



Agave lechuguilla waste can be applied as biochar-adsorbent to remove arsenic from water

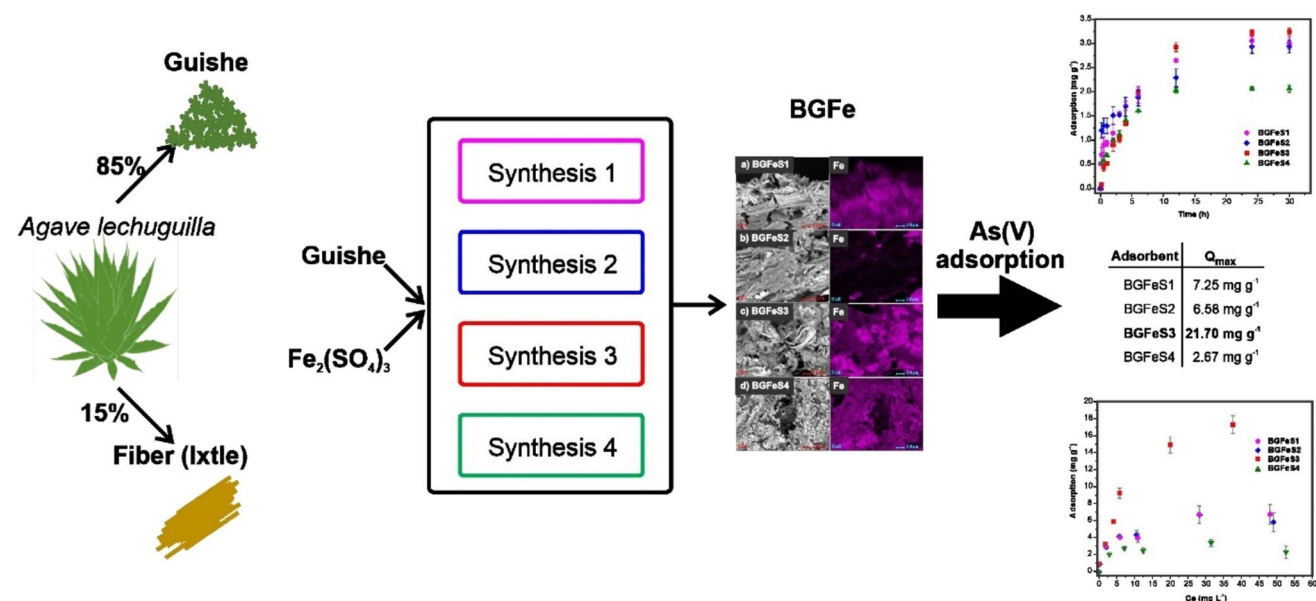
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Abstract

Fiber extraction from *Agave lechuguilla* generates approximately 150,000 tons of guishe, a byproduct currently lacking significant commercial value. The production of efficient and inexpensive biochar-adsorbents from guishe can potentially solve the issue of arsenic-contaminated groundwater in Mexico, particularly in arid and semi-arid regions. In this report, the synthesis of four iron-modified guishe biochars was presented. The adsorbents were characterized using various techniques, and their performance as an adsorbent for arsenate was assessed by examining the impact of pH, kinetics, and adsorption isotherms. The findings suggest that all biochars can effectively remove arsenic from aqueous solutions. According to the Langmuir model, the maximum adsorption capacity of arsenic on iron-modified guishe biochar ranged from 2.67 to 21.70 mg g⁻¹. The utilization of these adsorbents presents a potential alternative solution to the issue of arsenic-contaminated water. Moreover, synthesizing these adsorbents involves using local waste material, representing a cost-effective and sustainable approach to waste management.

Graphical abstract



Keywords Guishe · Biomass waste · Heavy metal removal · Water remediation · Langmuir model

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Introduction

Ixtle extraction from *Agave lechuguilla* is a significant economic activity for rural communities in arid and semi-arid zones of Mexico. *A. lechuguilla* is a succulent plant that wildly grows in some Mexican states (San Luis Potosí, Coahuila, Nuevo León, Zacatecas, Durango, and Tamaulipas) (Kalan Kash 2009; Díaz-Jiménez et al. 2019). However, the National Institute of Agricultural and Livestock Forestry Research (INIFAP) has proposed strategies to enhance the productivity of this plant by implementing systematic cultivation (Castillo-Quiroz, Cano-Pineda and Berlanga-Reyes, 2012). While obtaining the ixtle, a juicy and fibrous residue (guishe) is generated, burned, or thrown in the open field, leading to contamination and health problems (Díaz-Jiménez et al. 2019). Considering that for every ton of ixtle, 5.66 tons of guishe are produced, the generation of guishe reaches 150,000 tons annually (Castillo-Quiroz, Cano-Pineda and Berlanga-Reyes, 2012; Díaz-Jiménez et al. 2019); however, this amount is anticipated to rise five or seven times or 750,000 to 1,050,000 tons annually with the systematization of cultivation.

On the other side, it should be noted that groundwater is the only permanent source of water supply in Mexico's arid and semi-arid zones, where high concentrations of As have been detected. Osuna-Martínez et al. (2021) report that the groundwater with the highest As concentration in Mexico is found in San Luis Potosí (60 mg L^{-1}). High concentrations of As have also been detected in drinking water in Coahuila (0.408 mg L^{-1}), Durango (0.194 mg L^{-1}), San Luis Potosí (0.169 mg L^{-1}), Hidalgo (0.069 mg L^{-1}) and Chihuahua (0.052 mg L^{-1}) (Osuna-Martínez et al. 2021). It is estimated that 8.81 million Mexicans are exposed to water contaminated by As with a concentration above 0.010 mg L^{-1} (Alarcón-Herrera et al. 2020). Furthermore, crops cultivated using water with elevated arsenic levels will possess this toxic element. Extended exposure to elevated amounts of As can lead to the development of cancer in various organs and tissues, particularly the skin, bladder, liver, lung, and kidney (Armienta and Segovia 2008). In the arid states of northern and central Mexico, 13,070 new cases of cancer-related to As contamination is expected (Alarcón-Herrera et al. 2020).

Several methods can tackle this issue, including adsorption, electrocoagulation, filtration, ion exchange, or chemical precipitation. Adsorption is notable for its simplicity in operation and maintenance and its high efficiency, primarily due to the abundance of adsorbents (Yadav et al. 2021, 2022). Given the urgency of addressing the issue of As contamination in Mexico's water, it is imperative

to implement solutions using locally abundant resources, such as guishe. This material is a lignocellulosic residue with physicochemical characteristics that make it appropriate for generating adsorbents. Alcazar-Medina et al. (2014) used guishe extracts to remove Cu(II) in an aqueous solution by spherical agglomeration. This study found that guishe extracts have greater removal effectiveness for Cu(II) than sodium oleate. Romero-González et al. (2006) utilized guishe as an adsorbent for Cr(III). They proposed that Cr(III) is adsorbed through the carboxyl groups found on the surface of the guishe. Furthermore, Díaz et al. (2019) suggest utilizing existing market technologies to produce biochar using a biorefinery technique. This biochar can then be employed as an adsorbent.

Biochar is an up-and-coming alternative to conventional adsorbents since it is inexpensive, has a large surface area, contains many surface functional groups, and can be obtained from abundant biomass (Hassan et al. 2020; Kamali et al. 2021). However, pristine biochar exhibits a deficient performance in terms of As removal. Nevertheless, utilizing biochar as a support makes using all the above attributes feasible. Several investigations have focused on producing composite materials based on biochar and transition metals (Fe, Mn, Zn, Co, Ni, among others) in metallic or oxide form (Srivastav et al. 2022; Zhang et al. 2022). However, iron (Fe) exhibits a more remarkable ability to remove As, possesses minimal toxicity, is cost-effective, and is more readily accessible (Li et al. 2021a; Shaheen et al. 2022; Zhang et al. 2022). The incorporation of Fe or iron salts on the biochar surface can be done by different synthesis methods, including pre- or post-pyrolysis treatments and co-pyrolysis (Hassan et al. 2020; Li et al. 2021b). Through these methods, iron-modified biochars have been synthesized from corn straw (He et al. 2018), switchgrass (Bakshi et al. 2018), and rice straw (Nguyen et al. 2019; Nham et al. 2019), which have been applied to As adsorption. All of these residues possess a composition that resembles that of guishe, suggesting the possibility of using guishe biochar to produce an adsorbent modified with iron.

The main objective of this study was to produce iron-modified biochars using guishe as raw material and to analyze the impact of the synthesis method on the physicochemical properties and, consequently, the performance as an As(V) adsorbent. This approach provides a solution to address the issue of arsenic contamination in water and waste within the same application areas of the adsorbents. The performance of iron-modified guishe biochars was evaluated by studying the effect of pH, kinetics, and adsorption isotherm. This study was conducted at Cinvestav-Unidad Saltillo (Ramos Arizpe, Mexico) during 2023.



Materials and methods

Materials

The guishe was collected from the ixtle production area of Ramos Arizpe, Coahuila, Mexico (25°51'40"N, 101°16'31"W). This material was dried at room temperature for one week. It was then ground in a blade mill (Restch SM100, Han, Germany) and sieved to obtain a homogeneous particle size. The fraction retained between meshes No. 20 and 40 synthesized the adsorbents. The reagents used in this study were analytical or reagent grade and supplied by Sigma Aldrich (except NaOH). NaOH (99%) was Jalmek brand. The solutions used in the adsorption experiments were prepared from a stock solution with an As(V) concentration of 1000 mg L⁻¹, which was made from Na₂HAsO₄ 7H₂O (Sigma Aldrich, ≥ 98%) and distilled water. 0.1 M HCl and 0.1 M NaOH were used to adjust the pH of the solutions.

Synthesis of iron-modified guishe biochars (BGFe)

Four guishe biochars were produced using different methods to modify them with iron. The objective was to investigate the effect of the synthesis method on the adsorption capacity of the biochar (Fig. 1). A mass ratio of 0.18 Fe:guishe (or biochar) was used in all methods. The biochars were identified as BGFeSX, where X indicates the synthesis method.

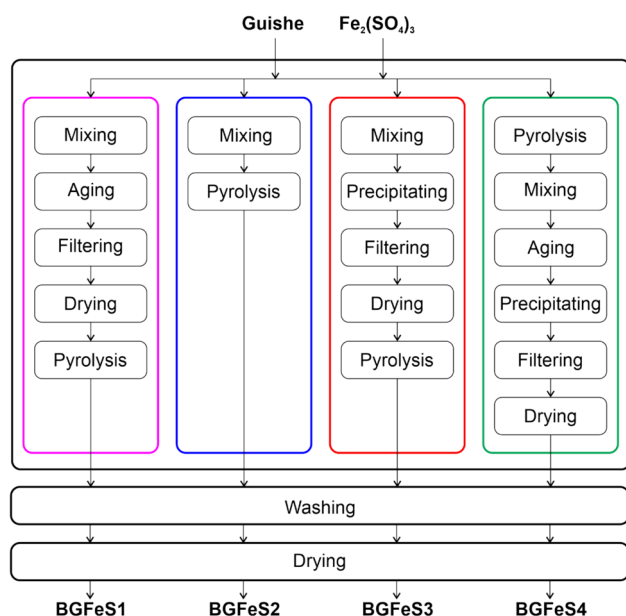


Fig. 1 Diagram of the synthesis of BGFe using different methods

Preparation of BGFeS1

The synthesis of the BGFeS1 adsorbent was carried out according to the previously reported method (Zhu et al. 2014; He et al. 2018), with some modifications. Firstly, 6.4 g Fe₂(SO₄)₃ were dissolved in deionized water to prepare 100 mL of 0.16 M Fe₂(SO₄)₃. Subsequently, 10 g guishe were submerged into a 0.16 M Fe₂(SO₄)₃ solution and stirred at 500 rpm for 30 min. After this time, the mixture was covered and aged at room temperature for 24 h. Afterward, the solids were separated by filtration, dried at 120 °C for 2 h, and then subjected to slow pyrolysis.

Preparation of BGFeS2

The co-pyrolysis of guishe and Fe₂(SO₄)₃ was performed by adapting the method described in (Bakshi et al. 2018). Briefly, 10 g of guishe and 6.4 g of Fe₂(SO₄)₃ were mixed mechanically until a homogeneous mixture of solids was achieved. Subsequently, the mixture was introduced into the tube oven to undergo a slow pyrolysis.

Preparation of BGFeS3

The BGFeS3 adsorbent was synthesized using a previously described method (Wu et al. 2018) with some modifications. Initially, a solution was prepared by dissolving 6.4 g Fe₂(SO₄)₃ in deionized water to prepare 200 mL with a 0.08 M Fe₂(SO₄)₃ concentration. After that, 10 g guishe were submerged into 0.08 M Fe₂(SO₄)₃ solution and stirred at 300 rpm for 1 h. Subsequently, a 5 M NaOH solution was added dropwise until the pH reached 10, and then the solution was stirred for an additional hour. After this time, the solids were filtered and dried at 120 °C for 4 h. A process of slow pyrolysis followed this.

Preparation of BGFeS4

The BGFeS4 adsorbent was synthesized following a reported method (Navarathna et al. 2019) considering the next modifications. In brief, slow pyrolysis initially generated guishe biochar (BG). Afterward, 10 g of BG was placed into 200 mL of a 0.08 M Fe₂(SO₄)₃ solution. The mixture was then stirred at room temperature for 24 h at 120 rpm. Subsequently, a 5 M NaOH solution was added dropwise until the pH reached 10. The solution was then stirred for an additional hour. After this time, the solids were separated using filtration and subsequently dried at 120 °C for 4 h.

The synthesis of BGFe involved a slow pyrolysis stage in a horizontal tubular furnace equipped with a quartz reactor (Vichi HT-1100). The temperature for pyrolysis was set to 700 °C with a heating ramp of 6 °C per minute and a residence time of 1 h under a N₂ atmosphere. Then, the reactor



was allowed to undergo a cooling process and reached a state at which point the biochar could be extracted. Afterward, the synthesized BGFe underwent many rinses with distilled water until the pH of the rinse water was an approximate pH of 7.

Biochar characterization

The elemental composition of biochar was determined using two CHNS/O analyzers (Thermo Scientific FlashSmart and LECO Corporation model CS230). The inorganic elements were determined by AA and ICP spectrometers (Thermo Scientific model ICE 3300 y Perkin Elmer model Optima 8300). FTIR spectra were obtained between 450 and 4000 cm^{-1} using an FTIR spectrometer (PIKE Technologies Inc. model Frontier FT-IR/NIR) with a diamond crystal attenuated total reflectance (ATR) accessory. The morphology and surface were analyzed by scanning electron microscopy (SEM) combined with energy dispersion spectroscopy (EDS) (Philips model XL-30 ESEM). The crystallinity of biochars was identified by X-ray diffractometry (XRD) (Malvern Panalytical model Empyrean). XRD patterns were recorded with Cu-K α radiation at 40 kV and 30 mA, over the 2θ range 10–80°. The point of zero charge PZC was determined by the immersion method (Fiol and Vil-laescusa 2009). Briefly, suspensions of adsorbent material (1.25 g) were prepared with 0.01 M NaCl solution (50 mL). The pH was adjusted to 4, 7, 9, and 11 using 0.1 M HCl and 0.1 M NaOH before adding the adsorbent material. The suspensions were agitated in an orbital incubator (Prendo, INO-650 M) at 120 rpm for 48 h at 25 °C. After this time, the pH of the supernatant liquid was measured with a pH meter (Thermo Scientific, Orion Star A211), and calculated the change in pH (ΔpH). The determination was performed twice.

Batch adsorption studies

pH effect on As adsorption

The pH effect was assessed at pH 5, 7, and 9 because As-contaminated groundwater is commonly seen within this range (Esteller et al. 2017; Pérez-Martínez et al. 2021). 25 mg of adsorbent and 25 mL of a 10 mg L^{-1} As(V) solution were placed in a 50 mL Erlenmeyer flask, which was then placed in an orbital incubator (Prendo, INO-650 M) maintained at 120 rpm and 25 °C for 24 h. 0.1 M NaOH and 0.1 M HCl solutions were used to adjust the pH. The experiment was performed three times. Once equilibrium was reached, the solution was filtered, and 2 drops of concentrated HNO_3 were added to preserve it (ASTM 2015). The remaining As (V) was determined by ICP-AES (Perkin Elmer model OPTIMA 8300).

The amount of As adsorbed was determined by the following equation:

$$q_e = (C_0 - C_e) \frac{V}{m} \quad (1)$$

where q_e is the amount of As adsorbed (mg g^{-1}) in the biochar at equilibrium; C_0 y C_e represent the initial and equilibrium concentration of As (mg L^{-1}) in solution, respectively; V (L) is the volume of the solution and m the mass of adsorbent (g).

Adsorption kinetics

The kinetic study was done by adding 125 mg of adsorbent to 125 mL of a 5 mg L^{-1} As(V) solution at pH 7. The samples were placed in an orbital incubator and agitated at 120 rpm at 25 °C. At 1, 10, 30, 60, 120, 180, 240, 360, 720, 1440, and 1800 min was taking out an aliquot to measure the remaining As(V) concentration by ICP-AES. The amount of As adsorbed was calculated by Eq. (1). Kinetic data were fitted to pseudo-first-order (PS-1, Eq. (2)), pseudo-second-order (PS-2, Eq. (3)), and Elovich (E, Eq. (4)) models.

$$q = q_e (1 - e^{-K_1 t}) \quad (2)$$

$$q = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (3)$$

$$q = \frac{1}{\beta} \ln(\alpha \beta t + 1) \quad (4)$$

where q y q_e is the adsorption capacity (mg g^{-1}) at any time and equilibrium, K_1 y K_2 are the rate constant for PS-1 (h^{-1}) y PS-2 ($\text{g mg}^{-1} \text{h}^{-1}$) models, respectively. In the E model E, α (h^{-1}) is the initial adsorption rate, and β (g mg^{-1}) is the desorption constant. While t is time (h).

Adsorption isotherms

The maximum adsorption capacity of BGFe was determined using a batch equilibration method. A 25 mg of adsorbent was added to a 50 mL Erlenmeyer flask with 25 mL of different As (V) initial concentrations (1, 5, 10, 15, 35, and 55 mg L^{-1}). The pH of the solutions was adjusted to 7 using solutions of 0.1 M NaOH and 0.1 M HCl. The experimental data were fitted to the Langmuir (5) and Freundlich (6) models.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where q_m (mg g^{-1}) is the maximum adsorption capacity and K_L (L mg^{-1}) is the ratio between the rate of adsorption and desorption.



$$q_e = K_F C_e^{1/n} \quad (6)$$

where K_F ($L^{1/n} \text{ mg}^{1-1/n} \text{ g}^{-1}$) and n are constants.

Results and discussion

Biochar characterization

Elemental composition

Elemental analysis of G, BG, and BGFe (Table 1) showed that the H/C and O/C ratios are higher in G compared to BG and BGFe. This behavior is because dehydration and decomposition reactions of organic compounds occur during pyrolysis (Xiao et al. 2018). The high concentration of Ca (6.61%) in G is proportional to the amount of calcium oxalate (CaC_2O_4) present in the *A. lechuguilla* Torrey (Figueroa-Díaz, Carlos-Hernández and Díaz-Jiménez, 2021). BG and BGFe have a higher Ca/C ratio than G due to the thermal decomposition of CaC_2O_4 to calcium compounds, such as CaCO_3 , CaO , and $\text{Ca}(\text{OH})_2$, during the pyrolysis process (Figueroa-Díaz, Carlos-Hernández and Díaz-Jiménez, 2021; González García et al. 2022). The fact that guishe biochar contains Ca from the precursor represents an advantage compared to biochar synthesized by external addition of Ca, such as those synthesized in (Wu et al. 2018).

On the other hand, the Fe concentration of BGFe is greater than BG, which suggests that the four synthesis methods performed in this research are feasible to produce Fe-modified biochar with the capacity to adsorb As. In addition, the difference in Fe and S contents among the BGFe is mainly due to the synthesis method since the same amount of $\text{Fe}_2(\text{SO}_4)_3$ was used in each one. The lower S content on BGFeS3 and BGFeS4, is an example of the effect of the synthesis method, which includes a step where the dissolved Fe is precipitated by the addition of NaOH, resulting in the formation of Na_2SO_4 . Consequently, a substantial amount of sulfur stays in solution (as SO_4^{2-}) and is eliminated during filtration.

Finally, BGFeS1, BGFeS2, and BGFeS3 have higher Fe concentration and O/C ratios than BG and BGFeS4. This

trend implies that BGFeS1, BGFeS2, and BGFeS3 could have a higher fraction of iron oxides (He et al. 2018). The iron content in biochar could be directly related to its capacity to adsorb As, as stated in different reports (Xi et al. 2021; Xu et al. 2021).

XRD

Figure 2a shows the diffractograms of BG and BGFe. The X-ray diffraction (XRD) spectrum of BG indicates the presence of calcite (CaCO_3), quartz (SiO_2), and portlandite ($\text{Ca}(\text{OH})_2$) (PDF 005–0586, 033–1161 and 044–1481, respectively). The presence of calcium compounds, such as CaCO_3 , $\text{Ca}(\text{OH})_2$, and CaO , is an inherent characteristic of guishe biochar (Figueroa-Díaz, Carlos-Hernández and Díaz-Jiménez, 2021; González García et al. 2022). It has shown that CaCO_3 can provide additional adsorption sites for As, which improves the capacity of biochar to adsorb this pollutant (Román-Ross et al. 2006; Shah et al. 2022). In addition, CaCO_3 has a buffering capacity and acts as a pH regulator (Wu et al. 2018; Xu et al. 2021). The presence of this compound in guishe biochar provides a distinct advantage over other adsorbents. This inherent characteristic may allow the use of these adsorbents in acidic conditions since CaCO_3 neutralizes the pH during the adsorption (Wu et al. 2018).

BGFeS1 and BGFeS4 show characteristic peaks of anhydrous and hydrated sulfate. BGFeS1 contains anhydrite (CaSO_4 , PDF 037–1496) and basanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, PDF 033–0310), whereas BGFeS4 comprises $\text{Ca}(\text{SO}_4)(\text{H}_2\text{O})0.5$ (PDF 01–083-0438). Both syntheses need an aging stage in which G or BG is immersed in a $\text{Fe}_2(\text{SO}_4)_3$ solution for 24 h. During this period, it is feasible that dissolved iron (Fe) was substituted with calcium (Ca) in G or BG, forming the calcium sulfates mentioned above. Calcium sulfates can remove As from water by substituting sulfate ions or co-precipitation (Chen et al. 2013; Jia et al. 2020). However, this is only possible at specific temperature and pH conditions. Chen et al. (2013) reported that using anhydrous CaSO_4 as an adsorbent can achieve 95.97% As(V) removal at pH 12.5. Jia et al. (2020) determined that As(V) ions replace sulfate ions in $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ at 95 °C and pH 7.3. Furthermore, in BGFeS1, the presence of Fe is observed in the form of hematite (Fe_2O_3) and magnetite (Fe_3O_4) (PDF 033–0664 and

Table 1 Elemental content and mass H/C, O/C, Ca/C ratios of G, BG, and, BGFe

Material	C (%)	H (%)	O (%)	N (%)	S (%)	Ca (%)	Fe (%)	H/C	O/C	Ca/C
G	34.39	4.827	32.84	1.047	0.048	6.61	0.205	0.140	0.955	0.192
BG	47.47	1.87	16.53	2.406	0.02	12.4	0.192	0.039	0.348	0.261
BGFeS1	30.54	0.889	16.79	0.573	17.5	8.09	21.03	0.029	0.550	0.265
BGFeS2	28.37	0.831	15.39	0.535	14.8	6.21	26.07	0.029	0.542	0.219
BGFeS3	30.44	1.045	15.37	0.571	3.05	7.19	33.51	0.034	0.505	0.236
BGFeS4	45.17	1.595	17.25	1.085	2.82	9.30	6.48	0.035	0.382	0.206



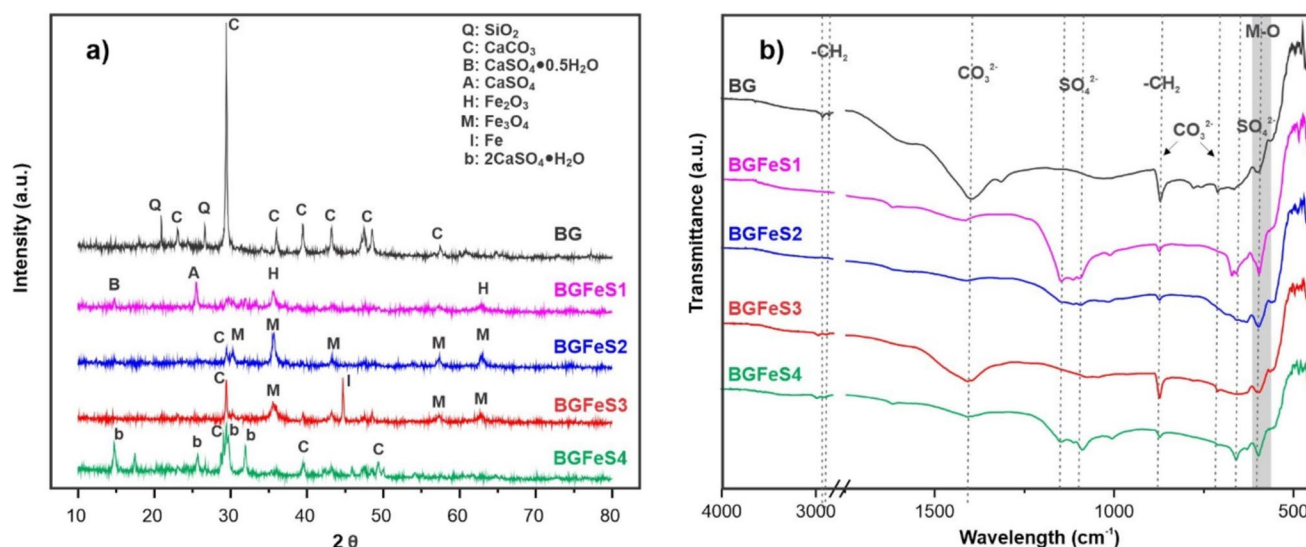
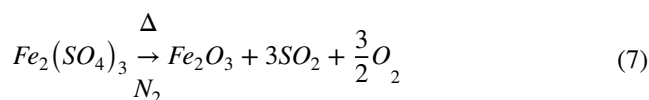


Fig. 2 **a** Diffractograms and **b** FTIR spectra of BG and BGFe

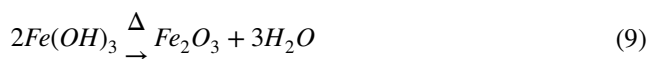
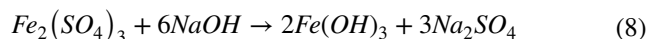
019–0629, respectively). However, in BGFeS4, no distinct crystalline phase consisting of Fe was detected. Nevertheless, BGFeS4 comprises 6% of Fe (as indicated in Table 1), which may potentially exist in amorphous forms. Fe in crystalline and amorphous forms can remove As(V) from water (Xu et al. 2021). Zhang et al. (2019b) synthesized two types of Fe-modified rice straw biochars: one containing amorphous Fe phases and the other hematite. Both types demonstrated the ability to remove As(V) from water.

On the other hand, the BGFeS2 diffractogram revealed the presence of magnetite (Fe₃O₄) and calcite (CaCO₃) using PDF 019–0629 and PDF 005–0586, respectively. The synthesis of BGFeS2 involved the dry mixing and subsequent pyrolysis of G, and Fe₂(SO₄)₃. During this procedure, G undergoes thermal decomposition through various reactions, producing biochar and gases, including CO and CH₄ (Sharma et al. 2015). Furthermore, Fe₂(SO₄)₃ undergoes thermal decomposition according to reaction (7) (Zboril et al. 2003; Petkova and Pelovski 2008). Consequently, the gases generated during pyrolysis and carbonization can cause the reduction of Fe₂O₃ to Fe₃O₄ (Zboril et al. 2003). The release of SO₂ during the synthesis of BGFeS2 could cause corrosion of the pyrolysis equipment (Ruhl and Kranzmann 2013). This aspect should be considered if this method is chosen to produce absorbents.



Finally, the XRD spectrum of BGFeS3 revealed the existence of calcite (CaCO₃, PDF 005–0586), magnetite (Fe₃O₄, PDF 019–0629), and metallic iron (Fe⁰, PDF

006–0696). The synthesis of BGFeS3 involved conducting the precipitation reaction (8) as the initial step, wherein Fe(OH)₃ was deposited onto the surface of the G. During the subsequent drying stage, this compound was transformed according to reaction (9). Ultimately, in the pyrolysis process, Fe₂O₃ experienced a reduction to Fe₃O₄ and Fe⁰.



The presence of magnetite and Fe⁰ can increase the adsorption capacity of arsenic (As) on BGFeS3. It has been shown that the adsorption of As(V) by iron oxides and metallic iron is enhanced when both are combined and supported on materials such as biochar. For example, a biochar-supported nZVI/maghemite with an As(V) adsorption capacity of 124.5 mg g⁻¹ was synthesized by Wang et al. (2017).

FTIR

Figure 2b shows the FT-IR spectra of BG and BGFe. The bands at 2919 and 2850 cm⁻¹ are associated with asymmetric and symmetric C–H stretching, of the aliphatic groups contained in biochar (Zhang et al. 2020). The band at 871 cm⁻¹ may indicate bending stresses outside the C–H plane in aromatic compounds (Chen et al. 2008; Scheller and Ulvskov 2010). Conversely, the bands seen at 1411, 871, and 718 cm⁻¹ are associated with the asymmetric stretching and bending vibrations occurring beyond the O–C–O



plane. These vibrations are specific to calcite (CaCO_3) (Hajji et al. 2017) and are more prominent in BG and BGFeS3. The bands observed at 1145 and 1090 cm^{-1} in BGFeS1 and BGFeS4 can be attributed to the asymmetric and symmetric vibrations resulting from the stretching of the SO_4 tetrahedrons (Liu 2018). The bands observed at 660 and 595 cm^{-1} indicate the asymmetric bending vibrations of SO_4 ions (Liu 2018). These vibrations are typically found in hydrated calcium sulfate compounds such as basanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) (Nosov et al. 1976). In addition, it has been reported that signals in the range of 620 to 560 cm^{-1} typically correspond to stretching and bending of the M–O bond of metal oxides, such as calcite (CaCO_3) (Hajji et al. 2017), magnetite (Fe_3O_4) and hematite (Fe_2O_3) (Namduri and Nasrazadani 2008; Wan et al. 2020). These results were consistent with those obtained by XRD analysis (Fig. 2a).

SEM

The micrograph of BGFeS1 (Fig. 3a) shows the presence of needle-shaped particles distributed over a portion of the biochar surface. The morphologies observed in the crystals are typical of anhydrite (CaSO_4) (Mahmoud et al. 2004; Chen et al. 2013), as validated by elemental mapping using EDS (Fig. 3e). The analysis showed that the needles are mainly composed of calcium (Ca), oxygen (O), and sulfur (S). In addition, the mapping in Fig. 3e demonstrates that the distribution of Fe is uniform over both the anhydrite (needle-shaped crystals) and biochar surface. This distribution will enhance the interaction between As(V) and the Fe contained in BGFeS1.

Figure 3b illustrates that BGFeS2 is a mixture of biochar particles (red oval) and particles in the form of smooth and rough hollow spheres (whole or in fragments). The shape of smooth hollow spheres is characteristic of ash with calcium (Zhang et al. 2019a), whereas rough spheres indicate ash with iron oxide (Derkowski et al. 2007). At a magnification of 1000x, the BGFeS2 particle has a smoother surface compared to the other BGFe. EDS elemental mapping in this zone (Fig. 3f) shows that Fe is concentrated mainly in the regions where ash fragments are found. This observation suggests that mechanically dry mixing guishe and $\text{Fe}_2(\text{SO}_4)_3$ before pyrolysis is insufficient to deposit Fe within the biochar pores. In contrast, Fe deposition occurs when the raw materials are mixed in a stirring medium, and ultrasound is used (Wang et al. 2015; Bakshi et al. 2018).

The micrograph of BGFeS3 (Fig. 3c) reveals that the biochar surface is entirely enveloped by variously shaped and sized aggregates, indicating a greater specific area. Figure 3g, shows that Fe is predominantly distributed across the surface, except for the Ca particles. In addition, the color is more pronounced in certain areas, indicating a greater iron concentration (Fe). This configuration will enhance the

interaction between the As(V) dissolved in the solution and the Fe contained in BGFeS3. In addition, when iron (Fe) is not present, calcium (Ca) is found in the form of calcite (Fig. 3g), which is known to have the ability to remove arsenic (As) from water (Román-Ross et al. 2006; Shah et al. 2022).

Finally, Fig. 3d shows that the surface of BGFeS4 is coated with clusters of comparable form and size. EDS elemental mapping (Fig. 3h) verifies the existence of iron (Fe) in BGFe4 (Table 1), which is uniformly distributed on the biochar surface. The effectiveness of the active sites is not hindered by the presence of Fe in amorphous phases (Fig. 2a). The biochar surface contains dispersed active sites that facilitate the interaction between arsenic (As) in solution and iron (Fe), thereby enhancing As removal.

PZC

Figure 4a shows the PZC of the BG and BGFe. The alkaline PZC of the adsorbents is mainly attributed to the existence of calcium compounds, which were identified through XRD analysis (Fig. 2a). Nevertheless, all BGFe materials exhibit a lower PZC compared to BG, primarily due to the presence of hematite ($\text{PZC} = 8.1$ (Mamindy-Pajany et al. 2011)) and magnetite ($\text{PZC} = 6.40$ (Mamindy-Pajany et al. 2011)) deposited on their surface. The PZC of iron-modified biochars derived from bamboo (Alchouron et al. 2020) and grape seeds (Frišták et al. 2018) decreased compared to the PZC of unmodified biochars.

When the pH is lower than the PZC, the surface of the adsorbent becomes positively charged due to protonation. This positive charge attracts anions and repels cations. On the other hand, if the pH is higher than the PZC, the surface of the adsorbent becomes coated with hydroxyl groups, leading to a negative charge that draws in cations and pushes away anions (Hassan et al. 2020). Groundwater typically has a pH range of 5 to 9 (Esteller et al. 2017; Pérez-Martínez et al. 2021). This pH range facilitates the adsorption of As(V) by electrostatic interactions, with the following order of ease: BGFeS3 > BGFeS1 > BGFeS4 > BGFeS2. Nevertheless, in addition to electrostatic forces, other factors influence the adsorption process, such as the amount of iron (Xi et al. 2021; Xu et al. 2021) and the degree of crystallinity of the iron compounds present in the biochar (Xu et al. 2021).

Batch adsorption studies using the four BGFe

pH effect on As adsorption

The relationship between the pH of the solution and the As(V) adsorption capacity of the BGFe is illustrated in Fig. 4b. The effect of pH was studied in a pH range of 5 to 9, encompassing the pH levels typically found in groundwater.



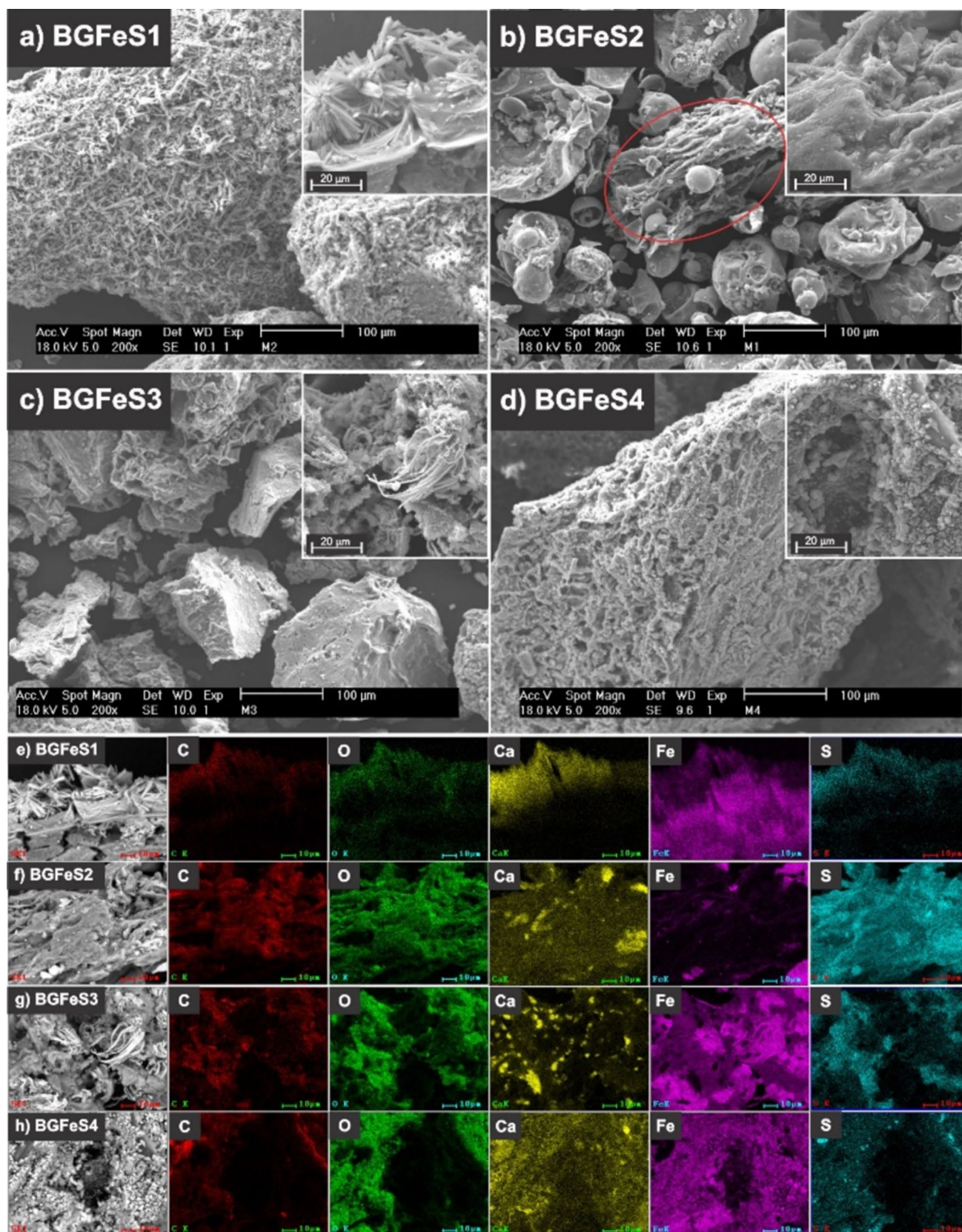


Fig. 3 a–d SEM images of the four BGFe and e–h SEM-EDS elemental distribution maps for e BGFeS1, f BGFeS2, g BGFeS3, and h BGFeS4



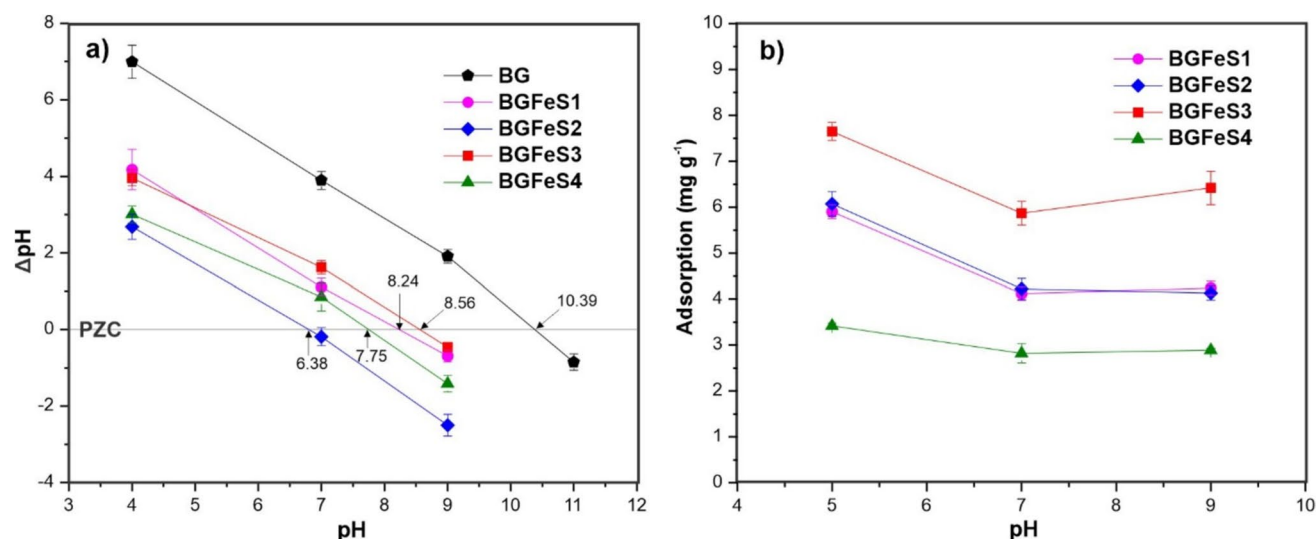


Fig. 4 a PZC of BG and BGFe determined by immersion method. b Effect of pH on As(V) adsorption ($C_0=10\ mg\ L^{-1}$, $T=25\ ^\circ C$ and 24 h)

The adsorption capacity of all BGFe samples was higher at pH 5. This is because acidic conditions cause H^+ ions to saturate the surface of the BGFe, thereby rendering it positively charged. This results in an enhanced the adsorption of As(V) anions through electrostatic interactions (Hassan et al. 2020). Conversely, an increase in pH to 7 led to a notable reduction in the adsorption capacity of all BGFe samples. At pH 9, the adsorption capacity exhibited minimal variation compared to that observed at pH 7. A comparable trend was evident in the adsorption of As(V) on biochar supported by nZVI (Wang et al. 2017), magnetite-modified water hyacinth biochar (Zhang et al. 2016), and iron-impregnated banana pith biochar (Lata et al. 2019). The decrease in adsorption capacity with the increasing pH of the solution can be attributed to two factors. Firstly, the presence of $H_2AsO_4^-$ and $HAAsO_4^{2-}$ anions, which are likely to be found in the pH range of 5 to 9, compete with OH^- for the active sites of the adsorbent as the pH of the solution increases (Zhang et al. 2016). Lately, the surface of the adsorbent has become more negative, which repels $H_2AsO_4^-$ and $HAAsO_4^{2-}$ anions.

Adsorption kinetics

Figure 5 shows the kinetics of As adsorption by BGFe. According to the findings, after 30 min BGFeS2 exhibited the highest As removal rate ($1.30\ mg\ g^{-1}$), followed by BGFeS1, BGFeS4, and BGFeS3. This finding could be due to the greater availability of magnetite as it is less trapped in BGFeS2 pores (as observed in SEM, Fig. 3b), which allows for faster interaction with As. After 24 h, when equilibrium was achieved, BGFeS3 exhibited the highest adsorption capacity of $3.21\ mg\ g^{-1}$. It was followed by

BGFeS1, BGFeS2, and BGFeS4, with adsorption capacities of 3.06, 2.94, and $2.07\ mg\ g^{-1}$, respectively.

In Table 2, the parameters of fitting the kinetics of As adsorption on BGFe to the pseudo-first-order (PS-1), pseudo-second-order (PS-2), and Elovich (E) models were presented. The E model is the most appropriate for representing the kinetics of As adsorption on BGFeS1, BGFeS2, and BGFeS4. This model postulates that the activation energy rises in proportion to the duration of adsorption and that the surface of the adsorbent is heterogeneous (Aharoni and Tompkins 1970), a finding that aligns with the SEM results. While the E model was initially created to explain the chemisorption of a gas in a solid material (Aharoni and Tompkins 1970), it has been more commonly employed to depict adsorption in liquid–solid systems (Wang and Guo 2020; Kushwaha et al. 2023). Previous research has demonstrated that the E model adequately describes the adsorption kinetics of As(V) in pinewood biochar modified with natural hematite (Wang et al. 2015) and in modified coffee husk and corn stover biochars with ZnO (Cruz et al. 2020).

On the other hand, the PS-1 model accurately represents the kinetics of As adsorption in BGFeS3 ($R^2_{adj} = 0.9922$). This model also elucidates chemisorption processes derived from Langmuir's kinetic model. The PS-1 model states that the diffusion of the adsorbate, whether external or internal, is the step that limits the process (Wang and Guo 2020). According to reports, the PS-1 model is more suitable for adsorbing As(V) on biochar derived from green algae (Senthilkumar et al. 2020) and biochar doped with N and modified with Fe_3O_4 (Ali et al. 2022) compared to the PS-2 model.



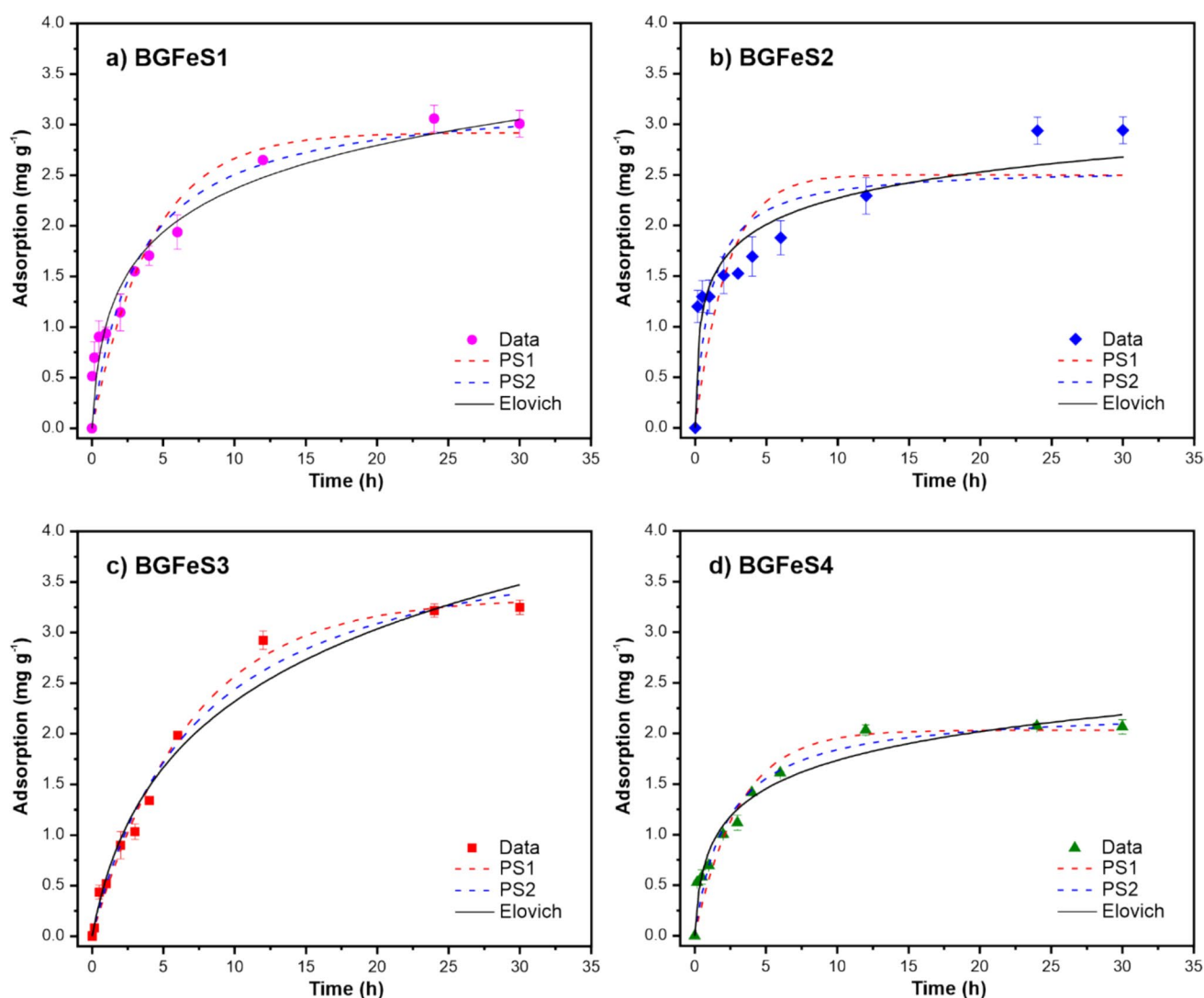


Fig. 5 As (V) adsorption kinetics by BGFe ($C_0=5 \text{ mg L}^{-1}$, $\text{pH}=7$, $T=25^\circ\text{C}$, and 24 h)

Table 2 Kinetic models and best-fit parameters for As(V) adsorption onto BGFe

	BGFeS1	BGFeS2	BGFeS3	BGFeS4
PS-1				
$q_e(\text{mg g}^{-1})$	2.9221	2.5107	3.3418	2.0319
$K_1(\text{h}^{-1})$	0.2437	0.4528	0.1462	0.3225
R^2_{adj}	0.8838	0.5691	0.9922	0.9289
PS-2				
$q_e(\text{mg g}^{-1})$	3.3014	2.5939	4.2099	2.2501
$K_2(\text{g mg}^{-1} \text{ h}^{-1})$	0.0957	0.3769	0.0327	0.1983
R^2_{adj}	0.9128	0.7203	0.9865	0.9508
Elovich				
$\alpha(\text{h}^{-1})$	2.5753	15.4761	0.7530	2.6909
$\beta(\text{g mg}^{-1})$	1.5760	2.6409	0.8729	2.4182
R^2_{adj}	0.9439	0.9050	0.9782	0.9621

bold values remark the best fitting to some of the proposed models for the kinetic study

Adsorption isotherms

The relationship between equilibrium As concentration and As adsorption capacity is presented in Fig. 6. The experimental data was described using the Langmuir and Freundlich models. The Langmuir model suggests that adsorption occurs in a monolayer with uniformly distributed adsorption sites, constant adsorption energy, and negligible interaction between adsorbate molecules (Langmuir 1918). The Freundlich model is an empirical model employed to depict the process of multilayer adsorption on heterogeneous surfaces (Freundlich 1907). The computed parameters of each model are displayed in Table 3. The Langmuir model demonstrates the highest correlation coefficient (R^2_{adj}), providing the most accurate fit to the experimental data. These results suggest that the adsorption of As on the BGFe surface occurs in a monolayer. The



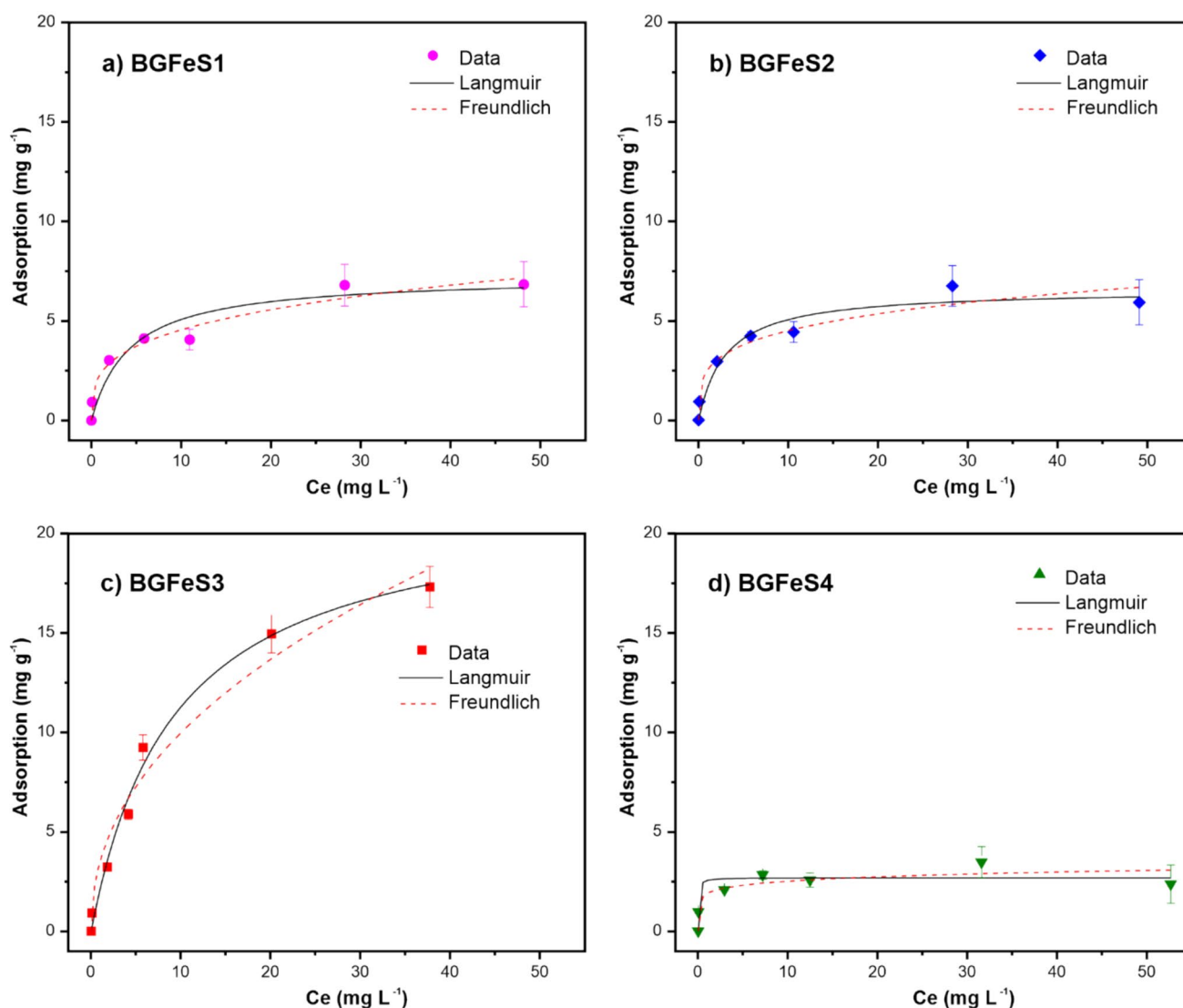


Fig. 6 As (V) adsorption isotherms by BGFe (pH=7, T=25 °C and 24 h)

Table 3 Isotherms models and best-fit parameters for As(V) adsorption onto BGFe

	BGFeS1	BGFeS2	BGFeS3	BGFeS4
Langmuir				
$q_m(\text{mg g}^{-1})$	7.251	6.568	21.70	2.674
$K_L(\text{L mg}^{-1})$	0.2323	0.3311	0.1079	19.2793
R^2_{adj}	0.9863	0.9861	0.9904	0.9911
Freundlich				
$K_F(\text{L}^{1/n} \text{mg}^{1-1/n} \text{g}^{-1})$	2.339	2.535	3.503	1.888
N	3.461	4.024	2.202	8.179
R^2_{adj}	0.9501	0.9496	0.9652	0.9707

Langmuir model also showed a better fit than Freundlich for As adsorption on iron-modified biochar (Nguyen et al. 2019; Nham et al. 2019), zero-valent iron-biochar (Wang et al. 2017; Bakshi et al. 2018), magnetic biochar (Zhang et al. 2013; Wang et al. 2015), and iron-impregnated biochar (He et al. 2018; Lata et al. 2019).

According to Langmuir, the maximum adsorption capacities were 21.70, 7.251, 6.568, and 2.674 mg g^{-1} for BGFeS3, BGFeS1, BGFeS2, and BGFeS4, respectively. BGFeS3 has the highest maximum adsorption capacity, while BGFe4 has the lowest. This suggests that the adsorption capacity can be directly related to the Fe content in each biochar, since BGFeS3 has the highest Fe content and BGFe4 has



the lowest (Table 1). However, the relationship between iron content and maximum adsorption capacity is not directly proportional. For example, BGFeS2 contains 22% less Fe than BGFeS3, but its maximum adsorption capacity decreases by 69% compared to BGFeS3. This suggests that other factors influence the adsorption capacity besides the Fe content.

The fact that BGFeS3 has the highest maximum adsorption capacity may be because the iron present in this material is in the form of Fe_3O_4 and Fe^0 . These iron phases may act in synergy, as reported in (Zubair et al. 2020). While calcium sulfates are present in BGFeS2 and BGFeS4, which could adsorb As. However, for calcium sulfates to perform well as adsorbents, the adsorption process must occur at $\text{pH} > 7$. Further testing is needed to confirm these hypotheses.

Comparison with other iron-modified biochars

Table 4 presents a comparative analysis of BGFe and other iron-modified biochars, all of which underwent slow pyrolysis in a nitrogen atmosphere. The iron modification was achieved through impregnation, co-pyrolysis,

or precipitation deposition, allowing for a comprehensive evaluation of BGFe synthesized using analogous methods.

According to Table 4, the four BGFe have As(V) adsorption capacities within the range reported in the literature for iron-modified biochars from lignocellulosic wastes. It is noteworthy that BGFeS3 has a higher maximum adsorption capacity than water hyacinth (Zhang et al. 2016), switchgrass, and red oak biochars (Bakshi et al. 2018), which contain about 40% more iron. Conversely, the adsorption capacity of BGFeS3 seems to be inferior compared to biochar derived from bamboo (Alchouron et al. 2020) and pinewood (Wang et al. 2017). The reason for this may be the presence of SiO_2 in the former, while in the latter, the adsorption capacity was determined at a pH of 4.1. However, the maximum adsorption capacity of BGFeS3 is predicted to increase under acidic conditions (Fig. 4b). In addition, the CaCO_3 present in BGFeS3 is expected to regulate the pH of the water, eliminating the need for external pH modifiers. Future research is required to verify this.

Table 4 As(V) adsorption comparison with other studies

Iron-modified biochar from	Fe content (%mass)	Iron phases	Adsorption conditions					Q_{max} (mg g^{-1})	References
			pH	Temperature ($^{\circ}\text{C}$)	Concentration (mg L^{-1})	Adsorbent/solution (g L^{-1})	Equilibrium time (h)		
Banana peel	NR	ND	6.5	25	0.05–0.5	2.5	8	0.12	(Lata et al. 2019)
Pinewood	2.95	Maghemite	7	22	1–60	2.5	20	0.4287	(Wang et al. 2015)
Guishe (BGFeS4)	6.48	ND	7	25	1–55	1	24	2.67	This study
Cottonwood	52.01	Maghemite	NR	22	5–200	2	24	3.147	(Zhang et al. 2013)
Guishe (BGFeS2)	26.07	Magnetite	7	25	1–55	1	24	6.56	This study
Corn straw	6.05	Hematite Magnetite	7	NR	0.25–100	5	48	6.8	(He et al. 2018)
Guishe (BGFeS1)	21.03	Hematite Magnetite	7	25	1–55	1	24	7.25	This study
Water hyacinth	54.56	Magnetite	5.3	25	2–105	NR	24	7.41	(Zhang et al. 2016)
Switchgrass	55.72	ZVI	7	21.5	1–25	1	48	7.92	(Bakshi et al. 2018)
Pomelo peel	NR	NR	7	30	0.05–20	1	24	15.28	(Nguyen et al. 2022)
Red oak	56.64	ZVI	7	21.5	1–25	1	48	15.58	(Bakshi et al. 2018)
Guishe (BGFeS3)	33.51	Magnetite ZVI	7	25	1–55	1	24	21.70	This study
Bamboo culms	17.9	Hematite Magnetite	7	25	2.5–1000	2	2	90	(Alchouron et al. 2020)
Pinewood	10.5	ZVI Maghemite	4.1	22	0–400	2	2	124.5	(Wang et al. 2017)

NR = Not reported; ND = Not determined.

data in bold corresponds with the results obtained in this study, which are being compared with data of other studies



Conclusion

It has been demonstrated that Fe-modified biochars can be prepared from guishe (bagasse from *Agave lechuguilla*) by practical synthesis methods, all capable of removing As(V) from water. According to the findings of the kinetic and isotherms investigation, the adsorption of As(V) on biochars takes place primarily on a monolayer. The maximum adsorption capacities of As(V) on BGFeS1, BGFeS2, BGFeS3, and BGFeS4 were 7.25, 6.56, 21.70, and 2.67 mg g⁻¹, respectively, at 25 °C and pH 7. These adsorbents, derived from abundant and locally sourced waste material, represent a notable advance in sustainability by reducing both the economic and environmental costs associated with material transportation. The simplicity of the synthesis methods not only suggests the feasibility of industrial-scale production but also underscores the potential for large-scale application. Nevertheless, further research is needed to optimize feedstock and energy utilization and understand the As(V) adsorption mechanism on guishe biochar. This deeper understanding will enable the refinement of remediation strategies, thereby establishing this approach as an effective and sustainable solution to arsenic contamination in water.

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Author contributions Ana Paloma González García: Conceptualization, Formal Analysis, Data curation, Methodology, Writing – Original draft; Salvador Carlos Hernández: Validation, Supervision, Writing – Review and Editing; Lourdes Díaz Jiménez: Conceptualization, Funding acquisition, Supervision, Resources, Writing – Review and Editing.

Data availability The data that support the findings of this study are available from the corresponding author, LDJ, upon reasonable request.

Declarations

Conflict of interests The authors have no relevant financial or non-financial interests to disclose.

Human or animal participants This article does not contain any studies with human participants or animals performed by any of the authors.

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