Supplementary Materials

Iron-loaded carbonized spent bleaching earth (Fe-SBE/C) composite used for arsenic removal from water

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Content

Text S1. Physicochemical characterization of material and methods

1. Physicochemical characterization of material

This study examined the thermal degradation of the material by utilizing thermographic analysis (TG) (STA PT1600 LINSEIS Germany) in an air environment. The heating rate was set at 5 ºC min^{-1}, starting from room temperature and reaching 1000 ºC. The value of pH_{PZC} was obtained using a Zeta potential analyzer (ZEN3690, Malvern, UK). The pattern of X-ray diffraction (XRD) was acquired by employing Cu-Kα radiation as a source of an X-ray powder diffractometer (Mini Flex600, Rigaku, Japan) with an operating configuration using a generator with 30 kV voltage and a tube current of 30 mA. The Fourier transform infrared spectroscopy (FTIR) was used to analyse the functional groups of materials. Subsequently, surface area and pore size distribution were quantified using a Belsorp-mini II, MicrotracBel, Japan, with calculations based on the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods within a P/P_0 range of 0.05 to 0.25. The surface and cross-sectional morphologies of the adsorbent were scrutinized using scanning electron microscopy (SEM), specifically the Sigma model from ZEISS, Germany. Lastly, the surface chemical states were characterized using X-ray photoelectron spectroscopy (XPS) (Thermo Kalpha; Thermo Escalab 250XI, USA).

2. Kinetic Study

For the kinetic study, the solution of As (III) and As(V) with a concentration of 50 µg L^{-1} was prepared in a 250 mL glass bottle reaction with the lid on. After adjusting the pH’s solution to neutral pH 7, the adsorbent 1 g L^{-1} was added and mixed in a water bath rotary shaker with a controlled temperature of 25±2 ºC. The experiment was held for 180 mins with samples taken at each time interval (0, 1, 5, 10, 20, 30, 60, 90, 120, 150, and 180 mins). The sample was taken and filtered through a 0.22µm PES filter and poured into a plastic tube, then immediately added 0.25 mL HCl 1:1 to stop the reaction and 0,25 mL thiourea-ascorbic acid solution. HG-AFS measured the concentration of As (III) and As (V) with As(total) configuration.

These models were determined by utilizing the respective equations assigned to each model.

The equation for pseudo-first-order is described as

$$\ln(q_e\text{-}q_t) = \ln(q_e) - k_1t \tag{1}$$

The simplified version of the Elovich kinetic model equation, commonly employed to describe chemisorption on adsorbents with significant heterogeneity, has been presented by Chien and Clayton 1980 [1]. Equation (3) provides the expression for this simplified model:

$$qt = \frac{1}{\beta}\ln(\alpha\beta) + \ln t\frac{1}{\beta} \tag{3}$$

The parameters α and β correspond to the initial rate of adsorption (expressed in $\mu g\ g^{-1}$ min^{-1}) and desorption constant (expressed in g µg-1), respectively.

The utilization of the intraparticle diffusion model allows for the investigation of whether the adsorption process entails the movement of adsorbate molecules through the pore of the adsorbent. Weber and Morris 1963 [2] established a framework that was employed to asses this kinetic model. The equation representing the intraparticle diffusion model is as follows:

$$qt = K_{diff.}t^{1/2} + C \tag{4}$$

The rate constant for intraparticle diffusion, denoted as K_{diff}, is expressed in $(g\ \mu g^{-1}\ min^{1/2})^{-1}$ units. The coefficient C ($\mu g\ g^{-1}$) is also linked to the magnitude of the boundary layer’s thickness.

3. Isotherm study

In an isotherm study, 1 g L^{-1} of adsorbent Fe-SBE/C was added to As(III) and As(V) solution in 250 mL glass bottle with a vary concentration range from 10 - 250 μg L^{-1} and mixed in a water bath rotary shaker with controlled temperature at 25±2 °C. HG-AFS measured the concentration of As (III) and As(V) with As Total configuration. The reactions were conducted with duplicate, and the initial pH was 7 for As(III) and pH 3 for As(V).

The adsorption isotherm concept describes how adsorbed molecules are distributed between the liquid and should phase at equilibrium. The present study evaluated the equilibrium adsorption data for As(III) and As(V) on Fe-SBE/C using three different isotherm models. First, the isotherm Langmuir model explains the quantitative information of monolayer molecules on the adsorbent's surface, which is affected by the concentration of the adsorbed substance in the liquid phase. Mathematically, the Langmuir model isotherm can be expressed by the equation [3]:

$$qe=q_{max}.CeK_L/(1+CeK_L) \quad (5)$$

In the context of this study, the variable qe (μg g^{-1}) represents the quantity of arsenic that has been adsorbed at the point of equilibrium. q_{max} (μg g^{-1}) denotes the maximum capacity of the adsorbent material to uptake arsenic. K_L (L μg g^{-1}) serves as the equilibrium constant, crucial in determining the overall adsorption process. Lastly, Ce (μg L^{-1}) represents the equilibrium concentration of arsenic.

Second, Freundlich isotherm, a renowned empirical equation, describes the adsorption phenomenon occurring on a surface that displays heterogeneity in its heat of adsorption distribution. This surface, which accommodates the adsorbed molecules interacting with each other, showcases diverse energetic characteristics. The Freundlich isotherm can be represented as follows [4]:

$$qe= K_F Ce^{1/n} \quad 6)$$

The parameter qe ($\mu g\ g^{-1}$) is the significant amount of adsorbed mass per unit of the adsorbent when equilibrium is reached. Ce ($\mu g\ L^{-1}$) is denoted as the equilibrium concentration of arsenic. K_F and 1/n are also essential as they denote the adsorption capacity and intensity, respectively.

Third, the Temkin isotherm model assumes that the decrease in the heat of adsorption for each molecule within the adsorbent layer follows a linear trend as the coverage increases. The phenomenon arises from the interactions between the sorbate and sorbent. The following equation represents this Temkin isotherm model [5]:

$$qe= B \ln A.Ce \quad 7)$$

The equation B=RT/bt represents the relationship between the heat of adsorption ($J\ mol^{-1}$) and the temkin isotherm constant ($L\ g^{-1}$). Here, R represents the gas constant (8.314 $J\ mol^{-1}\ K$), and T denotes the absolute temperature (K).

4. Thermodynamics

The investigation examined the adsorption kinetic across varying temperatures: 25 ºC, 35 ºC, and 40 ºC. The findings of this study align with the commonly observed phenomenon that higher temperatures tend to enhance the adsorption capacity. In order to ascertain the parameters of thermodynamics, including the standard Gibbs free energy (ΔG^o), change of enthalpy (ΔH^o), and change in entropy (ΔS^o), the established equation was utilized.

$$\Delta G^o= - RT\ln K_L \quad (8)$$

According to Maiti et al. [6,7], the equilibrium constant, denoted as KL, can be expressed as K_L = qe/Ce. In this equation, qe represents the equilibrium concentration of arsenic in the solution, while Ce refers to the concentration reduced by the adsorbent due to adsorption at equilibrium.

The equation below encompasses the relationship between the change in enthalpy (ΔH^o), and change in entropy (ΔS^o), and the Gibb's free energy:

$$\ln K_L = \Delta S^o/R - \Delta H^o/RT \qquad (9)$$

The values for both changes were derived from the intercept and slope of the $\ln K_L$ vs 1/T curves (Van't Hoff plot).

The activation energy (E_a, KJ mol^{-1}) has been calculated using Arrhenius equation [8,9]:

$$\ln k_{app} = \ln A - Ea/RT \qquad (10)$$

k_{app} is the apparent pseudo-first order rate constant, A is the Arrhenius constant (J mol^{-1} K^{-1}). In equations (9) and (10), T denotes the temperature in Kelvin and R denotes the universal gas constant (J mol^{-1} K).

5. Regeneration and reusability study

Four consecutive cycles were conducted to evaluate the regeneration and reusability of the composite through adsorption-desorption experiments. The adsorbent's surface becomes negatively charged when exposed to an alkaline solution. As a result, As(III) primarily exists as a divalent anion. This causes the adsorbed arsenic to be released from the surface of the materials [10]

The desorption of the composite loaded with As(III) is performed with a 0.1 mol L-1 NaOH as the agent for desorption. An adsorbent with a concentration of 1 g L^{-1} was individually mixed with NaOH solution. The mixture was then placed in a thermostatic shaker and agitated for 180 minutes at 250 rpm. Upon concluding the experiment, the solution underwent filtration and was subsequently stored for subsequent analysis. The solid was rinsed in three cycles using Ultrapure water and then utilized for another adsorption process. The adsorption process was repeated three times consecutively.

Suplementary of Figure

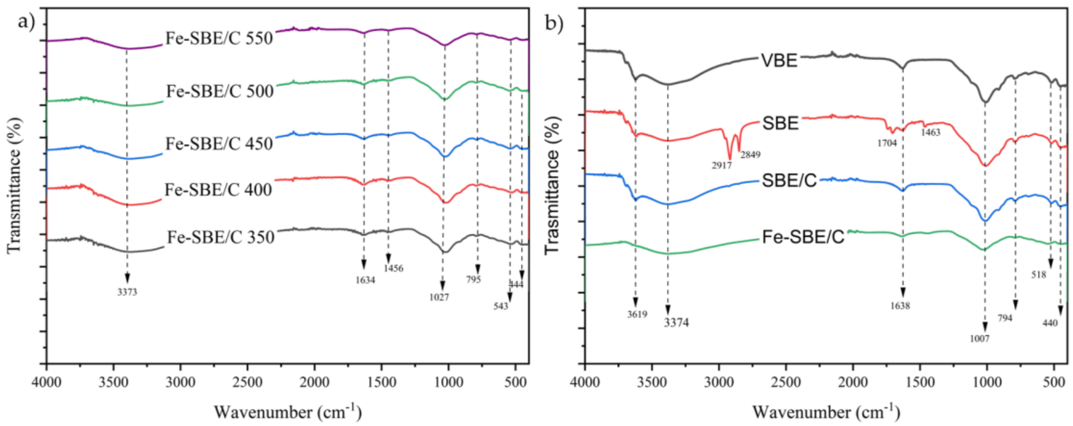

Figure S1. FTIR spectra for (**a**) the modified materials at different calcination temperatures and (**b**) the materials VBE and SBE, SBE/C, and Fe-SBE/C

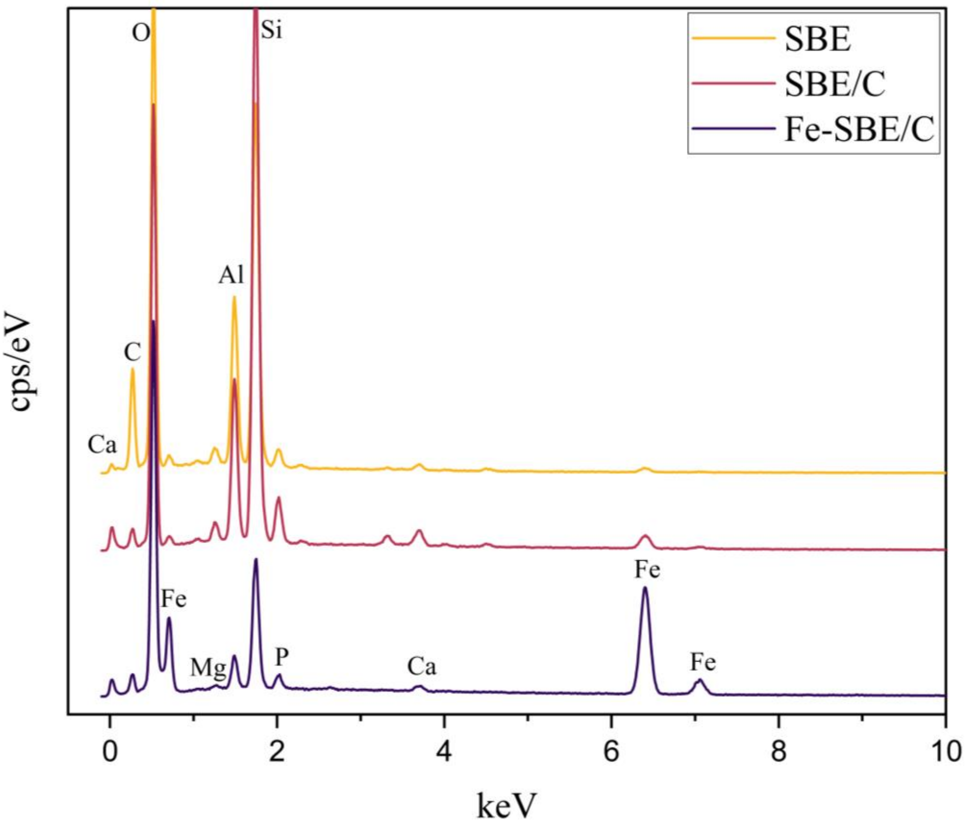

Figure S2. The energy-dispersive X-ray spectroscopy (EDS) element in the material.

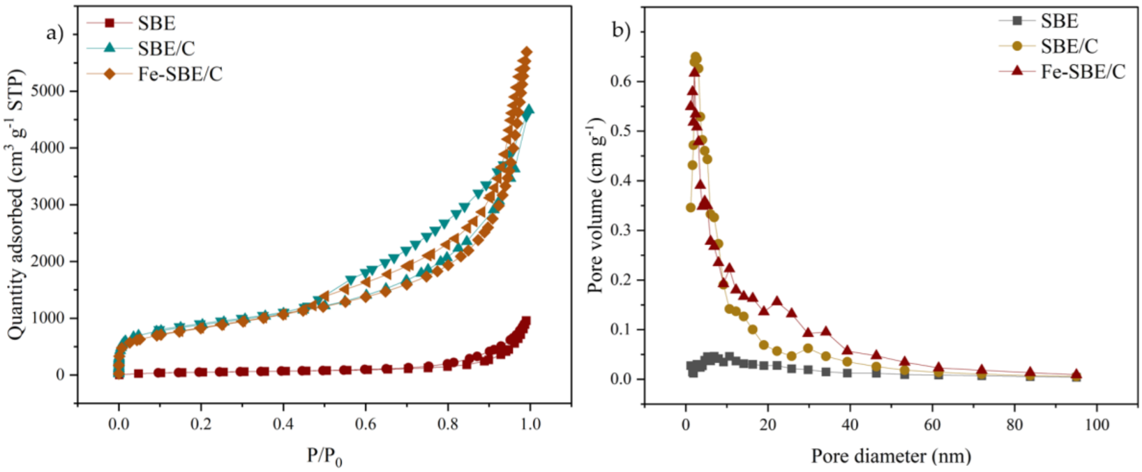

Figure S3. (**a**) Adsorption and desorption curves of N_2, (**b**) distribution of pore size.

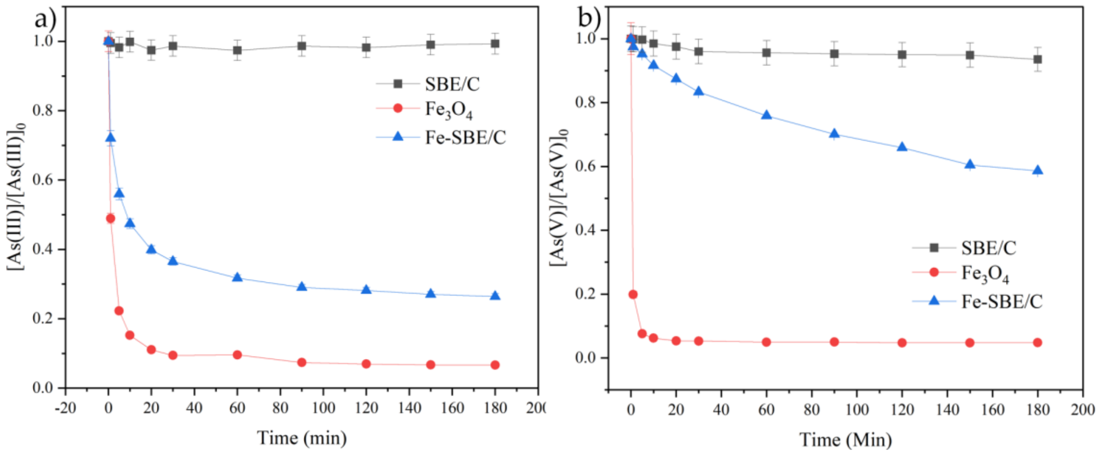

Figure S4. Comparison of (**a**) As(III) and (**b**) As(V) removal between SBE/C 500 ºC-3h, Fe_3O_4, and Fe-SBE/C 500 ºC. Experimental conditions: Adsorbent dosage = 1 g L^{-1}; V= 250 mL; initial concentration of arsenic = 50 µg L^{-1}; pH = 7; T = 25ºC; S= 250 rpm; t= 3 h.

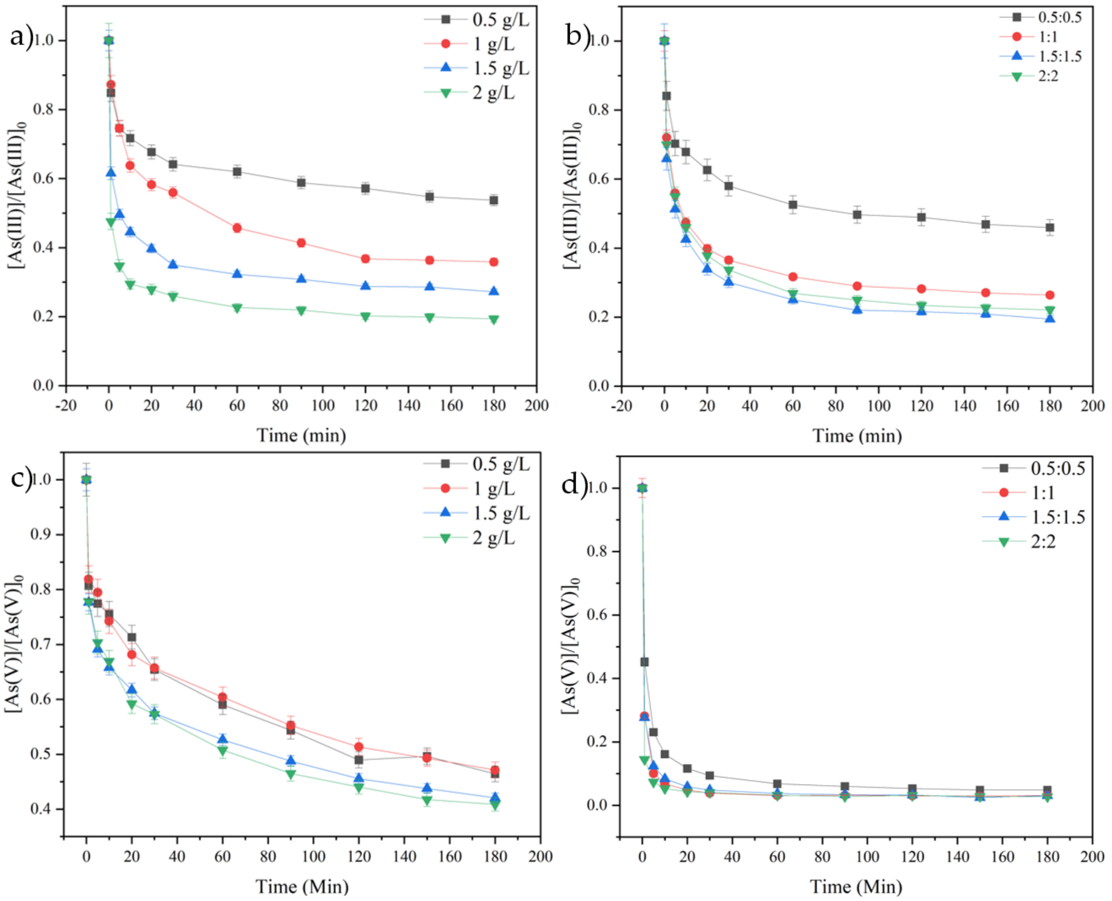

Figure S5. The influences of adsorbent dosage (**a** and **c**), the ratio of Fe(III)/Fe(II) (**b** and **d**) on As(III)/As(V) adsorption, respectively. Experimental conditions: (iron ratio; Adsorbent dosage = 1 g L^{-1}); V= 250 mL; Initial concentration of arsenic = 50 µg L^{-1}; (adsorbent dosage: pH = 7 (As(III)) and pH 3 (As(V))) T = 25ºC; S= 250 rpm; t= 3 h.

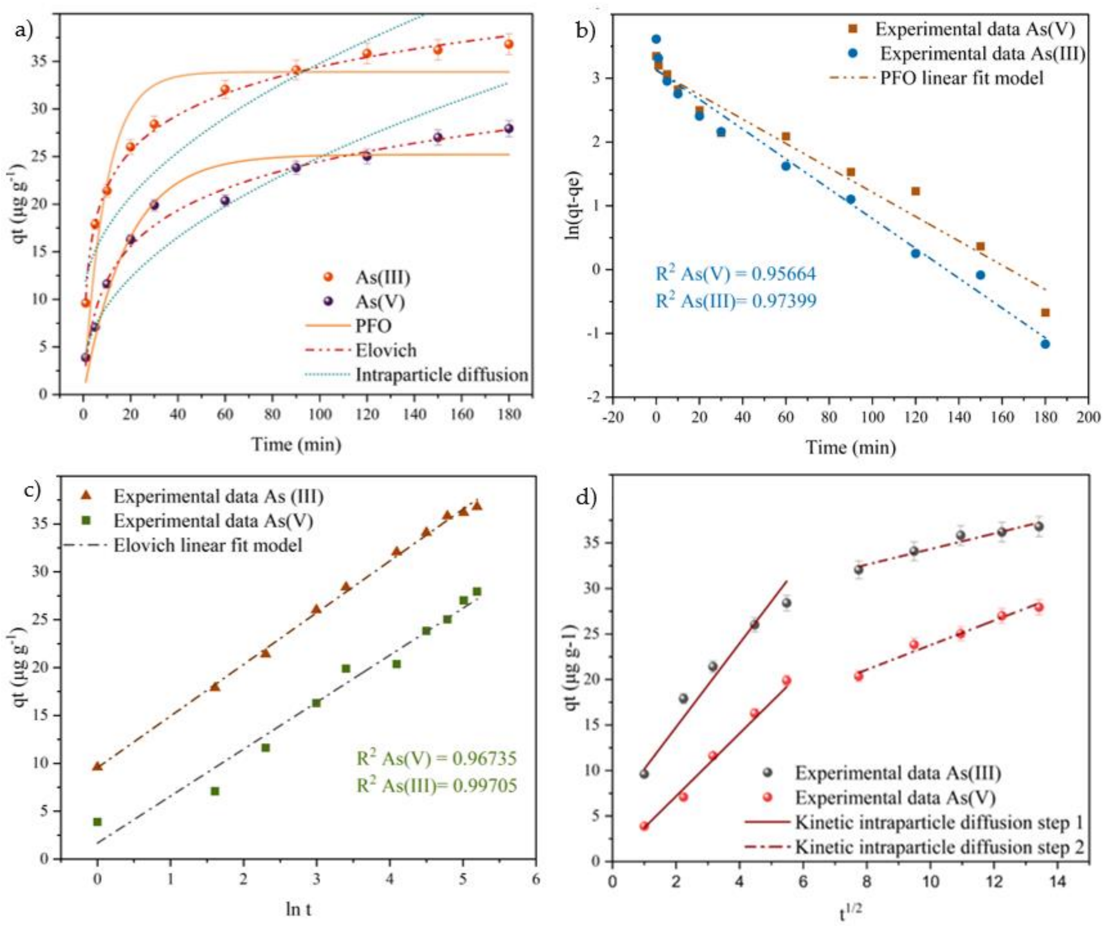

Figure S6. Adsorption kinetic studies of As(III) and As(V), (**a**) Kinetic models, (**b**) Pseudo-first-order linear fit model, (**c**) Elovich linear fit model, (**d**) Intraparticle diffusion model. Experimental conditions; Adsorbent dosage = 1g L^{-1}; V= 250 mL; Initial concentration of arsenic 50 µg L^{-1}; pH= 7; T= 25 ºC; S= 250 rpm; t= 3 h.

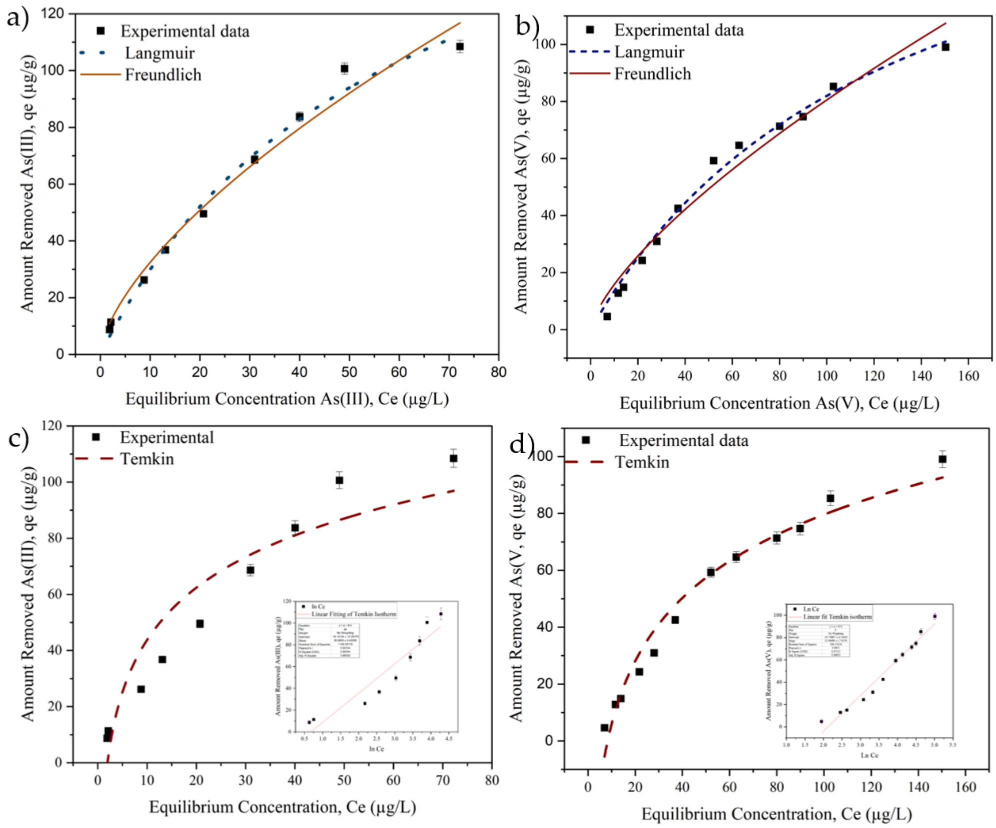

Figure S7. Isotherm Langmuir, Freundlich, and Temkin model of As(III) (**a** and **c**) and As(V) (**b** and **d**) adsorption. Experimental conditions; Adsorbent dosage= 1g L^{-1}, V = 250 mL; T= 25 ºC; t= 3 h; S= 250 rpm; pH= 7 (As(III)), pH=3 (As(V)).

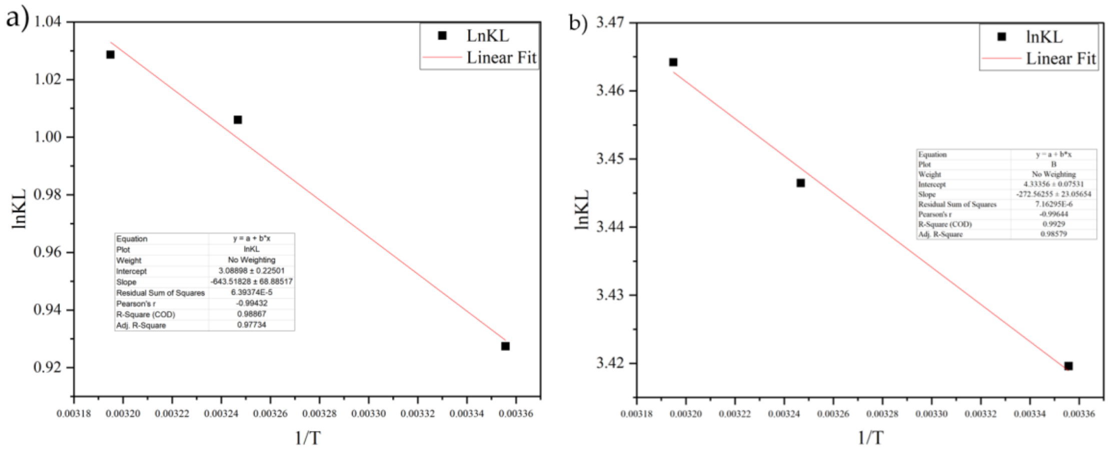

Figure S8. Adsorption thermodynamic (Van't Hoff) plots for adsorption of As(III) (**a**) and As(V) (**b**). Experimental condition; Adsorbent dosage = 1 g L^{-1}; V= 250 mL; Initial concentration of arsenic = 50 µg L^{-1}; T= 25 ºC, 35 ºC, and 40 ºC; t = 3 h; S= 250 rpm, pH = 6 for As(III) and pH = 3 for As(V).

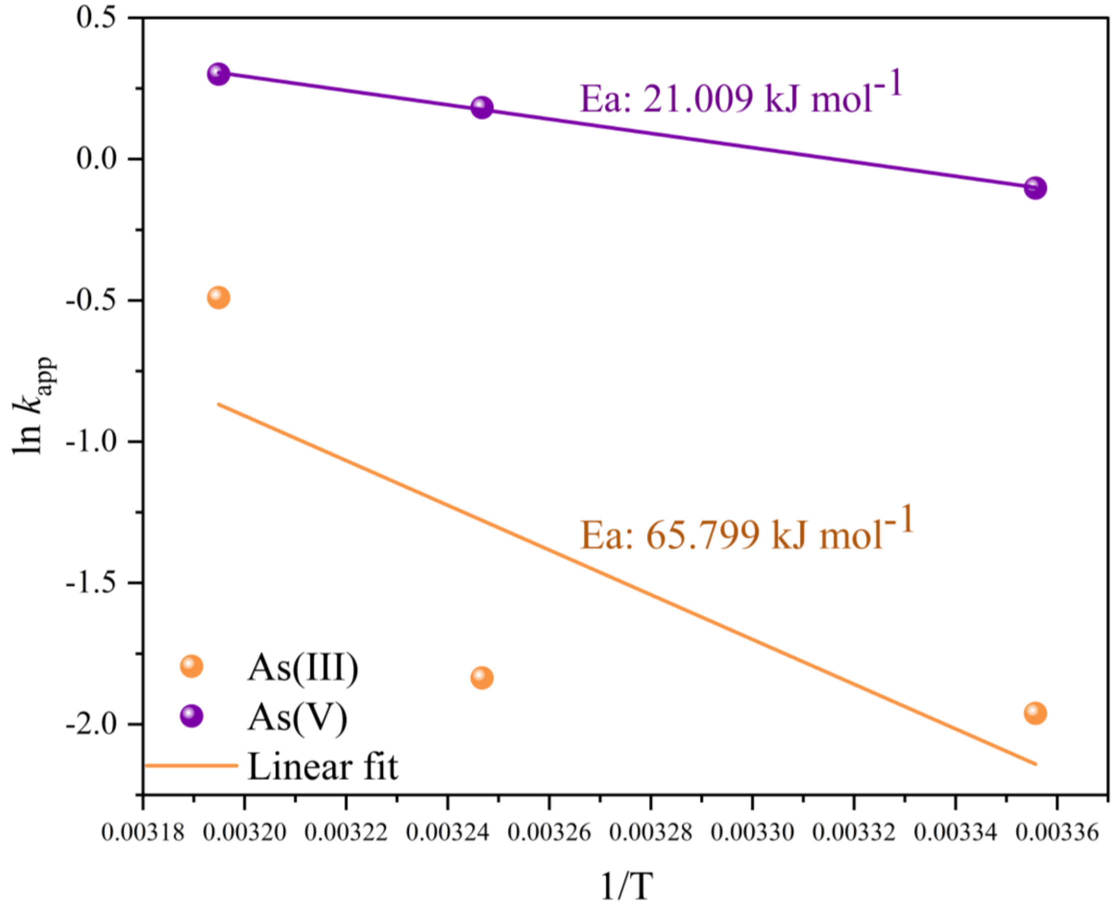

Figure S9: Arrhenius plot of As(III) and As(V) adsorption. Experimental condition; Adsorbent dosage = 1 g L^{-1}; V= 250 mL; Initial concentration of arsenic = 50 µg L^{-1}; T= 25 ºC, 35 ºC, and 40 ºC; t = 3 h; S= 250 rpm, pH = 6 for As(III) and pH = 3 for As(V).

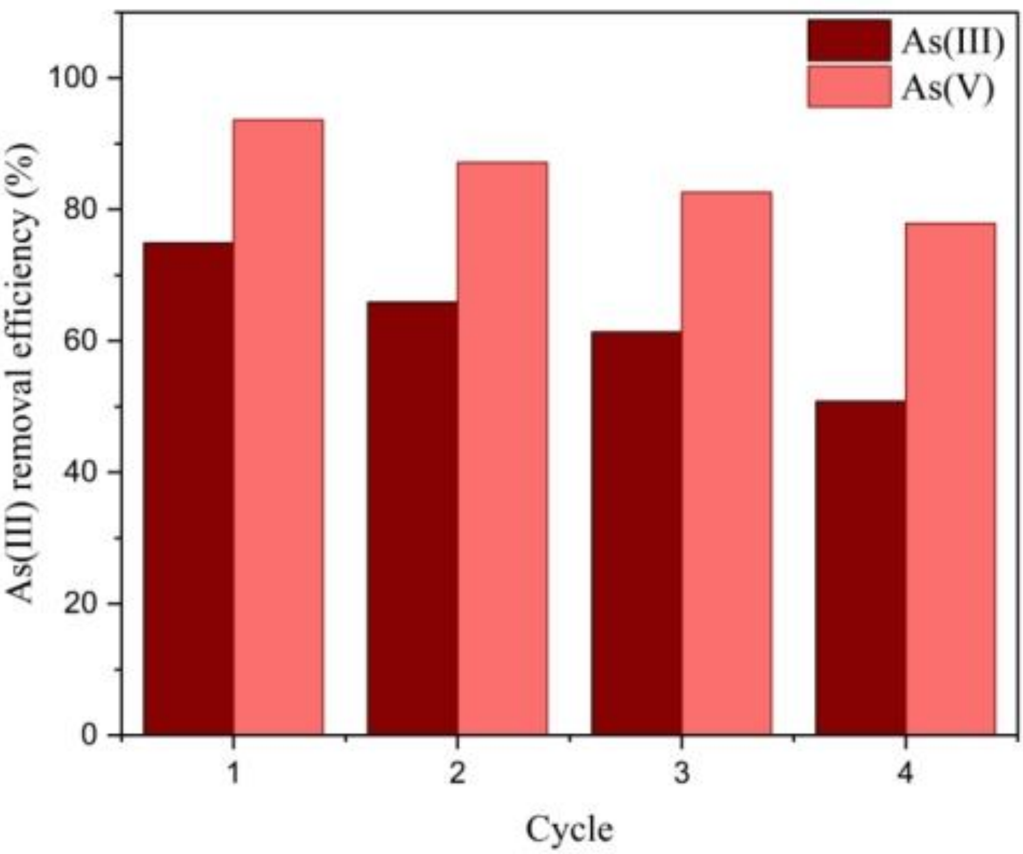

Figure S10. Reusability cycle of Fe-SBE/C for As(III) and As(V) adsorption. Experimental conditions; Adsorbent dosage= 1 g L^{-1}, V = 250 mL; Initial concentration of arsenic = 50 µg L^{-1}; T= 298K; t= 3 h; S= 250 rpm; pH= 7 for As(III) and pH=3 for As(V).

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