

Supplementary Information

Efficient removal of tetracycline in water using modified eggplant straw biochar supported green nanoscale zerovalent iron: synthesis, removal performance, and mechanism

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Text S1 The synthesis of B-nZVI/ESBC composite

B-nZVI/ESBC composite was synthesized by the following liquid phase reduction method using NaBH_4 as the reducing agent. Typically, 0.5 g of ESBC and 0.8297 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were added to a 250 mL three-necked flask containing 100 mL of deoxygenated water, and stirred thoroughly for 2 h at room temperature. Then, 10 mL of NaBH_4 solution was added dropwise to the mixed solution and stirred for another 1 h. In this process, Fe^{2+} was reduced to nZVI and bound to the surface of ESBC to form B-nZVI/ESBC composite. The above reactions were carried out under nitrogen protection. The formed solid composite was collected by centrifugation and washed three times with deoxygenated water and anhydrous ethanol, respectively. Finally, B-nZVI/ESBC composite was vacuum dried at 80 °C for 12 h and stored in a nitrogen-filled bottle for further use.

Text S2 The characterization of as-synthesized materials

Field emission scanning electron microscopy (FE-SEM, JSM 7500F, Japan) was used to examine the morphological characteristics of as-synthesized materials at a voltage of 5 kV. The surface areas, pore volumes and pore sizes of the materials were measured with a Brunauer–Emmett–Teller (BET) analyzer (Micromeritics ASAP2460, USA) by N₂ adsorption/desorption method at -196 °C. The crystal structures of as-synthesized materials were analyzed with a D8 Advance X-ray diffractometer (Germany) equipped with a Cu-K α radiation (45 kV, 40 mA). Samples were scanned from 10° to 90° 2 θ at a speed of 3° 2 θ /min. Fourier transform infrared (FTIR) analyses of as-synthesized materials were performed with a FTIR spectrometer (Vertex 70, Bruker, Germany). Samples were mixed with KBr at a ratio of 1:100 (w/w), pressed into thin slices, and scanned at a resolution of 4 cm⁻¹ within the range of 4000-400 cm⁻¹. The chemical compositions of materials were analyzed using an X-ray photoelectron spectrometer (XPS, ESCALAB 250XI, Thermo, USA) with an Al K α radiation source. The zeta potentials of P-nZVI/ESBC composite were measured using Zetasizer Nano (EKYS-130, Malvern UK) at solution pH from 2 to 11.

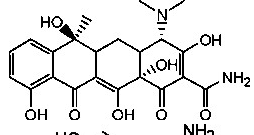
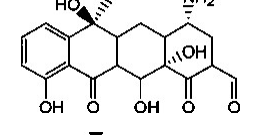
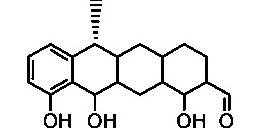
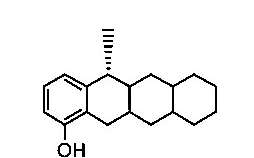
Table S1 Specific surface area and porosity of material.

Material	BET Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	BJH Pore Size (nm)
P-nZVI/ESBC	203.81	0.1186	10.34

Table S2 Comparison of adsorption capacities of different materials for TC.

Materials	Reaction condition	q_m (mg g ⁻¹)	Reference
nZVI		105.46	
pumice supported nZVI composite	Materials: 5 g L ⁻¹ , TC: 25-300 mg L ⁻¹ , pH: 8, 25 °C	115.13	Guler ¹
ZVI/BC (co-pyrolysis of hematite and pinewood)	Material: 1 g L ⁻¹ , TC: 25-400 mg L ⁻¹ , 25 °C	301.39	Shi et al. ²
Fe/BC (blue-green microalgae)	Material: 2 g L ⁻¹ , TC: 25-1000 mg L ⁻¹	95.86	Peng et al. ³
Biochar R600 (rice straw)	Material: 3 g L ⁻¹ , TC: 0.5-32 mg L ⁻¹ , 25 °C	14.185	Wang et al. ⁴
Fe loaded biochar (sewage sludge)	Material: 0.2 g L ⁻¹ , TC: 2-45 mg L ⁻¹ , pH: 6, 25 °C	123.35	Fan et al. ⁵
P-nZVI/ESBC composite	Material: 1 g L ⁻¹ , TC: 50-400 mg L ⁻¹ , pH: 6, 25°C	304.62	This work

Table S3 The major reductive degradation products of TC by P-nZVI/ESBC composite.

Compound	m/z	Molecular weight	Formula	Molecular structure
TC	444.9	444.4	C ₂₂ H ₂₄ N ₂ O	
product A	387.1	389.5	C ₂₀ H ₂₃ NO ₇	
product B	329.5	330.5	C ₂₀ H ₂₆ O ₄	
product C	270.9	270.3	C ₁₉ H ₂₆ O	

During the reaction, three major degradation products with m/z of 270.9, 329.5 and 387.1 in the filtrate were observed, as shown in Table S1 (Supplementary Information). Previous studies ^{6, 7} indicated that C-N bonds on TC were prone to be broken due to the lower bond energy. The product A (m/z 387.1) was generated from TC decomposition through the loss of dimethylamino group at C4, an amino group, and a hydroxyl group at C3. Product B (m/z 329.5) was derived from product A (m/z 387.1) degradation via removing an amino group at C4 and three hydroxyl groups at C6, C12, and C12a, meanwhile the carbonyl groups at C1 and C11 were hydrogenated to form hydroxyl groups. Product B (m/z 329.5) further lost two hydroxyl groups and a formyl group to yield product C (m/z 270.9).

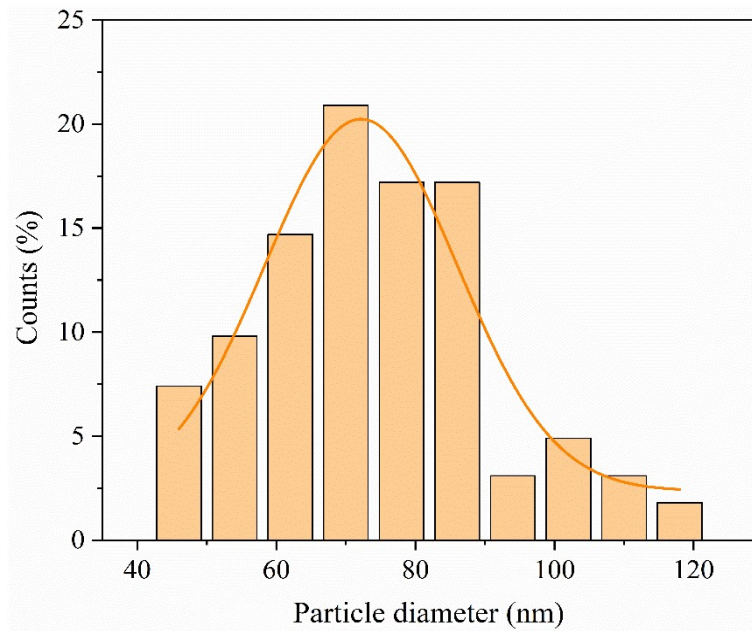


Fig. S1. The size distribution of nZVI obtained by Nano Measurer software statistics.

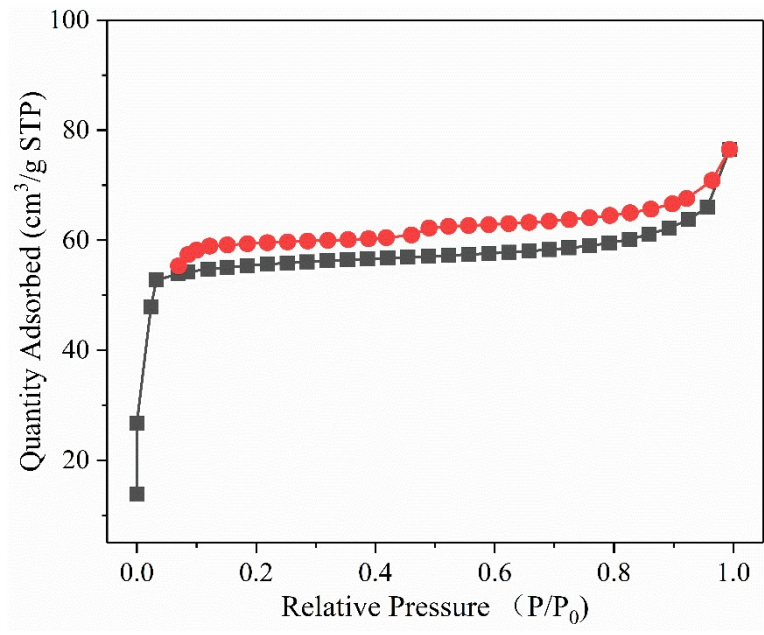


Fig. S2. Nitrogen adsorption–desorption isotherms of P-nZVI/ESBC composite.

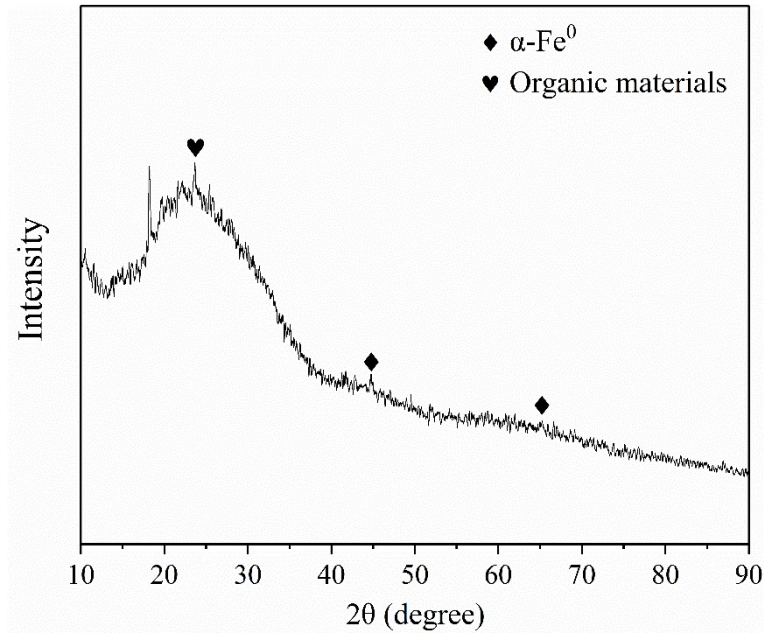


Fig. S3. XRD pattern of P-nZVI.

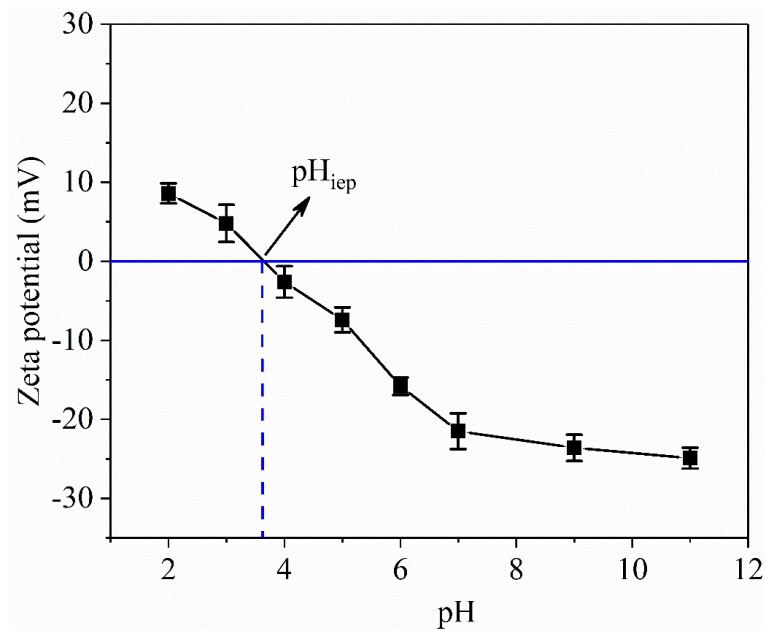


Fig. S4. The zeta potential of P-nZVI/ESBC composite at different solution pH.

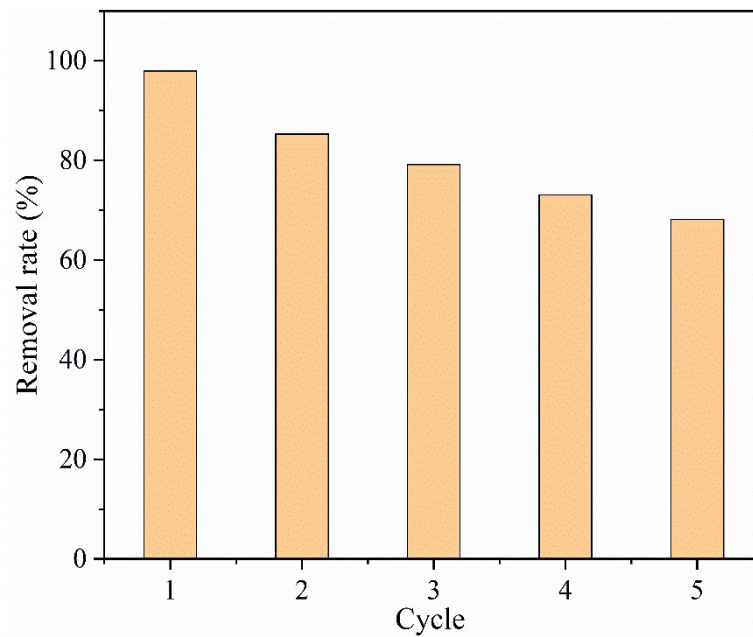


Fig. S5. Reusability test of P-nZVI/ESBC composite.

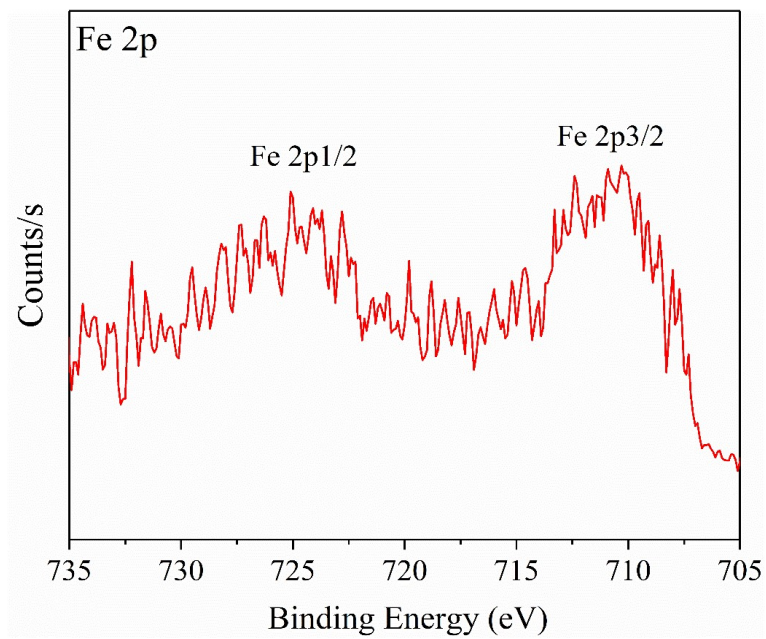


Fig. S6. The high-resolution Fe 2p spectrum of P-nZVI/ESBC composite after reaction with TC.

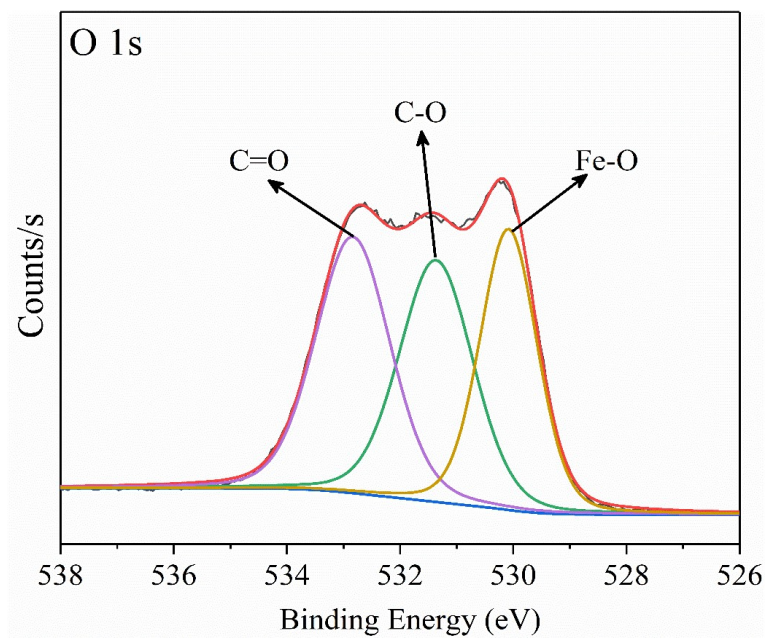


Fig. S7. The high-resolution O 1s spectrum of P-nZVI/ESBC composite after reaction with TC.

References

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