Supporting information

Development of Vitamin B6-Mediated Biochar with Nano Zero-Valent Iron Coating for Oxytetracycline Removal through Adsorption and Degradation under Harsh Acidic Conditions

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Contents

1. Adsorption isotherm models

Four adsorption isotherm models were simulated to study the adsorption characteristics of modified biochar for OTC[1]. The equations are as follows:

Langmuir:

$$Q_e = \frac{Q_m K_l C_e}{1 + K_l C_e} \quad (1)$$

where C_e (mg/L) is the initial and equilibrium concentrations, Q_m (mg/g) is the theoretical maximum adsorption capacity, and K_l (L/mg) is the Langmuir equilibrium constant related to the surface heterogeneity representing the adsorption strength.

Freundlich:

$$Q_e = K_f C_e^{\frac{1}{n}} \quad (2)$$

where K_f (mg/g·(L/mg)$^{1/n}$) is the Freundlich adsorption capacity, and n is the Freundlich constant related to the surface heterogeneity representing the adsorption strength.

Temkin:

$$Q_e = Aln(K_T) + Aln(C_e) \quad (3)$$

where K_T (L/mg) is the equilibrium binding constant, and A (J/mol) is the Temkin adsorption heat-related coefficient.

2. Kinetic models

Three kinetic models were simulated to study the adsorption and removal characteristics of modified biochar for OTC[2]. The equations are as follows:

1) The pseudo-first-order:

$$Q_t = Q_e(1 - \exp(K_1 t)) \quad (4)$$

The linear pseudo-first-order:

$$ln(Q_e - Q_t) = lnQ_e - K_1 t \quad (5)$$

where K_1 (min^{-1}) is the pseudo-first order adsorption rate constant, Q_e (mg/L) is the initial and equilibrium concentrations, Q_t (mg/g) is the adsorption capacity at different time..

2) The pseudo-second-order:

$$Q_e = \frac{Q_e^2 K_2 \mathrm{t}}{1+Q_e K_2 t} \quad (6)$$

Linear pseudo-second-order:

$$\frac{t}{Q_t} = \frac{1}{Q_e} t + \frac{1}{Q_e^2 K_2} \quad (7)$$

where Q_e (mg/L) is the initial and equilibrium concentrations, Q_t (mg/g) is the adsorption capacity at different time K_2 (g/(mg·min)) is the pseudo-second-order adsorption rate constant.

3) Intra-particle diffusion:

$$Q_t = K_{int} t^{\frac{1}{2}} + C \quad (8)$$

where K_{int} ($mg/(g \cdot min^{1/2})$) is the intraparticle diffusion rate constant, Q_t (mg/g) represents the amounts of OTC adsorbed or removed at time t (min), *C* is a constant related to the boundary layer thickness and decreases with increasing surface heterogeneity and the number of hydrophilic groups for biochar.

The fitting analysis of kinetics and isotherm modelling and illustrations were carried out with Origin 2021 software.

3. The removal rate in four cycle OTC exposure experiment by nZVI@BC and nZVI/B6@BC.

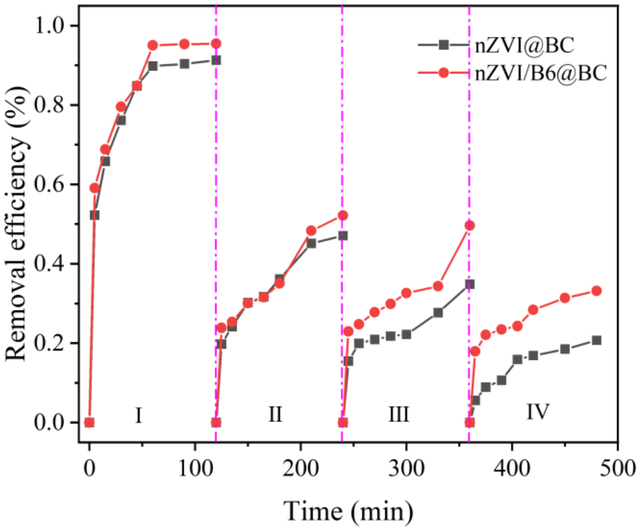


Figure S1 The removal rate in four cycles OTC exposure experiment by nZVI @BC and nZVI/B6@BC.

4. Dissolution of iron of nZVI/B6@BC and nZVI@BC

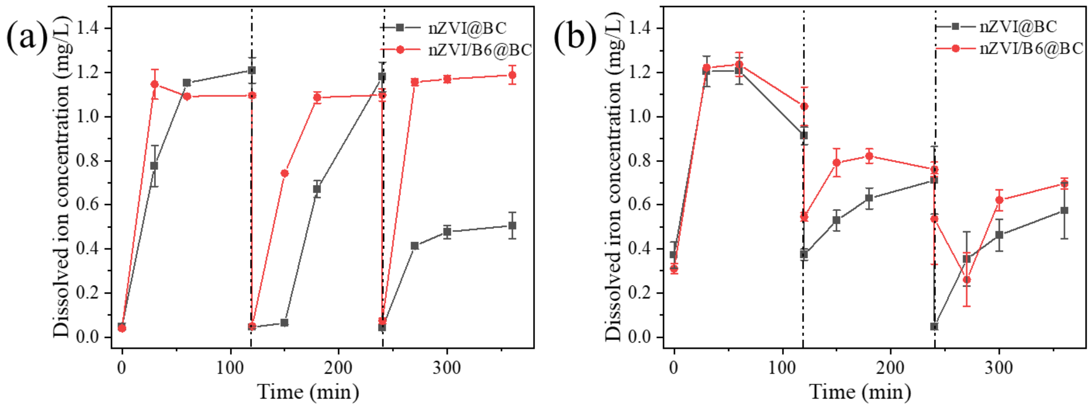


Figure S2: Dissolution of iron of nZVI/B6@BC and nZVI@BC in acid conditions (pH = 3.5) exposure cycles under a) pure deionized water adjusted by acid hydrochloric acid and b) 500 mg/L OTC solutions.

5. HPLC method

The Thermo Ultimate 3000 HPLC-system (Thermo Fisher Scientific, Waltham, USA) was used for OTC detection, equipped with an autosampler (operated at 4 ◦C), a pump, and a thermos-stated column oven. The analytical column was an Agela Venusil MP C18 chromatographic column (4.6 mm × 150 mm, 5 μm, Agela, China) operated at 35 ◦C. UV detector operated at 355 nm. The mobile phases consisted of 0.01 mol/L aqueous NaH_2PO_4 (pH = 2.5, B) and acetonitrile (A) and the flow rate was 1.0 mL/min. Gradient elution adjusted by time: 0-1 min, 90% B, 1-4 min: 90-80% B, 4-10 min: 80% B, 10-12 min: 80-90% B. The OTC peaks approximately appeared at 7.8 min.

6. Zeta potential of different composites in aqueous water.

Table S1 Zeta potential of different composites in aqueous water.

Composite type	Zeta potential (mV)	Conductivity (mS/cm)
BC	-23	0.1005
B6@BC	-17.3	0.00429
nZVI@BC	10.2	0.0337
nZVI/B6@BC	11.37	0.0201

7. The isotherm parameters of oxytetracycline adsorption

Table S2 The isotherm parameters of oxytetracycline adsorption onto BC and B6@BC at 25 °C and pH = 3.5.

Isotherm model	Parameters of BC			Parameters of B6@BC		
Langmuir	Q_m (mg/g)	K_l (L/mg)	R^2	Q_m (mg/g)	K_l (L/mg)	R^2
	47.898	0.0068	0.9420	52.7869	0.0349	0.9973
Freundlich	K_f (mg/g·(L/mg)$^{1/n}$)	n	R^2	K_f (mg/g·(L/mg)$^{1/n}$)	n	R^2
	11.945	2.235	0.9693	2.465	4.448	0.9473
Temkin	K_T (L/mg)	B (J/mol)	R^2	K_T (L/mg)	B (J/mol)	R^2
	0.6747	11.158	0.9699	0.02205	8.3187	0.9551

8. The kinetic parameters of oxytetracycline adsorption

Table S3 The kinetic parameters of oxytetracycline adsorption onto BC and B6@BC at 25 °C and pH = 3.5.

Kinetic model	parameters		
Pseudo-first order	K_1 (min^{-1})	Q_e (mg/g)	R^2
BC	0.0249	67.38	0.9545
B6@BC	0.0205	51.21	0.9808
Pseudo-second order	K_2 (g/(mg·min))	Q_e (mg/g)	R^2
BC	0.0006	89.28	0.9865
B6@BC	0.0104	90.09	0.9928
Intramolecular diffusion	K_{int} (mg/(mg·min$^{1/2}$))	C (mg/g)	R^2
BC	6.0202	17.182	0.9885
B6@BC	4.8496	34.166	0.987

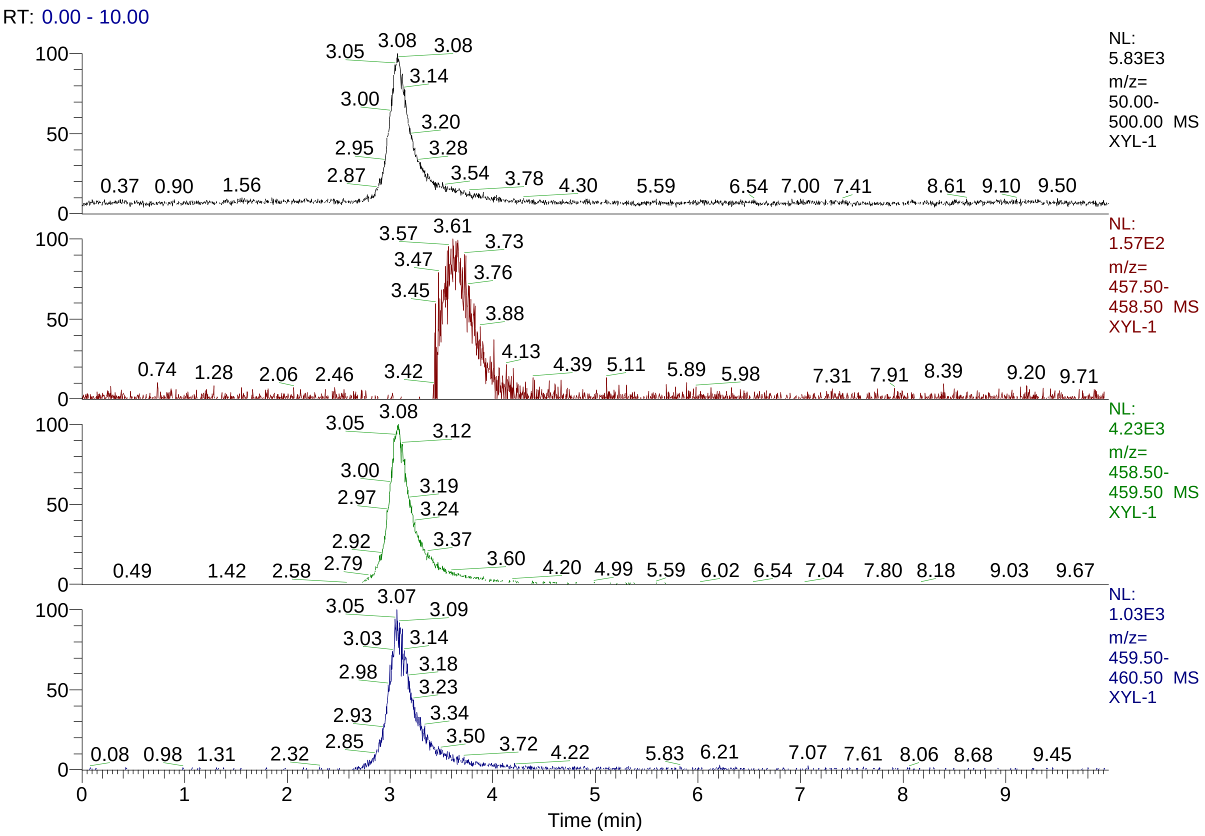
9. The kinetic parameters of oxytetracycline removal

Table S4 The kinetic parameters of oxytetracycline removal onto nZVI@BC and nZVI/B6@BC at 25 °C and pH = 3.5.

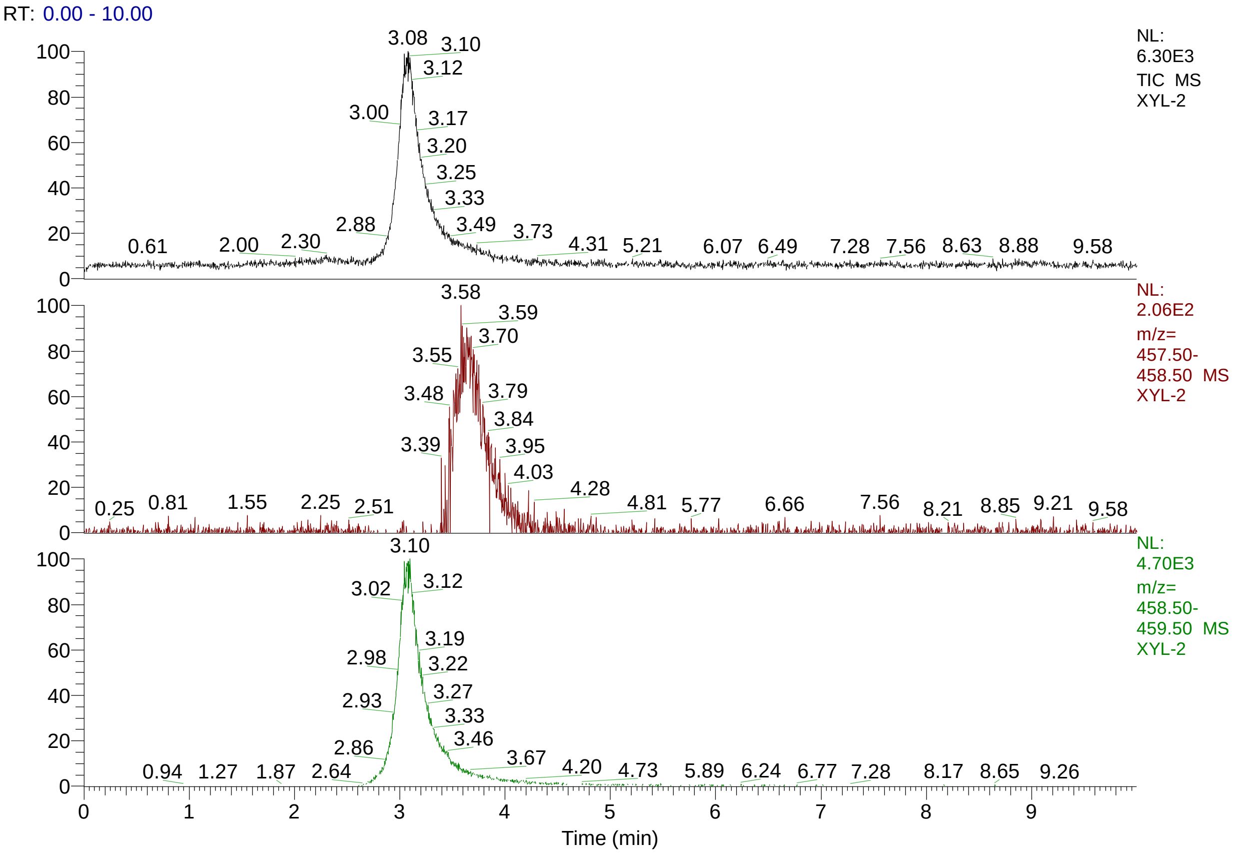
Kinetic model	parameters		
Pseudo-first order	K_1 (min^{-1})	C_e (mg/L)	R^2
nZVI@BC	0.00504	117.91	0.8149
nZVI/B6@BC	0.00458	80.479	0.5430
Pseudo-second order	K_2 (g/(mg·min))	C_e (mg/L)	R^2
nZVI@BC	0.000275	490.196	0.99986
nZVI/B6@BC	0.000403	490.196	0.99992

10. The results of HPLC-MS

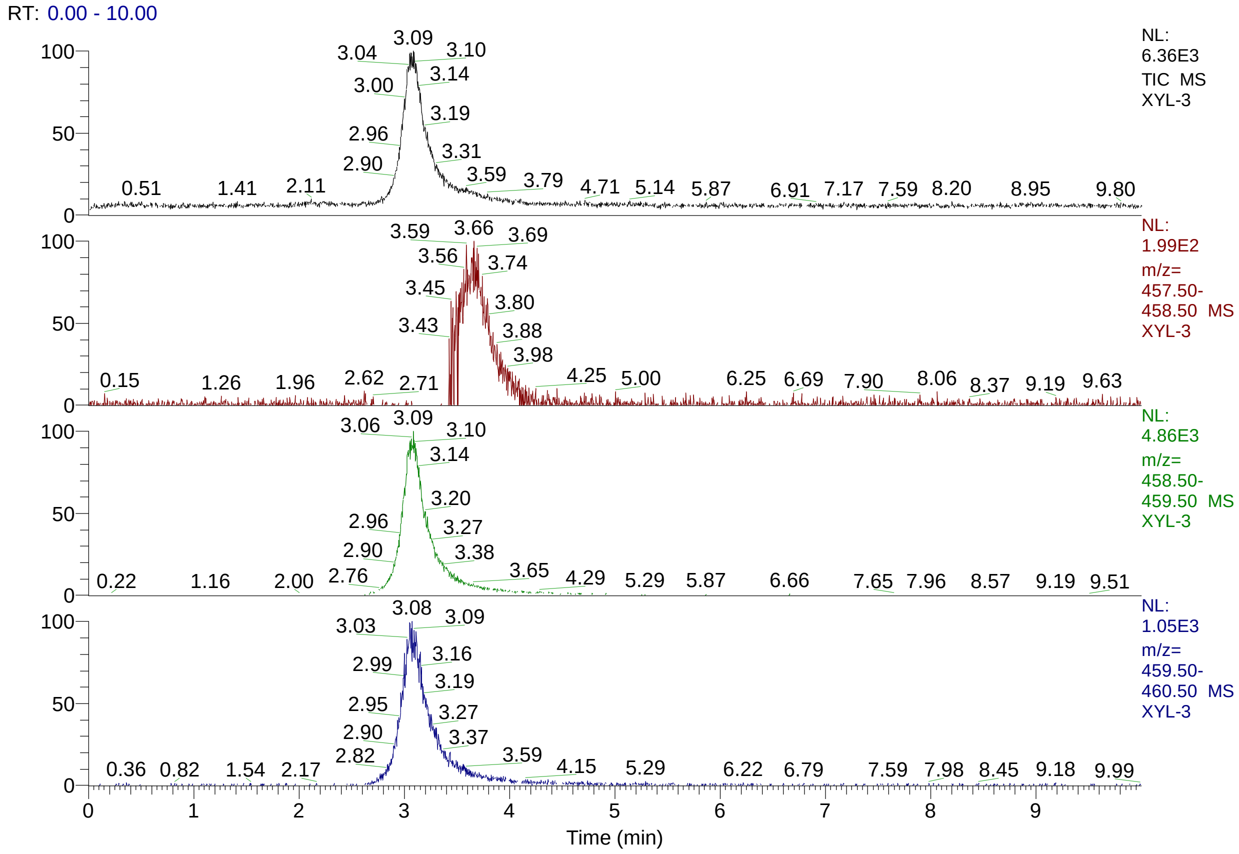
(1) OTC blank



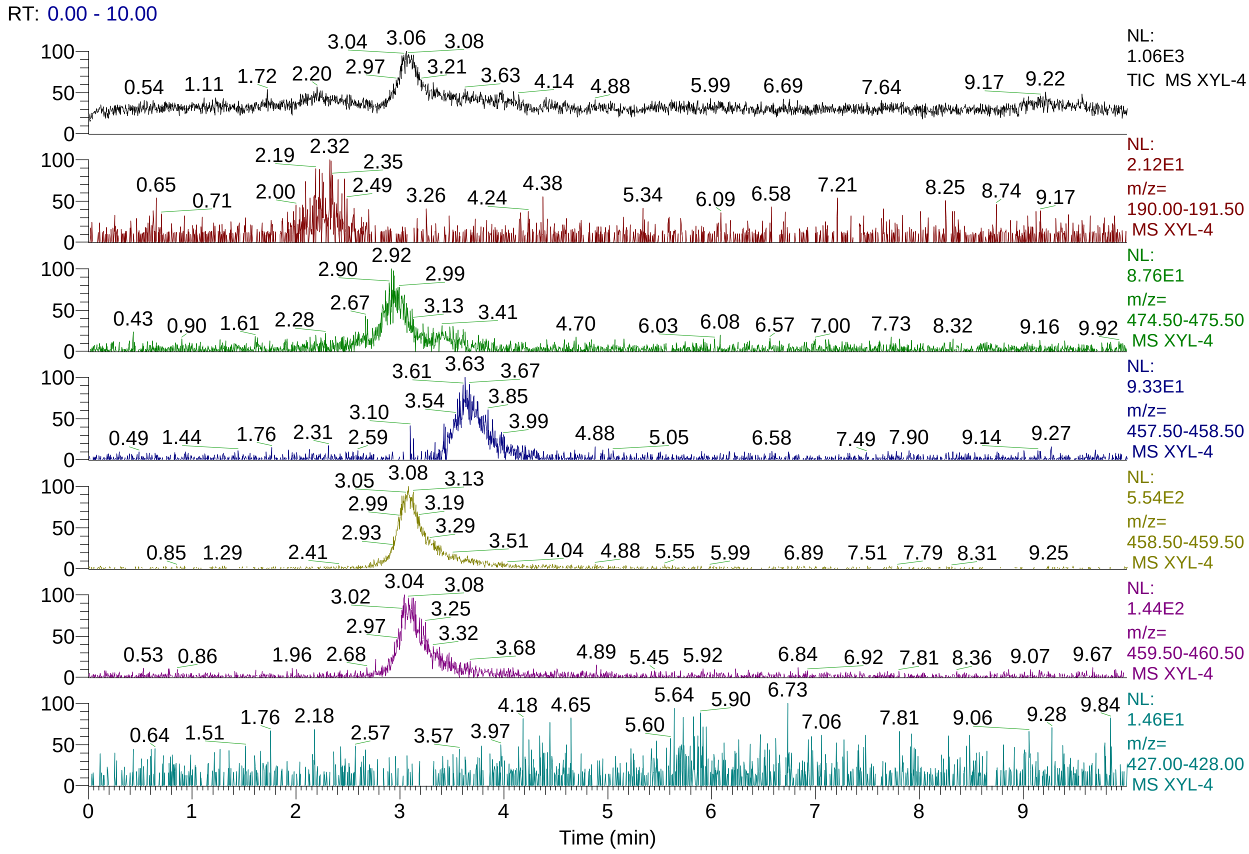
(2) The HPLC-MS of BC after 120 min



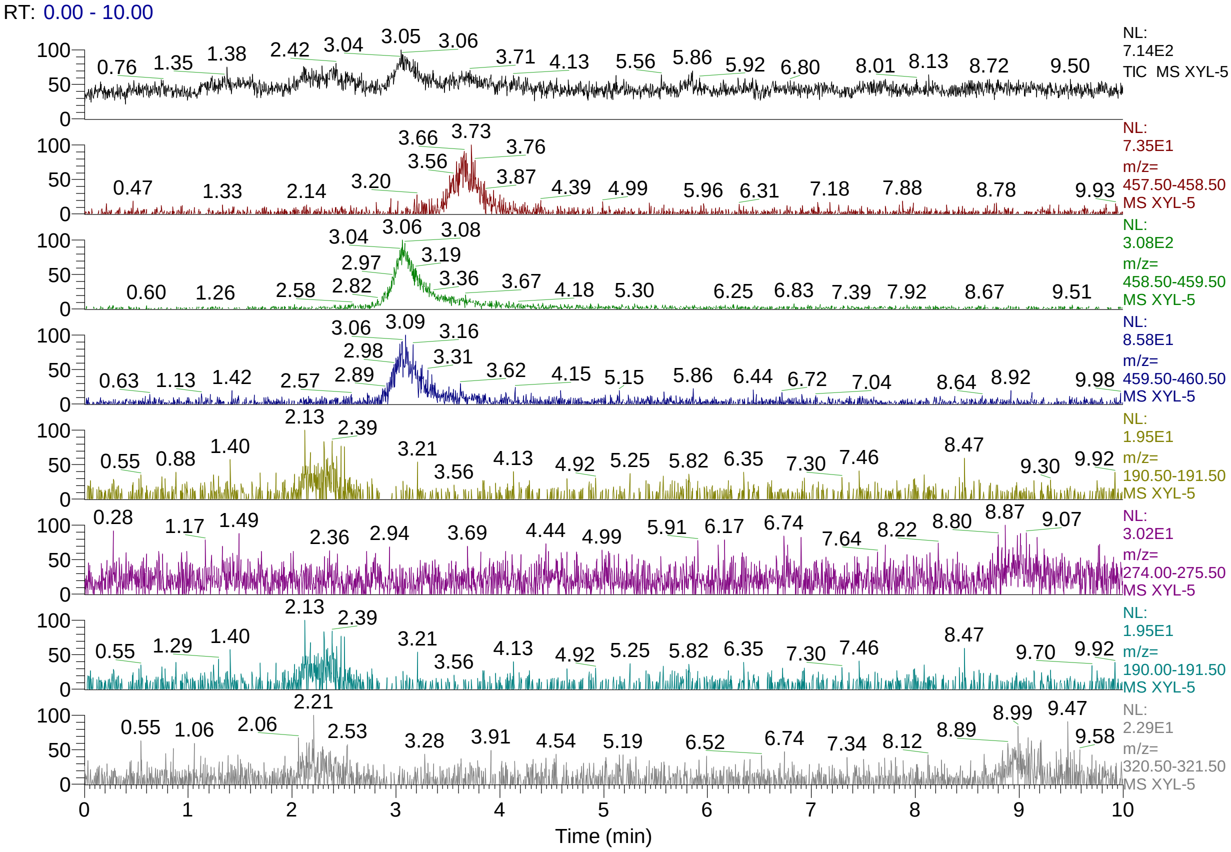
(3) The HPLC-MS ofB6@BC after 120 min.



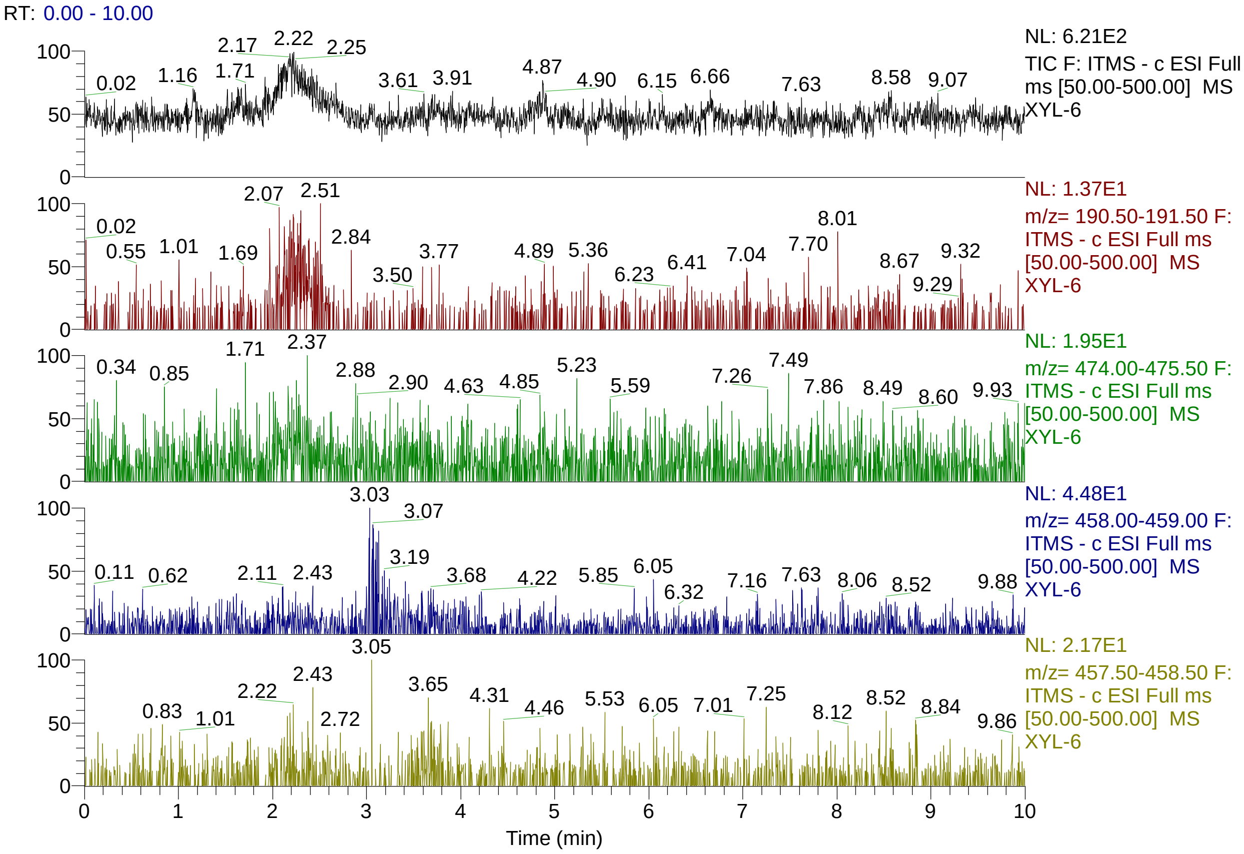
(4) The HPLC-MS of nZVI@BC after 5 min



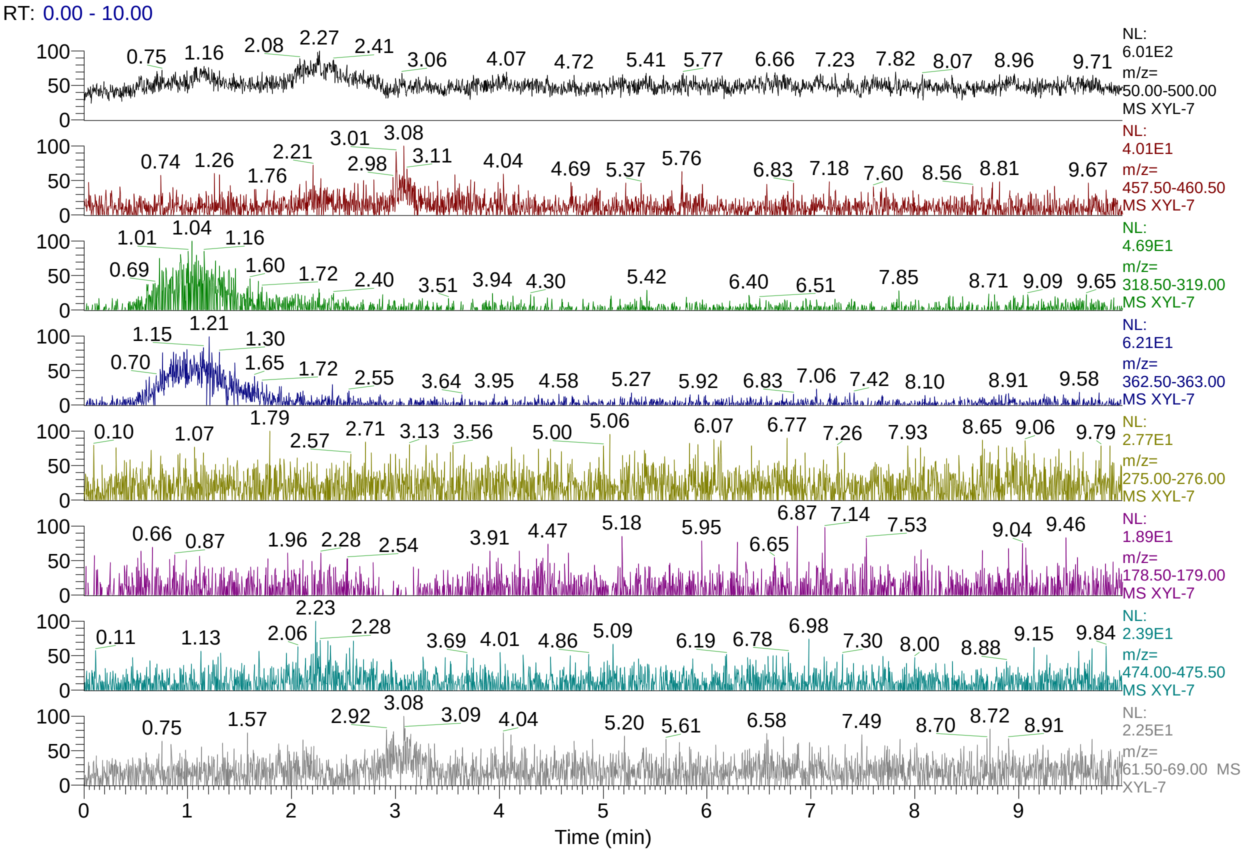
(5) The HPLC-MS of nZVI/B6@BC after 5 min



(6) The HPLC-MS of nZVI @BC after120 min.



(7) The HPLC-MS of nZVI/B6@BC after120 min.



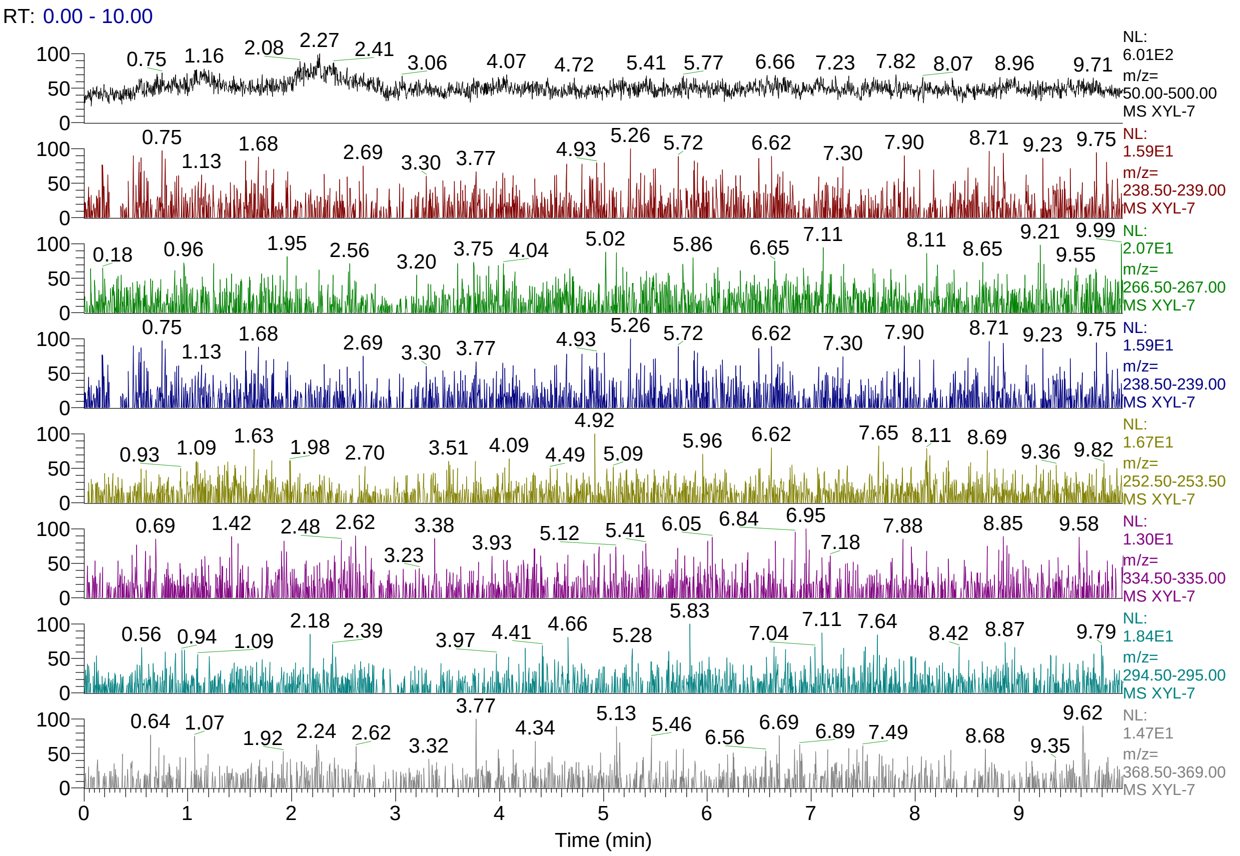


Figure S3 The HPLC-MS of (1)OTC blank, (2)BC, (3)B6@BC after 120 min, (4) nZVI @BC, (5) nZVI/B6@BC after 5 min, (6) nZVI @BC, and (7)nZVI/B6@BC after120 min.

References

1. Saremi, F.; Miroliaei, M. R.; Shahabi Nejad, M.; Sheibani, H., Adsorption of tetracycline antibiotic from aqueous solutions onto vitamin B6-upgraded biochar derived from date palm leaves. *Journal of Molecular Liquids* **2020,** *318*.
2. Zhang, H.; Wang, J.; Zhou, B.; Zhou, Y.; Dai, Z.; Zhou, Q.; Chriestie, P.; Luo, Y., Enhanced adsorption of oxytetracycline to weathered microplastic polystyrene: Kinetics, isotherms and influencing factors. *Environ Pollut* **2018,** *243*, (Pt B), 1550-1557.