation to describe adsorption kinetic processes. It is described as:

$$q_t = q_e[1 - \exp(-K_L t)] \quad (2)$$

Where  $q_e$  and  $q_t$  (mg/g) are the adsorption capacities at equilibrium and time,  $t$  (min), respectively.  $K_L$  ( $\text{min}^{-1}$ ) is the pseudo-first-order rate constant for the kinetic model.

Elovich equation has been usually reported for chemisorption of gases on solids. This equation can be expressed as follows:

$$q_t = 1/\beta \ln(1 + \alpha \beta t) \quad (3)$$

Where  $q_t$  represents the amount of gas adsorbed at time  $t$ ,  $\beta$  is the desorption constant, and  $\alpha$  the initial adsorption rate [17].

The pseudo-second-order kinetic model [18] can be described on its nonlinear form as:

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (4)$$

Where  $q_t$  (mg/g) and  $q_e$  (mg/g) are the amounts of metal ion adsorbed at time  $t$  and at equilibrium, respectively, and  $K_2$  is the rate constant  $\text{g}/(\text{mg} \cdot \text{min})$ .

Table 1 shows the arsenate adsorption kinetic parameters of the empirical models. It has been found that the pseudo-second-order model is the model that best describes As(V) adsorption onto FeGS, according to the correlation coefficient obtained from the regression ( $R=0.977$ ). This fact suggests that As(V)-FeGS adsorption system presents chemisorption on the surface of the adsorbent, which supports the FTIR results that indicated a strong interaction between arsenate and hydroxyl and carboxyl groups on the surface of FeGS. As(V) sorption kinetics is relatively fast since almost 90% of adsorption occurs in the first 50 min of contact, this indicates that FeGs can be used in continuous adsorption systems and could perform well.

Table 1. Model parameters of arsenate adsorption on FeGS.

Model		
Lagergren	Pseudo-second-order	Elovich
$K_L(\text{min}^{-1}) = 0.1640$	$K_2 (\text{g/mg}\cdot\text{min})=0.059$	$\alpha\beta(\text{mg}/\text{min})=2685$
$q_e (\text{mg}/\text{g})= 0.0359$	$q_e (\text{mg}/\text{g})=0.0751$	$\beta\gamma(\text{g}/\text{mg})=0.59$
$R= 0.9040$	$R = 0.9770$	$R= 0.9360$

### 3.4. Effect of biosorbent dose

The adsorbent dose is also an important parameter owing to its effect on adsorption efficiency and the amount of arsenate adsorbed per unit weight of biomass ( $q_t$ ). It was found that As(V) removal increases as the adsorbent dose increases until 1 g of FeGS is reached (Figure 7). It is known that adsorption increases at low doses ( $<0.4$  g) because all types of active sites had been saturated due to monolayer formation on the sorbent surface. The slight decrease at higher FeGS doses can be attributed to the agglomeration of adsorbent particles, leading to unavailable sorption sites, although a higher surface area is present in the system. Therefore, the optimal dose for the further batch adsorption experiments was 1g in 10 mL of arsenate solution.

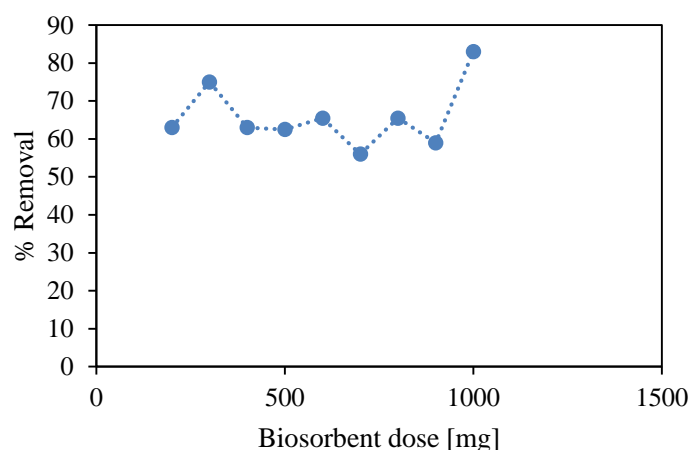


Figure 6. Effect of the adsorbent dose on the adsorption of arsenate by FeGS.

### 3.5. Adsorption isotherms

The sorption isotherm of arsenate for single solute systems using FeGS at pH 7 is shown in Figure 6. Adsorption performance by FeGS at low concentrations is significantly high, decreasing as the concentration rises. According to the Giles classification [19], arsenate sorption isotherm at pH 7 can be classified as L-type (L-1). The L-type isotherm, subgroup 1, indicates that the capacity of the theoretical monolayer does not reach saturation, and consequently, the slope is not null in the concentration interval studied. The L-type isotherms are characterized by an initially high slope that decreases as the equilibrium ion concentration increases. These types of isotherms result from a high affinity of FeGS for the adsorbate at low concentrations of As (V) and a decrease in the available surface functional groups as the solute equilibrium concentration increases [20]. This

behavior is essential for the application of FeGS adsorbent in fixed-bed systems since a strong affinity between adsorbent and adsorbate was noticed in As(V)-FeGS system, leading to a better performance of adsorbent in continuous operations. The maximum adsorption capacity obtained at these experimental conditions was 1.18 mg As/g FeGS.

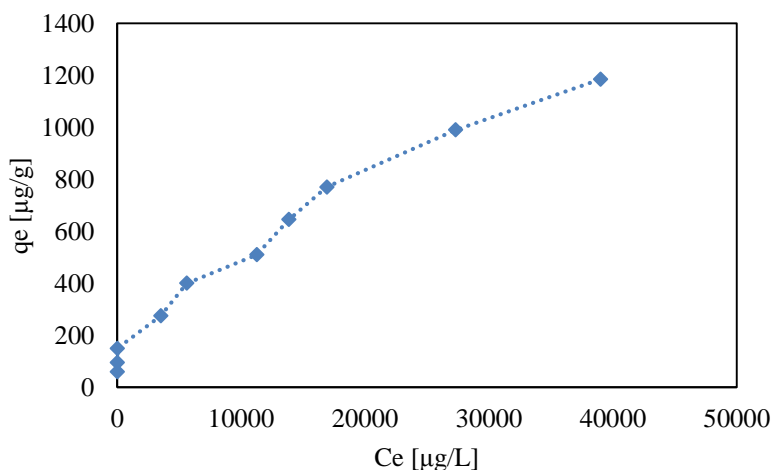


Figure 7. Sorption isotherm of arsenate on FeGS at 25 °C and pH 7.

Isotherm experimental data were fitted to the well-known isotherm models of Freundlich, Langmuir, and Langmuir-Freundlich [3] by nonlinear regression analyses (data not shown). Results showed that the Freundlich model best describes equilibrium data at these experimental conditions, according to the correlation coefficient ( $R=0.9970$ ). This fact indicates the heterogeneity of adsorption on surface functional groups present on the surface of FeGS. This fact also suggests that different arsenate mechanisms could happen in this adsorption system due to the interaction of adsorbate ions with functional groups related to fiber compounds of adsorbents as well as to those groups related to iron oxyhydroxides that could have been formed on the surface of adsorbent due to FeCl<sub>3</sub> modification.

A comparative analysis of arsenate sorption capacities in batch systems of different iron-modified biosorbents and other types of adsorbents is presented in Table 2. It can be observed that FeGS has a significantly higher sorption capacity (1.18 mg/g) compared to iron-modified adsorbents, except for sawdust. Compared to nano-adsorbents, FeGS has a lower but comparable sorption capacity; this could be attributed to the significantly higher surface area of nano-adsorbents; however, FeGSs are an excellent low-cost alternative for the removal of arsenates from aqueous solutions.

Table 2. Comparative analysis of As(V) adsorption capacities of various adsorbents.

Biosorbent	As(V) adsorption capacity (mg/g)	Reference
Iron-modified sawdust	12.85	[3]
Natural rock-iron oxide	0.04	[21]
Zeolite-FeCl <sub>3</sub> -NaCl 0.1M	0.0092	[22]
Zeolite- FeCl <sub>3</sub> - NaCl 0.01M	0.0084	[22]
Iron-modified lemon residues	0.474	[23]
nanochitosan	13.0	[24]
Iron oxide coated single-wall carbon nanotubes	49.65	[25]
Iron-modified guava seeds	1.18	This work.

### 3.6. Fixed-bed experiments

Fixed-bed column experiments were carried out to determine the sorption dynamic behavior of FeGS as well as the influence of some operational parameters of the continuous system, such as inlet concentration and flow velocity. Figures 8 and 9 show the breakthrough curves ( $C/C_0$  vs. time) for the sorption of arsenate using FeGS at different initial solution concentrations. For the case of 20 mg/L inlet arsenate concentration



(Figure 8), it can be observed similar behavior in each curve and a tendency to follow an “S” shape which is characteristic of ideal sorption in column systems; this behavior is typical of sorbents with a small molecular diameter and simple structure [26]. Furthermore, the concentration of the effluent from the first column (Z= 15 cm) increases faster than the concentration in the effluent from the third column, and therefore the S shape of the curves is more notorious in the third column (Z=45 cm) than in the first. This behavior is similar to the one observed using FeGS at a higher concentration (20 mg/L), Figure 9; however, the efficiency is lower at higher concentrations since the service and rupture times are lower under the same experimental conditions. Consequently, larger volumes of As(V) polluted solutions can be treated, particularly at low levels of arsenate in a continuous system [13].

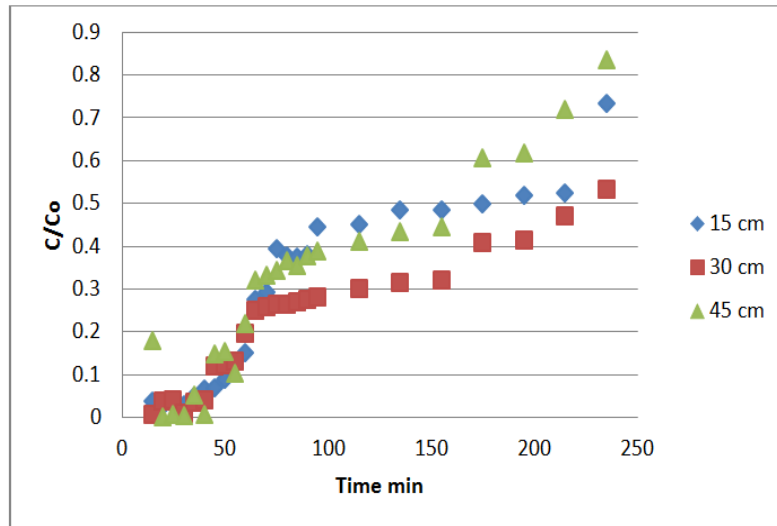


Figure 8. Breakthrough curves for arsenate using packed columns of FeGS at 4 mg/L inlet concentration (pH = 7, flow rate=10mL/min).

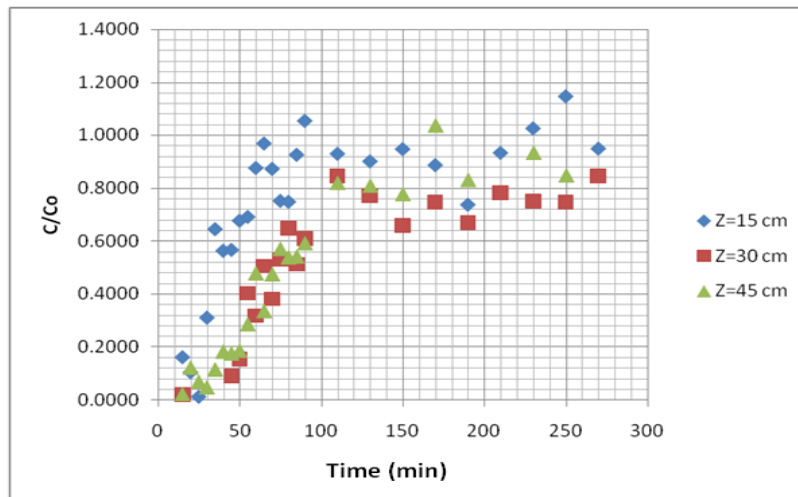


Figure 9. Breakthrough curves for arsenate using packed columns of FeGS at 20 mg/L inlet concentration (pH = 7, flow rate=10mL/min).

The sorption capacity of the bed was calculated using the following expression [13]:

$$q_b = \frac{Q_v t_{10\%} C_0}{m_c} \quad (5)$$

where,

$q_b$  = quantity of the adsorbed solute in the breakpoint (mg/g adsorbent)

$t_{10\%}$  = service time (minutes) considered when the concentration of the effluent reached 10 % of the concentration of the influent.

$C_0$  = concentration of arsenate in the influent (mg/L)

$Q_v$  = flow of the influent (L/min)

$m_c$  = mass of the adsorbent (g)

Tables 2 and 3 show the fixed-bed capacities ( $q_b$ ) for FeGS at different inlet concentrations, 4 and 20 mg/L, respectively. The selected breakpoint ( $C_b$ ) for these experiments was 10%. The capacity of the column series at 20 mg/L ( $q_b = 0.0880$  mg As/g FeGS) is lower than the maximum sorption capacity determined in the batch experiments (1.184 mg As/g FeGS), the efficiency was only 6.7 % of the maximum efficiency determined in the batch system. The same behavior was observed for the column system at 4 mg/L,  $q_b = 0.0294$  mg As/g FeGS, which is lower than the maximum sorption capacity determined in batch, the capacity in the column system was about 1.7% compared to the batch system. Low et al. [27] reported that the sorption in column systems does not reach equilibrium. Therefore, the flow may only allow the necessary time to distribute the arsenate ions in some sorption sites of the zeolitic materials, and for this reason, the sorption capacities decreased in column systems compared to batch systems. It is important to note that the sorption efficiencies in column systems depend on the flow of the influent solution. However, the efficiencies for the sorption of arsenate in column systems using FeGS are relatively high. According to  $q_b$  values (Tables 3 and 4), the sorption capacity of arsenate is higher for 20 mg/L inlet concentration than for 4 mg/L inlet concentration. However, the column's service time ( $t_{10\%}$ ) is significantly higher for a lower inlet concentration, providing significantly higher water-treated volumes ( $V_b$ ). The obtained value of service time ( $t_{10\%}$ ) for low inlet concentration is crucial since it provides a great perspective of applying the adsorbent once the system can be scaled up to continuous operations of arsenate-polluted water treatment.

Table 3. Fixed-bed sorption capacity ( $q_b$ ) and service time ( $t_{10\%}$ ) of FeGS for As(V) adsorption in fixed-bed columns ( $C_0 = 4$  mg/L,  $Q_v = 0.01$  L/min,  $C_b = 10\% C_0$ ).

Height (cm)	$m_c$ (g)	$V_b$ (mL)	$t_{10\%}$ (min)	$q_b$ (mg/g)
15	65	124.4	42.26	0.0260
30	130	3171	74.31	0.0228
45	195	4067.4	143.76	0.0294

Table 4. Fixed-bed sorption capacity ( $q_b$ ) and service time ( $t_{10\%}$ ) of FeGS for As(V) adsorption in fixed-bed columns ( $C_0 = 20$  mg/L,  $Q_v = 0.01$  L/min,  $C_b = 10\% C_0$ ).

Height (cm)	$m_c$ (g)	$V_b$ (mL)	$t_{10\%}$ (min)	$q_b$ (mg/g)
15	65	422.6	19.24	0.0592
30	130	743.1	60.32	0.0928
45	195	1437.6	86.54	0.0880

On the other hand, the influence of inlet flow velocity was examined for low arsenate inlet concentration. An experiment with 4 mg/L inlet concentration and 20 mL/min flow rate was conducted to compare the results with those obtained at 10 mL/min at the same As(V) concentration. Breakthrough curves for this experiment are shown in Figure 10, and the values of fixed-bed sorption capacity and column service time are presented in Table 5. For this case, in which the flow of the column was increased to 20 mL/min, it is observed that the "S" shape in the curves is less evident, although they still have that same tendency. The fixed-bed adsorption capacity for this case was  $q_b = 0.00929$  mg/g. As expected, the first column ( $Z = 15$  cm) saturates much faster than the other two ( $Z = 30$  and 45 cm); however, the removal percentages found for this case were high even in the last minutes of operation of the columns, which lengthens the service time of the column system. Compared to the experiment at a lower flow (10 mL/min), the service time and, therefore, the efficiency of the column increase. Contrary to the expected, it can be established that the system responds well to a rise in the flow velocity, which is an excellent operational parameter for this type of adsorbent in fixed beds.

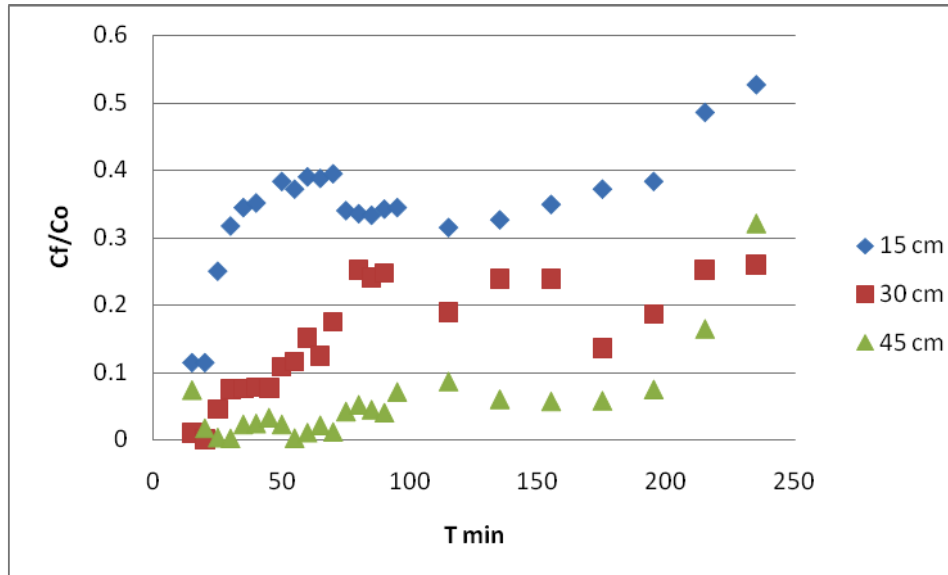


Figure 10. Breakthrough curves for arsenate using packed columns of FeGS at 4 mg/L inlet concentration (pH = 7, flow rate=20mL/min).

Table 5. Fixed-bed sorption capacity ( $q_b$ ) and service time ( $t_{10\%}$ ) of FeGS for As(V) adsorption in fixed-bed columns ( $C_0 = 4$  mg/L,  $Q_v = 0.02$  L/min,  $C_b = 10\% C_0$ ).

Height (cm)	$m_c$ (g)	$V_b$ (mL)	$t_{10\%}$ (min)	$q_b$ (mg/g)
15	65	124.4	6.22	0.000729
30	130	317.1	158.55	0.00794
45	195	4067.4	203.37	0.00929

#### Application of the BDST model

In the design of column systems, the main objective is to determine the service time until the effluent has a concentration higher than the predetermined limit. The Bed Depth Service Time (BDST) method relates the service time of a fixed bed with the bed height of the adsorbent material in the column. This model is one of the most used in the design of systems for the treatment of water. The equation that describes the BDST model is the following [13]:

$$t = \frac{N_0}{c_0 u} \left[ Z - \frac{u}{k N_0} \ln \left( \frac{c_0}{c_b} - 1 \right) \right] \quad (6)$$

Where  $t$  is the service time (min),  $u$  is the linear rate of the influent (cm/min),  $Z$  is the bed height (cm),  $k$  is the rate constant of sorption (L/mg.min),  $N_0$  is the total capacity of the column (mg/L),  $C_0$  is the influent concentration (mg/L) and  $C_b$  is the influent concentration in the breakthrough point (mg/L).

At 50 % of the saturation or  $C/C_0 = 0.5$ , the ratio  $C_0/C_b = 2$ , the logarithm part of Eq. 6 is reduced to zero, and the equation has a linear relation. Therefore, a plot of the model is a straight line that passes through the origin (only at 50 % of the saturation), the shape of the breakthrough curves has a form of an “S,” and they are symmetric at the 50 % of the saturation, and it can be said that the sorption data follow the BDST model [28, 29]. The data of Table 6 show the dynamic arsenate sorption capacity  $N_0 = 4.97$  mg/L at 20 mg/L inlet concentration at a flow rate of 10 mL/min using FeGS as adsorbent. This value can be considered relatively high since inlet concentration is also very high. However, at  $N_0$  decreases significantly when the flow rate increases to 20 mL/min at the same arsenate concentration; this could be attributed to a broadening of the mass transfer zone when linear velocity in the column rises.

Table 6. BDST parameters for arsenate sorption by FeGS at different flow rates ( $C_0=20$  mg/L, pH=7).

Flow rate	t (min)	$N_0$ (mg/L)	K (L/mgh)	$Z_0$ (cm)	$q_b$ (mg/g)
10 mL/min	86.54	4.97	0.09	3.92	0.088
20 mL/min	148.66	2.921	0.162	3.361	0.0037

Dynamic adsorption capacities ( $N_0$ ) for column systems at 4 mg/L arsenate inlet concentrations are shown in Table 7. It can be observed that  $N_0$  increases significantly when the flow rate rises. This fact means that, despite the correspondent broadening of the mass transfer zone due to an increase in linear velocity in the column, the column system supports well such an increase in flow rate. This behavior is closely related to the suitable kinetic and equilibrium parameters shown by FeGS in batch systems, as well as to the low inlet concentration in the system. This behavior represents a good first operational parameter for FeGS application in removing As(V) ions from polluted waters at relatively large volumes.

Table 7. BDST parameters for arsenate sorption by FeGS at different flow rates ( $C_0=4$  mg/L, pH=7).

Flow rate	t (min)	$N_0$ (mg/L)	K (L/mgh)	$Z_0$ (cm)	$q_b$ (mg/g)
10 mL/min	143.76	2.96	0.138	4.27	0.00324
20 mL/min	203.37	9.94	0.239	0.679	0.00807

#### IV. CONCLUSIONS

In general, guava seeds have desirable properties for the adsorption of arsenates from aqueous solutions, which are significantly enhanced by modifying their surface with iron compounds. The experimental isotherm data was classified as an L-Type, involving high affinity of the adsorbent for As(V) ions. These results also indicate that the mechanism involved in the As(V) adsorption in the iron-modified guava seeds is related to chemisorption on heterogeneous surfaces. This adsorbent showed excellent dynamic behavior in fixed-bed column systems for removing arsenate from aqueous solution, particularly at a high flow rate and relatively low Arsenate concentrations. Thus, it can be considered a novel and low-cost adsorbent with the potential for use in the decontamination of arsenic-polluted waters.

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