Supplementary Materials

Batch and Continuous Reactor Studies for the Adsorption of As(III) from wastewater using a hybrid biochar loaded with transition metal oxides: Kinetics and Mass Transfer Analysis

Isotherm Modeling

Langmuir isotherm model is represented in Eq. (1):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{1}$$

where q_m is the maximum adsorption capacity of As(III) ions in mg/g and K_L is the Langmuir constant in *L/mg*. Evaluation of the separation factor (R_L) determines the feasibility of the adsorption process. It can be calculated using Eq. (2):

$$R_L = \frac{1}{1+K_L.C_i} \tag{2}$$

The isotherm is considered to be linear if $R_L = 1$, favourable if $0 < R_L < 1$, unfavourable if $R_L > 1$ and if $R_L = 0$ indicates irreversible process.

Freundlich isotherm model is represented in Eq. (3):

$$logq_e = \left(\frac{1}{n}\right) logC_e + logK_F \tag{3}$$

where n indicates the degree of heterogeneity on the adsorbent's surface and K_F is the Freundlich constant in *L/mg*. For a favourable adsorption process, ($1/n$) < 1.

Temkin isotherm model is shown in Eq. (4):

$$q_e = \left(\frac{RT}{b_T}\right) lnA_T + \left(\frac{RT}{b_T}\right) lnC_e \tag{4}$$

where A_T is the equilibrium binding constant (*L/g*) and b_T is represents the heat of adsorption.

Dubinin–Radushkevich (D-R) isotherm equation and its parameter calculation are shown in Eqs. (5), (6) and (7):

$$ln q_e = ln q_m - k.\varepsilon^2 \tag{5}$$

$$\varepsilon = RT ln\left(1 + \frac{1}{C_e}\right) \tag{6}$$

$$E = \left[\frac{1}{\surd(-2k)}\right] \tag{7}$$

where *k* is the average adsorption energy required per mole of the adsorbate in mol^2/kJ^2. ε is the Polanyi potential which can be calculated from Eq. (6) and *E* is the mean free energy in *kJ/mol* determined from Eq. (7). *R* is the gas constant ($8.314\ J.mol^{-1}K^{-1}$) and *T* is the absolute temperature in *K*.

Breakthrough Curve Modeling

Eq. (8) shows the model equation for Adams-Bohart model equation:

$$ln\left(\frac{C_t}{C_o}\right) = k_{AB}C_o.t - k_{AB}N_o\left(\frac{Z}{u}\right) \tag{8}$$

where C_t and C_o are the instantaneous and initial As(III) ions concentration (mg/L), k_{AB} is the Adams-Bohart kinetic constant (L/mg.min), N_o is the adsorption capacity (mg/L), *u* is the velocity (cm/min) and *Z* is the bed depth (cm). N_o and k_{AB} are obtained respectively from the intercept and slope of the linear plot of $ln(C_t/C_o)$ versus time (*t*).

BDST model equation is shown in Eq. (9):

$$t = \left(\frac{N_o}{uC_o}x\right) - \left[\frac{1}{KC_o}ln\left(\frac{C_o}{C_B} - 1\right)\right] \tag{9}$$

where C_B is the breakthrough concentration (*mg/L*), K is the rate constant for adsorption (*L/mg.min*) and t is the service time (*min*). The above equation can be used to determine the service time (t) for a given bed depth (x) which must operated for a pre-determined values of linear feed velocity (u) for a laboratory test column.

Substituting $t = 0$ in Eq. (9), we get Eq. (10):

$$x_o = \frac{u}{KN_o} ln\left(\frac{C_o}{C_B} - 1\right) \tag{10}$$

where x_o is the minimum bed depth required to produce an effluent concentration C_B. It s also called as the *Critical Bed Depth*. It is the theoretically obtained bed depth necessary to ensure that the effluent concentration does not exceed breakthrough concentration at time (t) = 0 **[1]**.

In BDST model, Hutchins proposed a modified Bohart-Adams equation of the form shown in Eq. (11):

$$t = ax + b \tag{11}$$

where

$$a = slope = \frac{N_o}{uC_o} \tag{12}$$

$$b = intercept = \frac{1}{KC_o} ln\left(\frac{C_o}{C_B} - 1\right) \tag{13}$$

Eq. (14) shows the Thomas model equation:

$$ln\left(\frac{C_t}{C_o} - 1\right) = \frac{k_{TH} q_o m}{Q} - k_{TH} C_o. \tag{14}$$

where k_{TH} is the Thomas rate constant (*mL/min.mg*), q_o is the maximum adsorbate concentration in solid phase (*mg/g*), m is the adsorbent mass (g) and Q is the volumetric flow rate (*mL/min*). q_o and k_{TH} are determined from the intercept and slope values from the linear plot of $ln[(C_t/C_o)-1]$ against time (*t*) for a constant flow rate.

Table S1. Proximate Analysis of Mustard Cake

Components	Weight percentages
Moisture	5.51
Volatile matter	82.27
Fixed carbon	6.07
Ash	6.15

Table S2. Elemental Compositions of Fe-Mn Biochar

Element	Weight %	Atomic %	Net Int.	Error %	K ratio	Z	A	F
O K	27.36	56.76	718.05	2.76	0.2011	0.7771	0.9455	1.0000
MnK	8.10	4.89	50.22	12.38	0.0585	0.6598	1.0102	1.0845
FeK	64.54	38.35	321.05	4.30	0.4473	0.6850	1.0090	1.0027

Table S3. BET Surface Area, Pore Volume and Average Pore Diameter of the Native and Metal Oxides Loaded Biochar

Adsorbents	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
Native biochar	275.7	0.32	3.54
Fe-biochar	145.9	0.27	2.85
Mn-biochar	142.7	0.22	2.88
Fe-Mn-biochar	98.8	0.25	2.72

Table S4. Fixed Bed Column Parameters for As(III) using BCFM as Adsorbent

Parameters	Treated Volume (V_b) (mL)	Breakthrough time (t_b) (min)	As(III) adsorption capacity (q_{tot}) (mg)	As(III) removal %
Bed Depth, h (cm)[a]				
10 (m = 24.2 g)	2,010	250	28.48	78.65
20 (m = 46.5 g)	5,860	810	31.23	83.47
30 (m = 71.2 g)	10,380	1250	34.61	88.28
Flow Rate, Q (mL/min)[b]				
5	2,545	530	32.78	82.52

7.5	2010	250	28.48	78.65
10	850	140	18.56	55.27
Initial Concentration, C_o (mg/L)[c]				
0.5	4,390	510	27.98	80.32
1.0	2010	250	28.48	78.65
2.0	720	190	30.89	63.55

Breakthrough concentration = 0.045 mg/L

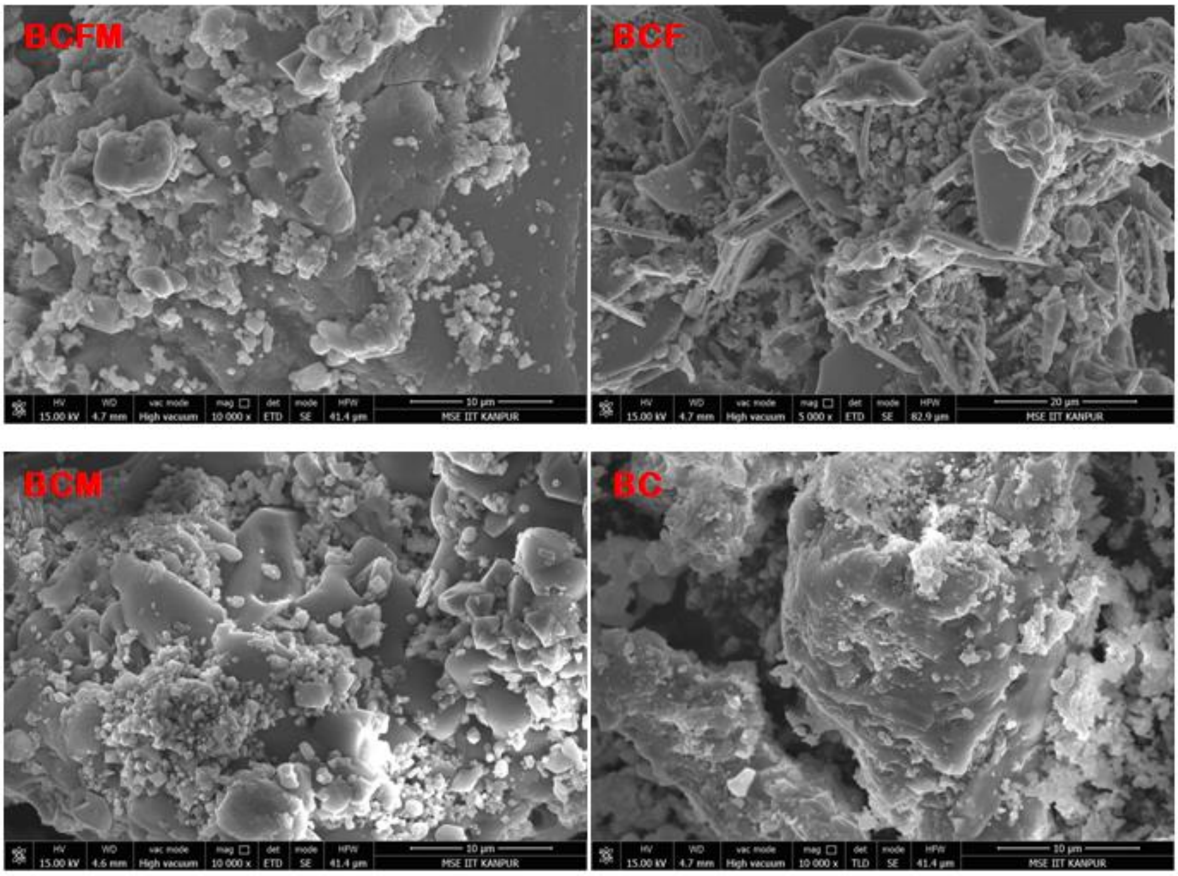
[a]C_o = 1.0 mg/L; Q = 7.5 mL/min

[b]C_o = 1.0 mg/L; h = 10 cm

[c]Q = 7.5 mL/min; h = 10 cm

Table S5. Estimated BDST Model Parameters at Different Breakthrough (*Q* = 7.5 mL/min; C_o = 1.0 mg/L; *ID* = 2.5 cm)

Breakthrough (%)	***a* (min/cm)**	***b* (min)**	**N_o (mg/L)**	***K* (L/mg.min)**	**R^2**
0.5	50	236.68	76.44	0.03	0.98
90	52.5	16.68	80.27	0.35	0.99



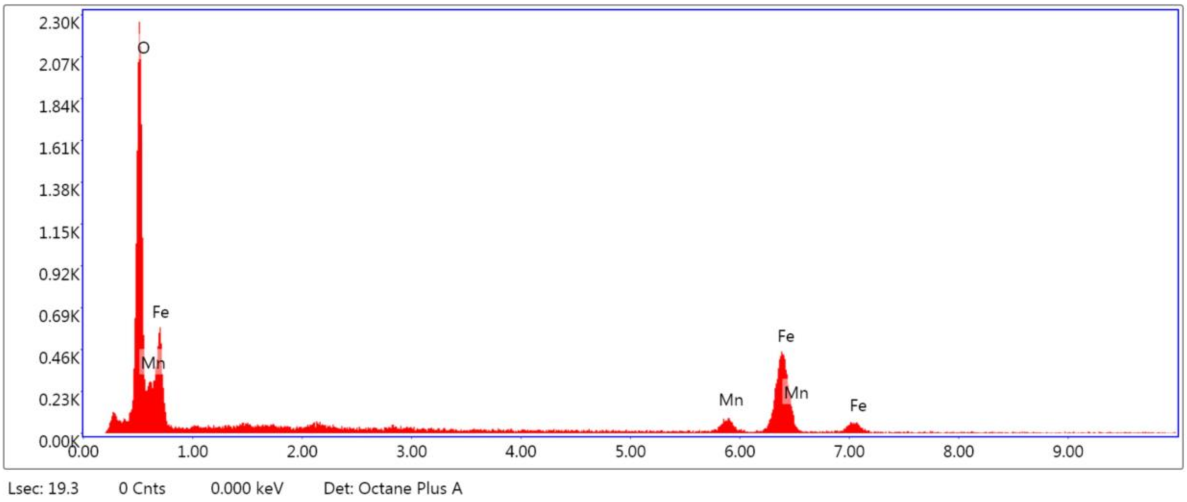


Fig. S1. SEM micrographs of the native and loaded biochar and EDX spectra of Fe-Mn oxides loaded biochar.

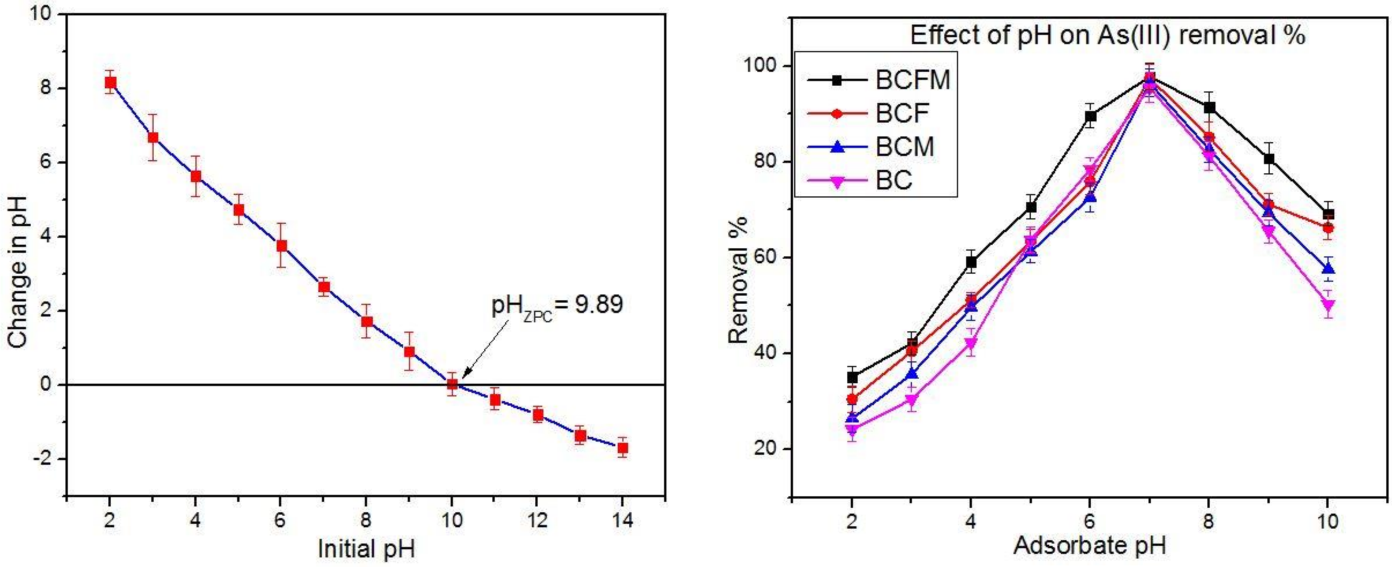


Fig. S2. (a) Point of zero charge (pH_{PZC}) for Fe-Mn loaded biochar; (b) Influence of pH on the removal% of As(III) ions using native and loaded biochar.

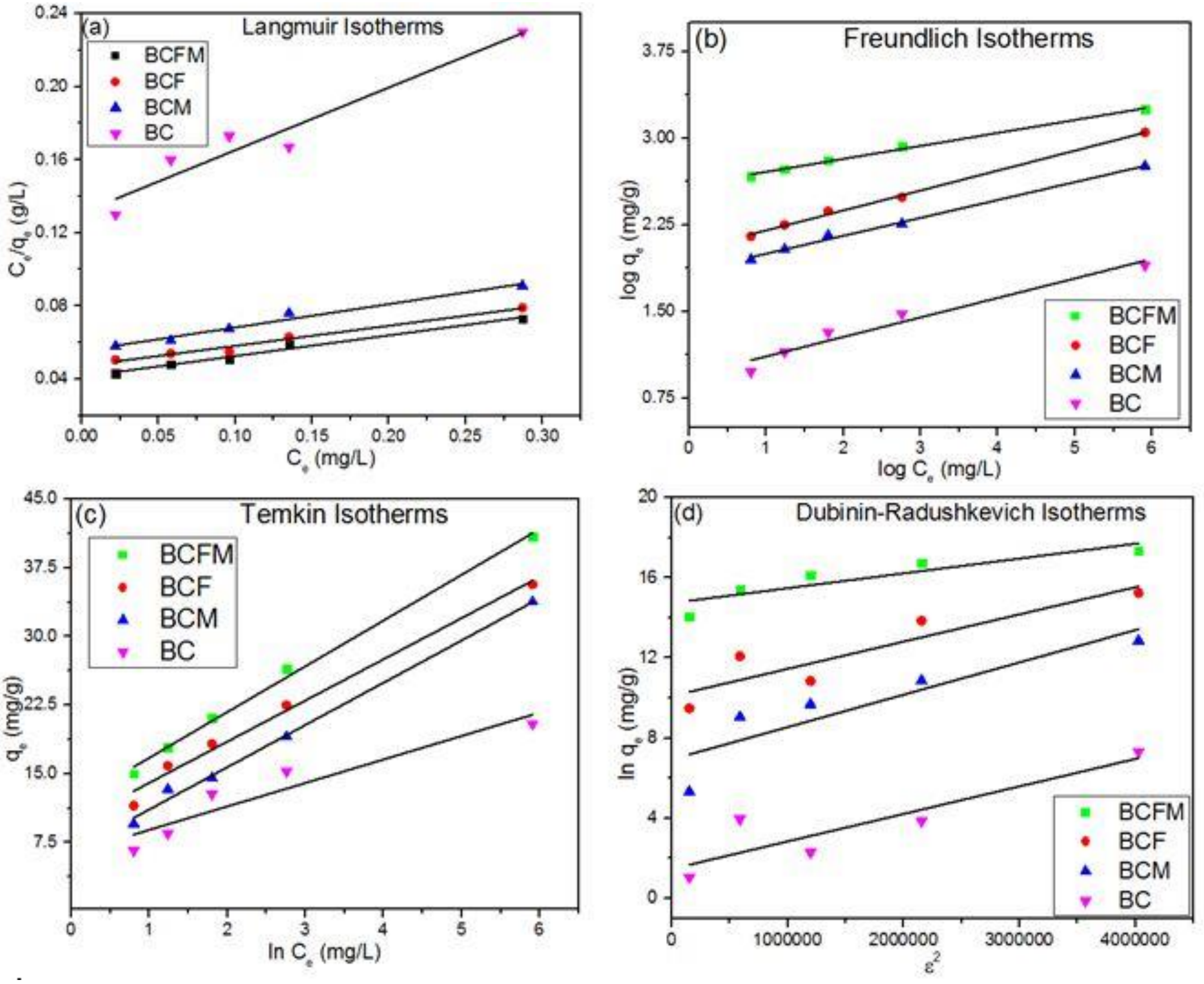


Fig. S3. Isotherms As(III) ions adsorption using native and loaded biochar.

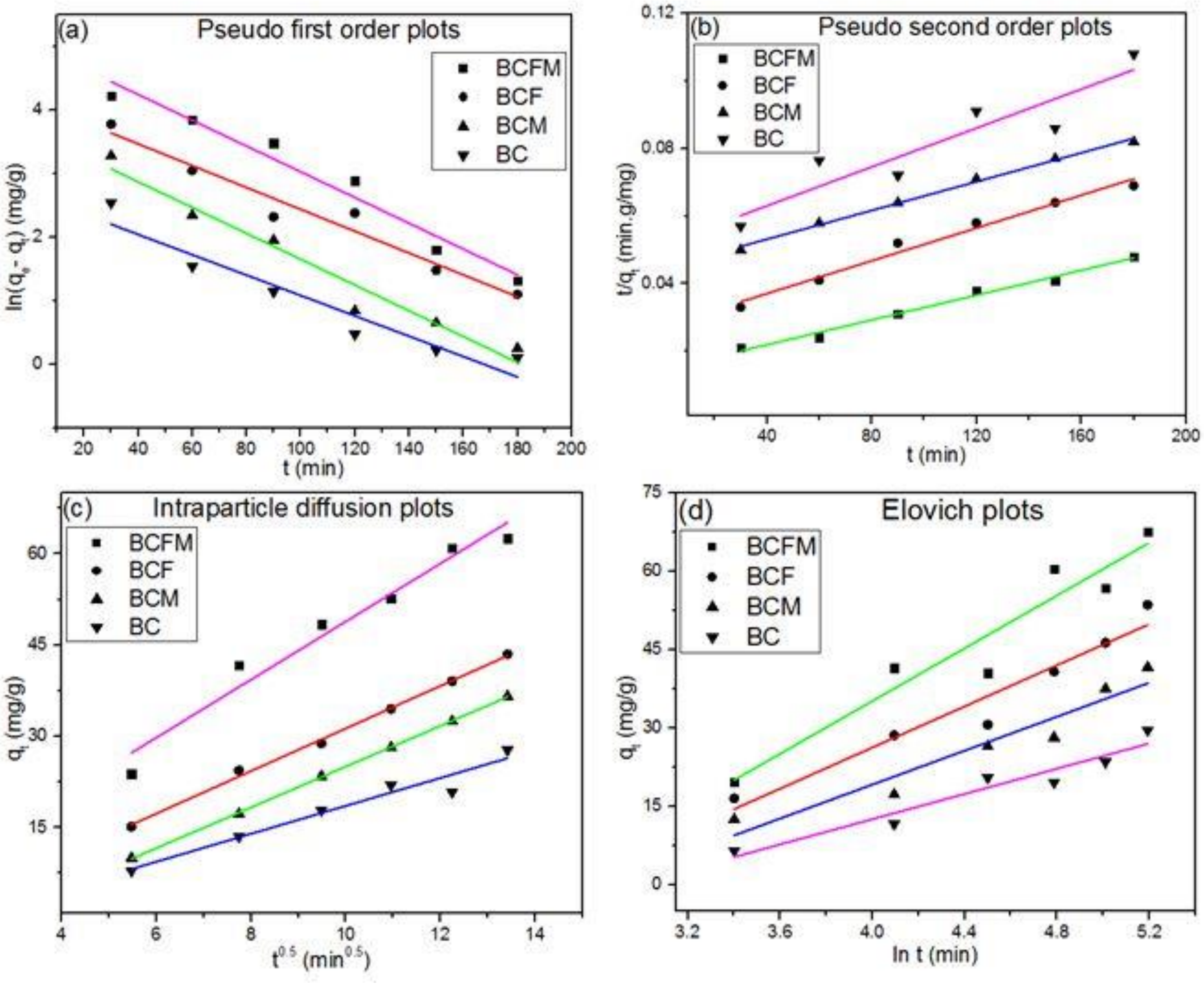


Fig. S4. Kinetic plots for As(III) adsorption using native and modified biochar

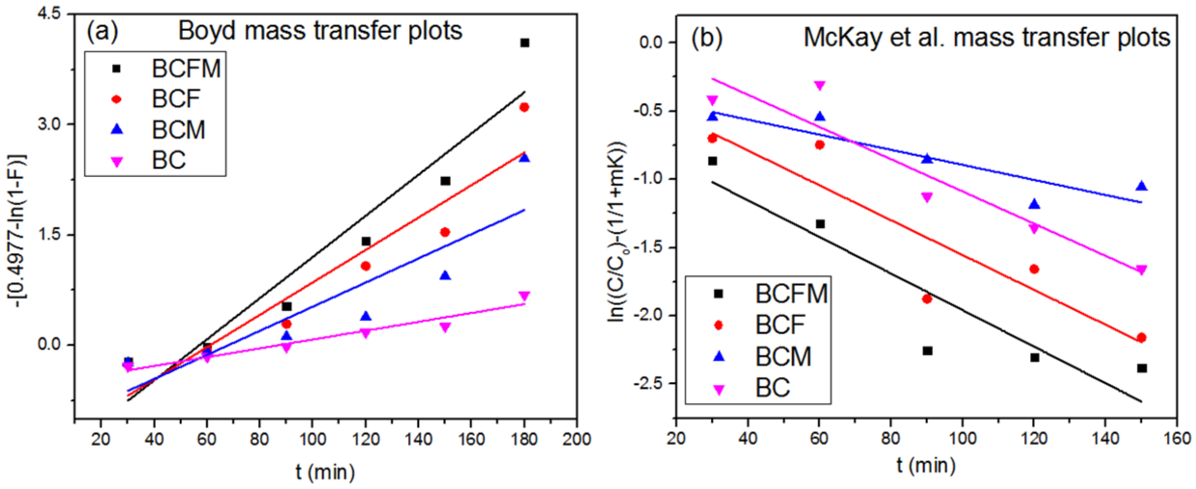


Fig. S5 (a) Boyd and (b) McKay et al. mass transfer plot for As(III) sorption using native and oxides loaded biochar.

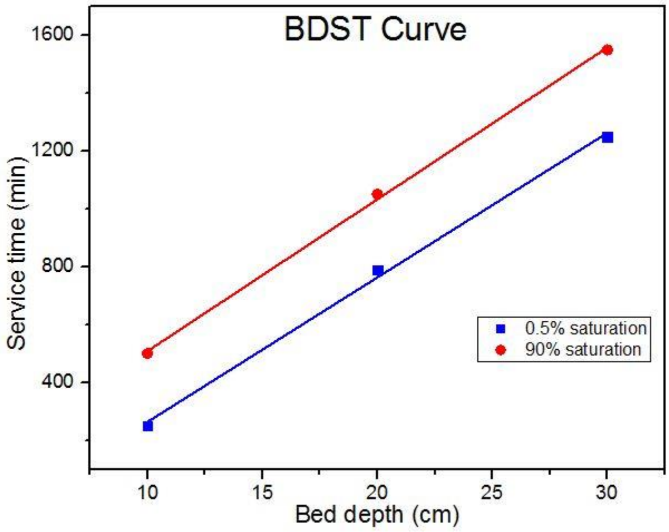


Fig. S6. Bed depth service time (BDST) plots for As(III) sorption.
(h = 10 *cm*; Q = 7.5 *mL/min*; C_o = 1.0 *mg/L*)

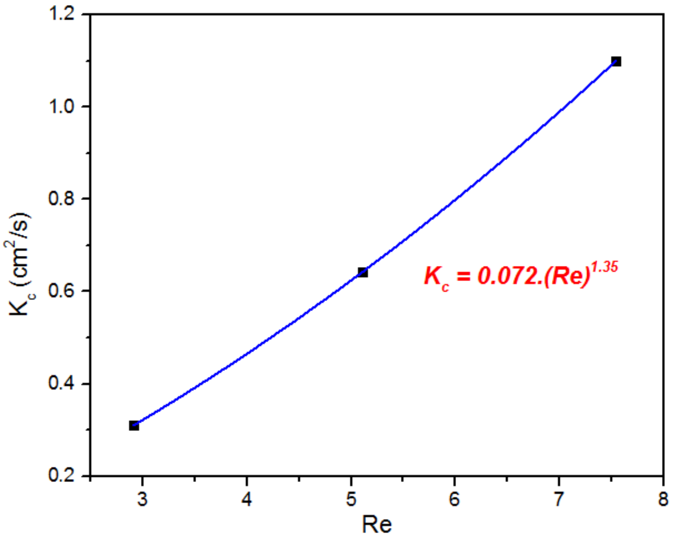


Fig. S7. Influence of mass transfer coefficients on Reynold's number in fixed bed As(III) adsorption.

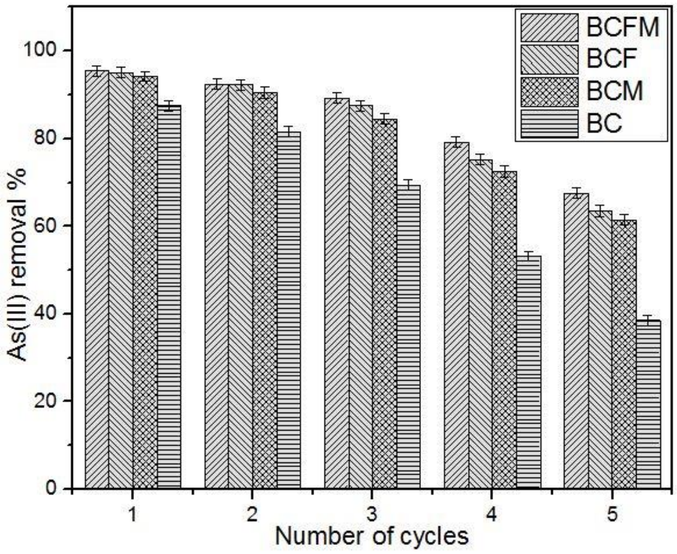


Fig. S8. Removal % of As(III) ions as a function of regeneration cycles.

Reference

1 Patel H. Fixed-bed column adsorption study: a comprehensive review. *Appl. Water Sci.* 2019;9:45.