Supporting Information

Adsorption-desorption behavior of arsenate using single and binary iron modified biochars: thermodynamics and redox transformation

Md. Aminur Rahman⁎, Dane Lamb, Mohammad Mahmudur Rahman, Md Mezbual Bahar, Peter Sanderson

⁎Global Centre for Environmental Remediation (GCER), College of Engineering, Science and Environment, The University of Newcastle, Callaghan, NSW 2308, Australia

Department of Public Health Engineering (DPHE), Zonal Laboratory, Khulna-9100, Bangladesh

Chemical and Environmental Engineering, School of Engineering, RMIT University, Melbourne, Victoria, 3000, Australia

⁎Corresponding Author:
Md. Aminur Rahman
Global Centre for Environmental Remediation (GCER), College of Engineering, Science and Environment
The University of Newcastle, Callaghan, NSW 2308, Australia
S1. Reagents and materials

Analytical grade reagents were obtained from Sigma-Aldrich, Australia. The glassware and plastic ware used during the experiment were washed with 3% HNO$_3$ solution followed by rinsing three times with ultrapure water. Stock solution of 1000 mg/L arsenate (As$^{V}$) was prepared from sodium arsenate dibasic heptahydrate (Na$_2$HAsO$_4$. 7H$_2$O). Zirconium (IV) oxychloride octahydrate (ZrOCl$_2$.8H$_2$O), iron chips (Fe), iron (III) chloride hexahydrate (FeCl$_3$.6H$_2$O), sodium nitrate (NaNO$_3$), potassium nitrate (KNO$_3$), magnesium nitrate (Mg(NO$_3$)$_2$), calcium nitrate (Ca(NO$_3$)$_2$), sodium sulphate (Na$_2$SO$_4$), sodium carbonate (Na$_2$CO$_3$), sodium phosphate monobasic (NaH$_2$PO$_4$), nitric acid (HNO$_3$), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich. The biosolid biomass (BSBM) was obtained from Winmalee sewage treatment plant-Winmalee, NSW, Australia. The BSBM was stored at ambient temperature (approximately 24 °C) after being oven dried at 80 °C for 24 h and ground to a powder (<1 mm, 50 mesh).

S2. Characterization of adsorbents

S2.1 Zeta potential

Electrophoretic mobility of biochar, namely zeta potential (ZP), can be used to evaluate surface charge properties of particulate systems. ZP is the electrical potential of a sliding plane between the stern and diffuse layers of colloidal particles. 1, 2 ZP was determined for each biochar samples using a Zeta-Analyzer (NanoPlus HD, Micromeritics, USA). All samples were dried and passed through a No. 200 sieve prior to measurement. A solution containing 0.01 g biochar in 50 mL (0.02%, w/V) NaNO$_3$ (0.01 M) was prepared. A small amount of the solution was placed into the cell. The velocity of particles moving toward a positively charged electrode, which is determined to compute the ZP of each sample using Zeta-Meter. This measurement was taken in triplicate and average values were recorder for each biochar samples.

S2.2 Point of zero charge (PZC)

The pH at which the net charge of a solid surface is zero, is referred to as point of zero charge (PZC), which is one of the most important parameters used to describe variable-charge. 3, 4 A Zeta-Analyzer (NanoPlus HD, Micromeritics, USA) was used to determine the PZC, where 0.02 g (0.02 % w/V) biochar was taken in a centrifuge tube using NaNO$_3$ (0.01 M) as a background electrolyte. The pH of biochar suspension was adjusted to 1.0–10 using 0.1 M HNO$_3$ and/or NaOH and then kept in a rotary shaker for 24 hours. The samples were placed in a sonicator for 15 minutes after being reached to equilibrium and then biochar suspension was
injected into the Zeta-analyzer. After successful calibrating the instrument, the PZC was determined from plotting the pH vs zeta potential (where intersects the curve).

S2.3 Cation exchange capacity (CEC)
Surface charge properties of biochars were determined by CEC and electrophoretic mobility property of biochars. Cation exchange capacity (CEC) is an indicator of abundance charge on the surface of a material, which can be balanced by exchangeable cations. In this study, CEC of biochar was determined by BaCl\(_2\) compulsive exchange modified method as described by Gillman and Sumpter (1986). Results are inserter in Table S2.

S2.4 BET-N\(_2\) surface area
Specific surface area (SSA) of biochar samples (<2 mm) were measured with nitrogen (N\(_2\)) adsorption isotherms under liquid N\(_2\) (-196 °C) by a Surface Area and Porosity Analyzer (TristarII 3020, Micromeritics, USA). Biochar samples were degassed overnight at 60 °C under at 2 Torr before N\(_2\) adsorption (micromeritics VacPrep 061 Sample Degas System). The BET (Brunauer-Emmett-Teller) equation were used to calculate the surface area of the biochar samples. BET and Langmuir adsorption isotherms were generated to determine the single-point surface area. Pore volume and pore diameter of all biochars were measured using a gas adsorption analyzer by BET method. The mean diameter of the biochar was measured using a Zeta plus particle size analyzer (NanoPlus HD, USA). The lower detection range of the particle size of the analyzer is 2 nm to 3 µm.

S2.6 Determination of C, N and S
Air-dried biochars (at 80 °C) were placed into glass vials. The contents of C, N, and S (wt %) were determined for each biochar samples by a CNS analyzer using a LECO TruMac operated in CHN mode. Results were tabulated in Table S3.

S2.7 Fourier transform infrared (FT-IR)
Fourier transform infrared (FT-IR) spectra were recorded using a Cary 600 Series (Agilent Technologies, USA) spectrometer in order to obtain the interactions between surface functional groups of biochar and As\(^V\). This was done by applying a dehydrated KBr disc technique, where biochar samples (150 µm) were mixed with spectroscopic grade KBr. The biochar to KBr ratio was maintained to 1:100 before scanning to produce suitable transmittance. Spectra over the
range between 4000–400 cm\(^{-1}\) were obtained by the co-addition of 64 scans with a resolution of 4 cm\(^{-1}\) and a mirror velocity of 0.6329 cm/s.

**S2.8 X-ray diffraction (XRD)**

X-ray diffractometer (Bruker D8 Advance) was used to collect the crystallinity of biochar samples before and after adsorption with As\(^{\text{V}}\). All samples were dried for 24 h at 80 °C prior to the XRD analysis. The samples were scanned from 5 to 80º using 30 mV current and 40 kV voltage with Co K\(\alpha\) radiation (1.5478 Å). The scanning rate was 1 ° (2\(\theta\)) min\(^{-1}\) with a step size of 0.04 °. A Match3 software (Crystal Impact, Germany) was used to interpret the XRD peaks of biochar samples.

**S2.9 Scanning Electron Microscope (SEM)**

Surface morphology of the Fe-modified, Zr-Fe modified and corresponding As-loaded biochar samples were determined using an Environmental Scanning Electron Microscope (SEM, Zeiss Sigma, Germany) which is equipped with a Bruker energy dispersive X-ray spectroscopy (EDS) detector. The purpose of this study was produce high-resolution surface morphology image with less electrostatic distortion. Prior to SEM imaging, biochar samples were placed on a sample holder, followed by coating with C applied a high vacuum coater (Cressington 208 carbon coater, USA). The SEM images were obtained from various regions of biochars at multiple magnifications with an accelerating voltage of 15 kV.

**S2.10 Transmission Electron Microscope (TEM)**

Microstructural analysis of biochar samples were determined using a high-resolution transmission electron microscope (HRTEM, JEM-2100F, Japan). Before TEM analysis, the grounded biochar samples were dispersed in ethanol, sonicated for 15 minutes and then one drop of biochar-suspension were placed on a copper grid (Lacey carbon film, 100 µm thickness, 300 mesh, copper material). Finally, the samples were inserted on a sample holder and immediately placed in a JEOL-JEC-4000DS pumping station. The high-resolution images were taken using a HTEM (JEM-2100F-HR, Japan) at an acceleration voltage of 200 kV in the 0–20 keV energy range. In addition, high-resolution elemental mapping was captured at 5000–30000 cps and T3 mode using an energy dispersive x-ray spectroscopy (JEOL-JED-2300).
S2.11 X-ray Photoelectron Spectroscopy (XPS)

To explore the oxidation state of As, Zr, and Fe bound to biochar surface, before and after As(V) adsorption was analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Scientific, ESCALAB 250Xi, UK). XPS measurements were performed using a monochromated Al Kα X-ray source (1486.6 eV) at 120 W with the pass energy of 20 eV for region scans and the step size of 500 μm steps. The background vacuum in the analysis chamber was better than 2 x10^{-9} mbar. The narrow scan spectra for Fe2p_{3/2} and As2p_{3/2} were calibrated by setting carbon 1s binding energy at 284.6 eV and fitted with a nonlinear least-squares curve-fitting program (Advantage software). The peaks were identified based on both literature and analytically derived data.

S2.12 pH and electrical conductivity measurement

pH and electrical conductivity (EC) of unmodified and modified biochars were measured in both water and CaCl₂ maintaining a 1:20 biochar to solution ratio (w/V). pH values were measured using a pH meter (Mettler Toledo FF28, Australia), supplied with a combined electrode, calibrated using commercial pH 4.01, 7.01 and 9.23 buffers. All analysis were performed in triplicate and the average values were recorded. Results were shown in Table S2.

S2.13 Major cations analysis

Determination of As and other major metals such as Na, K, Mg, Ca, Fe, Al, and P of biochars were extracted by microwave digestion in aqua regia following USEPA 3051 40 method. An inductively coupled plasma optical-emission spectrometer (ICP-OES, PerkinElmer Avio 200, USA) setting with dual view (axial and radial) were used to determine the concentration of As and other major metals.

S3. Adsorption kinetic models

The pseudo-first-order kinetic model can be expressed using equation Eq. S1.

\[ \log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \]  

(Eq. S1)

Where \( k_1 \) is the pseudo-first-order rate constant (h⁻¹) and \( q_e \) (mg/g) is the adsorption capacity at equilibrium and \( q_t \) (mg/g) is the adsorbed amount of As\(^V\) after time \( t \) (h). Lagergren’s first-order rate constant \( k_1 \) and \( q_e \) were calculated from the slope and intercept of plots of \( \log(q_e - q_t) \) vs \( t \).
The pseudo-second order model is commonly used to describe adsorption kinetics in which chemical adsorption controls the adsorption rate. The number of active adsorption sites on the adsorbent surface and the number of adsorbate ions in the liquid phase together determines the adsorption capacity. The formation of chemical bond between adsorbate and number of adsorbing sites is the rate-limiting step. A close agreement between the theoretical and experimental adsorption capacities supports the adsorption process which is well described by pseudo second order kinetic model.

The pseudo-second-order kinetics have been applied for analysing chemisorption kinetics from aqueous solutions which can be expressed using equation Eq. S2.

\[
\frac{t}{q_t} = \frac{1}{k_2} \cdot \frac{1}{q_e^2} + \frac{t}{q_e} \quad \text{(Eq. S2)}
\]

Where \( k_2 \) is the pseudo-second-order rate constant (g/mg/h). \( q_e \) and \( q_t \) represent the amount of adsorbed As\(^V\) (mg/g) at equilibrium and at any time \( t \) (h). The parameters \( q_e \) and \( k_2 \) can be calculated from slope and intercept of pseudo second order kinetics plot of \( t/q_t \) vs \( t \).

Elovic model: Zeldowitsch developed a kinetic model which assumes that solid adsorbent surface is generically heterogeneous and no lateral interaction takes place between the adsorbed solute. Elovich model is represented by the following expression Eq. S3.

\[
q_t = \beta \ln(\alpha \beta) + (\ln t) \quad \text{(Eq. S3)}
\]

Where \( q_t \) is the amount of adsorbed As\(^V\) by biochar at any time \( t \), \( \alpha \) is the adsorption kinetic at the initial time (mg/g.h) and \( \beta \) is the adsorption constant related to the extent of surface coverage and the activation energy for chemisorption (g/mg). The constants \( \alpha \) and \( \beta \) can be obtained from the slope and intercept of the linear plot of \( q_t \) vs \( \ln t \).

The kinetic and isotherms study help to identify the adsorption process, but it cannot predict the diffusion mechanism as well as rate-limiting step in the adsorption process. The transfer of solute from the aqueous phase to the adsorbent particle surface may be assumed in one or more steps, e.g. film or external diffusion, intra-particle or pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one-step. Generally, intra-particle diffusion is often controlled rate-limiting step. Weber and Morris proposed an functional relationship of intra-particle diffusion for an adsorption system. Intraparticle
diffusion is solely responsible for the rate controlling in the adsorption process if a plot of adsorbed As\textsuperscript{V} against the square root of reaction time generate a straight line. The Intra-particle diffusion model can be expressed using equation Eq. S4.

\[ q_t = k_{id} t^{1/2} + C \]  
(Eq. S4)

where, \( q_t \) is the adsorption capacity at any time \( t \) and \( k_{id} \) is the intra particle diffusion rate constant (mg/g h\( ^{1/2} \)) and \( C \) (mg/g) is the constant which gives an impression of the film thickness of the boundary layer. It is observed that the larger the intercept, the greater the contribution of the surface adsorption in the rate limiting step.\textsuperscript{19} The slope and intercept of the linear plot of \( q_t \) Vs \( t^{1/2} \) was used to calculate \( K_{id} \) and \( C \). If the plot of \( q_t \) vs \( t^{1/2} \) is linear and passes through the origin, i.e. \( C=0 \), then the adsorption process is considered to be controlled by the Intraparticle diffusion\textsuperscript{16} and multi-linear plot attributed to the process controlled by more than one mechanism.\textsuperscript{20}

**S4. Adsorption isotherm models**

Four sorption isotherm models were used to fit the equilibrium experimental data of As\textsuperscript{V} sorption to unmodified and modified biochars, namely the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) models (Table 2). The Langmuir isotherm assumes that the valid monolayer adsorbent homogenously covering the adsorbent surface consists of identical binding sites with equal adsorption activated energy and none of the binding sites of adsorbent affects its neighbours\textsuperscript{10, 21}, thus adopts uniform energies of adsorption on the surface and no transmigration adsorbate in the plane of the surface. The Freundlich isotherm is based on the assumption that multilayer adsorption on an energetically heterogeneous surface and can be used to describe the chemisorption process.

The equation Eq. S5 is used to describe in the Langmuir model (monolayer model).\textsuperscript{22}

\[ q_e = q_m C_e K_L/(1 + C_e K_L) \]  
(Eq. S5)

Where \( q_e \) is the adsorbed concentration of As\textsuperscript{V} at equilibrium in solid phase (mg/g), and \( q_m \) is the maximum adsorption capacity of As\textsuperscript{V} (mg/g). \( C_e \) (mg/L) is the concentration of As\textsuperscript{V} at equilibrium, and \( K_L \) is an equilibrium constant (L/mg) related to binding strength. The constant, \( K_L \) is calculated from slope and intercept of the linear plots of \( C_e/q_e \) versus \( C_e \), respectively.
Additionally, the important characteristics of the Langmuir isotherm can be explained by the separation factor ($R_L$), which is calculated by the equation Eq. S6.

$$R_L = \frac{1}{1+K_L C_0}$$  \hspace{1cm} (Eq. S6)

Where $C_0$ is the initial concentration of As$^V$ (mg/L). There are four probabilities for the $R_L$ value; (i) for favourable adsorption, $0 < R_L < 1$, (ii) for unfavourable adsorption, $R_L > 1$, (iii) for linear adsorption, $R_L = 1$, and (iv) for irreversible adsorption, $R_L = 0$.

The Freundlich model assumes a heterogeneous adsorption surface and active sites with different energy. The Freundlich equation (nonlinear model) is an empirical adsorption model usually expressed as the following equation (Eq. S7).  \hspace{1cm} (Eq. S7)

$$q_e = K_F C_e^{1/n}$$

Where $q_e$ and $C_e$ are defined previously, $K_F$ is a Freundlich affinity coefficient related to the measure of the adsorption capacity and $n$ is a Freundlich exponential coefficient measure of the adsorption intensity. Linear form of Freundlich equation is expressed by equation (Eq. S8).

$$\log q_e = \frac{1}{n} \log C_e + \log K_f$$  \hspace{1cm} (Eq. S8)

Temkin isotherm model considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms and suggested that, the heat of adsorption of all the molecules in the layer decreases linearly due to increasing surface coverage. Temkin isotherm is valid only for an intermediate range of ion concentrations. The linear form of Temkin isotherm has been generally applied in the following equation (Eq. S9).

$$q_e = B \ln A + B \ln C_e$$  \hspace{1cm} (Eq. S9)

Where $q_e$ is the amount of As$^V$ adsorbed at equilibrium (mg/g); $C_e$ is the concentration of As$^V$ in solution at equilibrium (mg/L). $B$ is a constant related to the heat of adsorption and it is defined by the expression $B = RT/b$, $b$ is the Temkin constant (J/mol), $T$ is the absolute temperature (K), $R$ is the gas constant (8.314 J/mol K), and $A$ is the Temkin isotherm constant.
From the plot of \( q_e \) vs \( \ln C_e \), \( B \) and \( A \) can be calculated from the slopes (\( B \)) and intercepts (\( B \ln A \)) respectively.

The classical derivation of the Temkin isotherm deals with structural heterogeneity and assumes a constant distribution of sites in a range of energies. It has also been suggested that the Temkin isotherm properly describes the case of induced heterogeneity among the biochar particles during the adsorption process.

The Dubinin-Radushkevich (D-R) isotherm model is an empirical model, which initially formulated for the adsorption process following a pore filling mechanism, gives insight into the biomass porosity as well as the adsorption energy. The D-R isotherm model can be used to determine whether the nature of the adsorption process is physical or chemical. It is generally applied to express the sorption process occurred onto homogeneous and heterogeneous surfaces. A distinguishing feature of the D-R isotherm is that it is temperature dependent; hence, when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed \( \text{As}^V \) versus the square of potential energy, all suitable data can be determined. The non-linear expression of Dubinin-Radushkevich isotherm model can be illustrated by equations Eq. S10–11.

\[
\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{Eq. S10}
\]

where \( q_e \) is the amount of \( \text{As}^V \) adsorbed per unit weight of adsorbent (mg/L); \( q_m \) is the maximum \( \text{As}^V \) adsorption capacity (mg/g); \( \beta \) is the activity coefficient related to the mean free energy of adsorption (D-R constant), \( E \) (mol\(^2\)/J\(^2\)); and \( \varepsilon \) is the Polanyi potential can be expressed as follows:

\[
\varepsilon = RT \ln(1 + 1/C_e) \tag{Eq. S11}
\]

The mean free energy of activation (E; kJ/mol) is expressed by the equation Eq. S12.

\[
E = 1/\sqrt{2\beta} \tag{Eq. S12}
\]

Where \( R \) is the gas constant (8.314 J/mol K) and \( T \) is the temperature (K). \( q_m \) and \( \beta \) (mol\(^2\)/kJ\(^2\)) can be calculated from the intercept and the slopes of the plot of \( \ln q_e \) vs \( \varepsilon^2 \). The information regarding the adsorption mechanism, whether physical or chemical in nature, can be determined from the E(kJ/mol) value.
**Table S1.** Zeta potential of pristine and modified biochars

| pH | BSBC | FeB      | FeCl₃B   | Zr-FeCl₃B |
|----|------|----------|----------|-----------|
| 2  | +5.21| +22.4    | +12.23   | +25.02    |
| 3  | +2.63| +17.84   | +16.2    | +21.15    |
| 4  | -2.03| +9.34    | +7.66    | +15.43    |
| 5  | -7.65| -4.33    | -1.46    | +9.98     |
| 6  | -10.28| -6.87    | -6.66    | +4.78     |
| 7  | -13.54| -15.93   | -6.86    | -13.79    |
| 8  | -14.73| -6.91    | -7.05    | -12.21    |
| 9  | -17.36| -7.23    | -10.13   | -16.45    |
| 10 | -20.59| -11.57   | -12.57   | -19.72    |
| 11 | -24.21| -19.81   | -15.36   | -25.68    |

**Table S2.** Physico-chemical characteristics of Fe-modified biochars

| Biochar | Specific surface area (BET), m²/g | Pore volume, cm³/g | Pore size/diameter, nm | Average particle size, nm | pH<sub>PZC</sub> | EC (mS/cm) | pH | CEC (cmol(+)/kg) |
|---------|----------------------------------|--------------------|------------------------|---------------------------|------------------|------------|----|------------------|
| BSBC    | 4.6                              | 0.006              | 6.51                   | 1292                      | 3.6              | 0.32       |    | 7.12             | 5.98             | 8.1               |
| FeB     | 6.6                              | 0.007              | 5.75                   | 909                       | 4.7              | 18.96      |    | 5.41             | 5.28             | 5.11              |
| FeCl₃B  | 24.02                            | 0.017              | 4.80                   | 249                       | 4.9              | 20.54      |    | 5.88             | 5.45             | 5.06              |
| Zr-FeCl₃B | 25.51                             | 0.019              | 3.92                   | 235                       | 6.3              | 18.57      |    | 5.64             | 5.17             | 5.63              |
### Table S3. Total elemental composition of biochars

| Biochar     | Mass %   | mg/g    |
|-------------|----------|---------|
|             | C        | N       | S      | Zr     | Na  | K    | Mg | Ca | Fe | Al | P   |
| BSBC        | 22.88    | 3.60    | 1.12   | -      | 1.99 | 4.24 | 7.76 | 22.97 | 100.69 | 29.65 | 54.86 |
| FeB         | 21.83    | 3.27    | 1.05   | -      | 71.54 | 1.82 | 4.19 | 12.37 | 176.21 | 19.26 | 43.47 |
| FeCl₃B      | 22.96    | 3.47    | 1.67   | -      | 12.75 | 2.34 | 4.05 | 15.04 | 228.17 | 22.10 | 42.86 |
| Zr-FeCl₃B   | 17.88    | 2.76    | 0.85   | 3.1    | 27.18 | 1.59 | 4.35 | 11.88 | 238.82 | 17.32 | 6.12  |

### Table S4. Major elemental composition of As-loaded biochars obtained from SEM–EDS analysis

| Element           | FeB + As | FeCl₃B + As | Zr-FeCl₃B + As |
|-------------------|----------|-------------|----------------|
|                   | [wt%]    | [at%]       | Error in wt.% (1 Sigma) | [wt%] | [at%] | Error in wt.% (1 Sigma) | [wt%] | [at%] | Error in wt.% (1 Sigma) |
| Oxygen (K-series) | 28.53    | 31.58       | 3.75            | 36.29 | 40.61 | 4.6             | 18.41 | 42.65 | 1.76          |
| Aluminium (K-series) | 3.52     | 2.31        | 0.20            | 4.73  | 3.14  | 0.26           | 2.14  | 2.94  | 0.10          |
| Silicon (K-series) | 2.54     | 1.60        | 0.14            | 2.16  | 1.38  | 0.12           | 1.97  | 2.60  | 0.08          |
| Phosphorus (K-series) | 4.08    | 2.33        | 0.19            | 7.43  | 4.29  | 0.32           | 8.11  | 9.71  | 0.24          |
| Calcium (K-series) | 1.03     | 0.45        | 0.07            | 0.98  | 0.44  | 0.06           | 0.20  | 0.13  | 0.038         |
| Sulfur (K-series)  | 2.26     | 1.24        | 0.11            | 0.36  | 0.2   | 0.05           | 1.27  | 1.47  | 0.06          |
| Iron (K-series)    | 24.78    | 7.86        | 0.70            | 15.32 | 4.91  | 0.45           | 46.24 | 30.69 | 0.87          |
| Arsenic (K-series) | 1.0      | 0.24        | 0.12            | 3.65  | 0.87  | 0.2            | 3.89  | 1.93  | 0.16          |
| Zirconium (L-series) | -       | -          | -               | -     | -     | -               | 16.84 | 6.84  | 0.47          |
| Biochar | T (K) | 1/T  | lnKc (J/mol.K) | R (J/mol.K) | Slope | Intercept | $\Delta H = \text{slope} \times R$ (J/mol.K) | $\Delta S = \text{Intercept} \times R$ (J/mol.K) | $\Delta G = \Delta H - T \times \Delta S$ (J/mol) | $\Delta G$ (KJ/mol) |
|---------|------|------|----------------|-------------|-------|-----------|---------------------------------|---------------------------------|---------------------------------------------|------------------|
| FeB     | 277  | 0.00361 | -0.36346       | 8.314       | -1.5844 | 5.4201    | 13.17                           | 45.06                           | -12469.20                                   | -12.47           |
|         | 288  | 0.003472 | 0.004808      | 8.314       | -1.5844 | 5.4201    | 13.17                           | 45.06                           | -12964.89                                   | -12.96           |
|         | 293  | 0.003413 | 0.058128      | 8.314       | -1.5844 | 5.4201    | 13.17                           | 45.06                           | -13190.20                                   | -13.19           |
|         | 298  | 0.003356 | 0.092298      | 8.314       | -1.5844 | 5.4201    | 13.17                           | 45.06                           | -13415.52                                   | -13.42           |
|         | 303  | 0.0033  | 0.136798      | 8.314       | -1.5844 | 5.4201    | 13.17                           | 45.06                           | -13640.83                                   | -13.64           |
|         | 313  | 0.003195 | 0.35478       | 8.314       | -1.5844 | 5.4201    | 13.17                           | 45.06                           | -14091.46                                   | -14.09           |
| FeCl$_3$B | 277  | 0.00361 | -0.32081      | 8.314       | -1.6497 | 5.6949    | 13.72                           | 47.35                           | -13101.51                                   | -13.10           |
|         | 288  | 0.003472 | 0.041419      | 8.314       | -1.6497 | 5.6949    | 13.72                           | 47.35                           | -13622.34                                   | -13.62           |
|         | 293  | 0.003413 | 0.108214      | 8.314       | -1.6497 | 5.6949    | 13.72                           | 47.35                           | -13859.07                                   | -13.86           |
|         | 298  | 0.003356 | 0.161039      | 8.314       | -1.6497 | 5.6949    | 13.72                           | 47.35                           | -14095.81                                   | -14.10           |
|         | 303  | 0.0033  | 0.198671      | 8.314       | -1.6497 | 5.6949    | 13.72                           | 47.35                           | -14332.55                                   | -14.33           |
|         | 313  | 0.003195 | 0.416442      | 8.314       | -1.6497 | 5.6949    | 13.72                           | 47.35                           | -14806.02                                   | -14.81           |
| Zr-FeCl$_3$B | 277  | 0.00361 | -0.18232      | 8.314       | -1.6358 | 5.752     | 13.60                           | 47.82                           | -13233.13                                   | -13.23           |
|         | 288  | 0.003472 | 0.108409      | 8.314       | -1.6358 | 5.752     | 13.60                           | 47.82                           | -13759.17                                   | -13.76           |
|         | 293  | 0.003413 | 0.194157      | 8.314       | -1.6358 | 5.752     | 13.60                           | 47.82                           | -13998.28                                   | -14.00           |
|         | 298  | 0.003356 | 0.265082      | 8.314       | -1.6358 | 5.752     | 13.60                           | 47.82                           | -14237.39                                   | -14.24           |
|         | 303  | 0.0033  | 0.314904      | 8.314       | -1.6358 | 5.752     | 13.60                           | 47.82                           | -14476.50                                   | -14.48           |
|         | 313  | 0.003195 | 0.52869       | 8.314       | -1.6358 | 5.752     | 13.60                           | 47.82                           | -14954.73                                   | -14.95           |
### Table S6. Atomic (%) of FeB, FeCl₃B and Zr-FeCl₃B biochars before and after adsorbed with As⁵⁺ by XPS analysis.

| Biochar       | Fe₂p½ as Fe³⁺ (711.76 eV) | Fe₂p½ as multiplets peak Fe³⁺ (715.76 eV) | Fe₂p½ Satellite peak (Fe³⁺ and Fe) (719.42 eV) | Zr as ZrO₂ (182.64 eV) | Zr as Zr-Zr (185.35 eV) | As⁵⁺ (43.58 eV) | As³⁺ (45.54 eV) |
|---------------|--------------------------|------------------------------------------|-----------------------------------------------|-------------------------|------------------------|-----------------|-----------------|
| FeB           | 3.0                      | 1.02                                     | 0.86                                          | -                       | -                      | -               | -               |
| FeCl₃B        | 4.02                     | 1.51                                     | 1.23                                          | -                       | -                      | -               | -               |
| Zr-FeCl₃B     | 3.44                     | 1.32                                     | 0.98                                          | 0.87                    | -                      | -               | -               |
| FeB + As      | 1.8                      | 0.52                                     | 0.42                                          | -                       | -                      | -               | 0.41            |
| FeCl₃B + As   | 2.48                     | 0.78                                     | 0.53                                          | -                       | -                      | 0.06            | 0.38            |
| Zr-FeCl₃B + As| 1.8                      | 0.59                                     | 0.4                                           | 1.28                    | -                      | 0.08            | 0.45            |

### Table S7. Experimental conditions used for As⁵⁺ adsorption

| Name of Experiment | Concentration of As(V) (mg/L) | Background electrolyte (NaNO₃) | pH | Biochar density (g/L) | Temperature (°C) |
|--------------------|------------------------------|--------------------------------|----|-----------------------|------------------|
| pH                 | 10                           | 0.01 M                         | 2–10 | 2                     | 22 ± 0.5         |
| Kinetics           | 10                           | 0.01 M                         | 5, 6 | 2                     | 22 ± 0.5         |
| Adsorption         | 1–250                        | 0.01 M                         | 5, 6 | 2                     | 22 ± 0.5         |
| Biochar dose       | 20                           | 0.01 M                         | 5, 6 | 1–10                  | 22 ± 0.5         |
| Ionic strength     | 20                           | 0.01–1.0 M                     | 5, 6 | 2                     | 22 ± 0.5         |
| Interfering ions (0.1 M) | 20         | 0.01 M                         | 5, 6 | 2                     | 22 ± 0.5         |
| Thermodynamics     | 20                           | 0.01 M                         | 5, 6 | 2                     | 4, 15, 20, 25, 30, and 40 |
| Desorption         | 20                           | 0.01 M                         | -   | 2                     | 22 ± 0.5         |

NaOH and HNO₃
Figure S1. Point of zero charge (PZC) of FeB, FeCl$_3$B and Zr-FeCl$_3$B
Figure S2. FTIR spectra of As-loaded region (A) 725–852 cm\(^{-1}\) and (B) 3602–3802 cm\(^{-1}\)
Figure S3. X-ray diffraction (XRD) pattern of biochars before (A), and after (B), $\text{As}^{V}$ sorption
Figure S4. XPS survey profile of As-loaded-FeB (A), FeCl$_3$B (B), and Zr-FeCl$_3$B (C)
Figure S5. XPS spectrum of O1s after reaction with As by FeB (A), FeCl3B (B), and Zr-FeCl3B (C), respectively.
S7. REFERENCES

1. Appel, C.; Ma, L. Q.; Rhue, R. D.; Kennelley, E., Point of zero charge determination in soils and minerals via traditional methods and detection of electroacoustic mobility. *Geoderma* **2003**, *113*, (1-2), 77-93.
2. Jiang, S.; Nguyen, T. A.; Rudolph, V.; Yang, H.; Zhang, D.; Ok, Y. S.; Huang, L., Characterization of hard-and softwood biochars pyrolyzed at high temperature. *Environmental geochemistry and health* **2017**, *39*, (2), 403-415.
3. Morais, F. I.; Page, A.; Lund, L., The Effect of pH, Salt Concentration, and Nature of Electrolytes on the Charge Characteristics of Brazilian Tropical Soils 1. *Soil Science Society of America Journal* **1976**, *40*, (4), 521-527.
4. Parks, G. A.; Bruyn, P. D., The zero point of charge of oxides.1. *The Journal of Physical Chemistry* **1962**, *66*, (6), 967-973.
5. Jiang, J.; Xu, R.-k.; Jiang, T.-y.; Li, Z., Immobilization of Cu (II), Pb (II) and Cd (II) by the addition of rice straw derived biochar to a simulated polluted Ultisol. *Journal of hazardous materials* **2012**, *229*, 145-150.
6. Mukherjee, A.; Zimmerman, A.; Harris, W., Surface chemistry variations among a series of laboratory-produced biochars. *Geoderma* **2011**, *163*, (3-4), 247-255.
7. Zhao, L.; Cao, X.; Zheng, W.; Wang, Q.; Yang, F., Endogenous minerals have influences on surface electrochemistry and ion exchange properties of biochar. *Chemosphere* **2015**, *136*, 133-139.
8. Gillman, G.; Sumpter, E., Modification to the compulsive exchange method for measuring exchange characteristics of soils. *Soil Research* **1986**, *24*, (1), 61-66.
9. Brunauer, S.; Emmett, P. H.; Teller, E., Adsorption of gases in multimolecular layers. *Journal of the American chemical society* **1938**, *60*, (2), 309-319.
10. Niazi, N. K.; Bibi, I.; Shahid, M.; Ok, Y. S.; Burton, E. D.; Wang, H.; Shaheen, S. M.; Rinklebe, J.; Lüttge, A., Arsenic removal by perilla leaf biochar in aqueous solutions and groundwater: an integrated spectroscopic and microscopic examination. *Environmental Pollution* **2018**, *232*, 31-41.
11. Ho, Y.-S.; McKay, G., Pseudo-second order model for sorption processes. *Process biochemistry* **1999**, *34*, (5), 451-465.
12. Sheela, T.; Nayaka, Y. A., Kinetics and thermodynamics of cadmium and lead ions adsorption on NiO nanoparticles. *Chemical Engineering Journal* **2012**, *191*, 123-131.
13. Ho, Y.-S., Review of second-order models for adsorption systems. *Journal of hazardous materials* **2006**, *136*, (3), 681-689.
14. Zeldowitsch, J., Adsorption site energy distribution. *Acta phys. chim. URSS* **1934**, *1*, 961-973.
15. Srivastava, V. C.; Mall, I. D.; Mishra, I. M., Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA. *Journal of hazardous materials* **2006**, *134*, (1-3), 257-267.
16. Chen, S.; Yue, Q.; Gao, B.; Li, Q.; Xu, X., Removal of Cr (VI) from aqueous solution using modified corn stalks: Characteristic, equilibrium, kinetic and thermodynamic study. *Chemical Engineering Journal* **2011**, *168*, (2), 909-917.
17. Han, R.; Zhang, L.; Song, C.; Zhang, M.; Zhu, H.; Zhang, L., Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode. *Carbohydrate Polymers* **2010**, *79*, (4), 1140-1149.
18. Weber, W. J.; Morris, J. C., Kinetics of adsorption on carbon from solution. *Journal of the Sanitary Engineering Division* **1963**, *89*, (2), 31-60.
19. Kannan, N.; Sundaram, M. M., Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study. *Dyes and pigments* **2001**, *51*, (1), 25-40.
20. Chio, C.-P.; Lin, M.-C.; Liao, C.-M., Low-cost farmed shrimp shells could remove arsenic from solutions kinetically. *Journal of hazardous materials* **2009**, *171*, (1-3), 859-864.
21. Baig, S. A.; Zhu, J.; Muhammad, N.; Sheng, T.; Xu, X., Effect of synthesis methods on magnetic Kans grass biochar for enhanced As (III, V) adsorption from aqueous solutions. *Biomass and Bioenergy* **2014**, *71*, 299-310.

22. Langmuir, I., The constitution and fundamental properties of solids and liquids. Part I. Solids. *Journal of the American chemical society* **1916**, *38*, (11), 2221-2295.

23. Sarı, A.; Şahinoğlu, G. n. r.; Tüzen, M., Antimony (III) adsorption from aqueous solution using raw perlite and Mn-modified perlite: equilibrium, thermodynamic, and kinetic studies. *Industrial & engineering chemistry research* **2012**, *51*, (19), 6877-6886.

24. Niazi, N. K.; Bibi, I.; Shahid, M.; Ok, Y. S.; Shaheen, S. M.; Rinklebe, J.; Wang, H.; Murtaza, B.; Islam, E.; Nawaz, M. F., Arsenic removal by Japanese oak wood biochar in aqueous solutions and well water: Investigating arsenic fate using integrated spectroscopic and microscopic techniques. *Science of the Total Environment* **2018**, *621*, 1642-1651.

25. Freundlich, H., Over the adsorption in solution. *J. Phys. Chem* **1906**, *57*, (385471), 1100-1107.