Supporting information for "Fungi-enabled hierarchical porous magnetic carbon derived from biomass for efficient remediation of As(III)-contaminated water and soil：performance and mechanism"

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Text S1

Chemicals

Sodium arsenite ($NaAsO_2$) was purchased from Anpel Laboratory Technologies Company (Shanghai, China). Sodium borohydride ($NaBH_4$) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$), sodium hydroxide (NaOH) and potassium hydroxide (KOH) were provided by Guangzhou Chemical Reagent Company (Guangzhou. China). All the above reagents were of analytical grade and were used directly in the experiments.

Text S2

Free radical detection

Electron spin resonance (ESR, JEOL FA-200, Japan) spectroscopy was used to detect superoxide anion radicals (O_2^-) and hydroxyl radicals (•OH) trapped by 5,5-dimethyl-l-pyrroline-N-oxide (DMPO). After 10 mg of FPC/nZVI was ultrasonically dispersed in 10 mL of deionized water for 5 min with the adjustment of pH, 200 μL of the suspension was taken out and immediately mixed with 50 μL of 0.1 M DMPO to form a DMPO-radical adduct, which was determined by the ESR spectrometer. The degradation intermediates of sulfadiazine were identified by an Agilent 1100 liquid chromatography and an electrospray ionization tandem mass spectrometry (LC/MS, USA) equipped with a Waters BEH-C18 column (5 μm, 4.6 × 150 mm).

Text S3

Isotherm models:

$$q_e = Q_{max}K_LC_e/(1 + bC_e) \qquad \text{Langmuir}$$

$$q_e = K_fC_e^{1/n} \qquad \text{Freundlich}$$

where C_e (mg/L) and q_e (mg/g) represent the equilibrium As(III) concentration in solution and adsorption capacity, respectively. Q_{max} (mg/g) represents the maximum equilibrium adsorption capacity. K_L (L mg^{-1}) and K_f (g mg^{-1} min^{-1}) represent adsorption equilibrium constants. *1/n* is a constant known as the heterogeneity factor related to the difficulty of adsorption. In addition, the dimensionless parameter of the equilibrium or adsorption intensity (R_L) was calculated using the Langmuir adsorption constant K_L and the initial concentration of As(III).

$$R_L = \frac{1}{1 + K_LC_0}$$

Kinetic models:

$$q_t = q_e(1 - e^{-K_1 t}) \qquad \text{Pseudo-first-order model}$$

$$q_t = {K_2 q_e^2 t}/{(1 + K_2 q_e t)} \qquad \text{Pseudo-second-order model}$$

Where t is the time of sampling, q_t and q_e refer to the adsorption capacity at instantaneous and equilibrium time, respectively. K_1 and K_2 represent kinetic constants.

Text S4

Plant cultivation

Rice (*Oryza sativa* L., Huanghuazhan) seeds were treated with 2% (W/V) of NaClO solution for 20 min and then washed with deionized water for three times. The sterilized rice seeds were evenly sprinkled on plastic nets immersed in deionized water and germinated in the black for three days. After germination, rice seedlings were transferred into barrels and grown in a growth chamber where the day and night temperatures were set to 27 °C and 23 °C and the photoperiod and light intensity were set to 14 hours and 400 μmol m^{-2} s^{-1}, respectively. The relative humidity of growth chamber was about 75-85%. After 12 days of growth, the rice seedlings would be transplanted into plastic square box filled with diverse soil containing different prepared materials.

Text S5

Arsenic concentration in water

The collected solution passed through a 0.22 um filter membrane, and then the concentrations of As(III) and As(V) were measured through an atomic florescence spectroscopy (SA-20, Jitian Inc., Beijing, China).

pH and available arsenic concentration in soil

5 g soil in the pot was put in 25 mL deionized water. After being shaken for 24 h, the resulting system was centrifuged (4500 rpm) for 5 min, and then the pH value of the supernatant was measured.

The concentrations of available arsenic in soil were determined as described in the previous study with some modifications [1]. In brief, 1.0 g soil was added to polyethylene centrifugation tubes and then treated with 25 mL $NH_4H_2PO_4$ (0.05 M) solution in a 65 °C water bath with shaking at 120 rpm for 2 h. The mixture was then centrifuged at 2500 rpm for 5 min, and arsenic concentration in the supernatant was measured.

Arsenic concentration in rice seedlings

The roots and shoots of rice seedlings were washed with deionized water for three times and then dried in an oven at 60 °C for 48 h. 0.25 g of dry samples were treated with 5 mL mixed acid (nitric acid and perchloric acid 3:1, v/v) in a Teflon bottle. After a night of soaking, the digestion solution was heated at 120 °C for 30 min followed by 180 °C for 30 min in a microwave reaction system. Following digestion, 2.5 mL aqua regia and 1 mL hydrofluoric acid were added to the digested extracts to dissolve any remaining material. The digested extracts were diluted to 50 mL using ultrapure water and then measured for the concentrations of As in solution.

Text S6

Regeneration and reusability experiments

0.5 g of FPC/nZVI was added to 50 mL of As(III) solution (10 mg/L, pH = 7.0) at 298 K with shaking at 200 rpm. The sampling time points set as 10, 30, 60, 120, 180, 240 and 300 min. After first use, the resulting FPC/nZVI-As was collected from the solution with a magnet. Then, the collected FPC/nZVI-As was added to 50 mL of HCl solution (0.5 M) for 5 hours of shock to desorb the adsorbed arsenic. Subsequently, the renewed FPC/nZVI was reused to adsorb As(III) from solution after magnetic separation, rinsing with water and drying. The concentration of As(III) and As(V) in solution from each sampling were all measured. After each cycle, Fe^{2+} concentration in solution was determined.

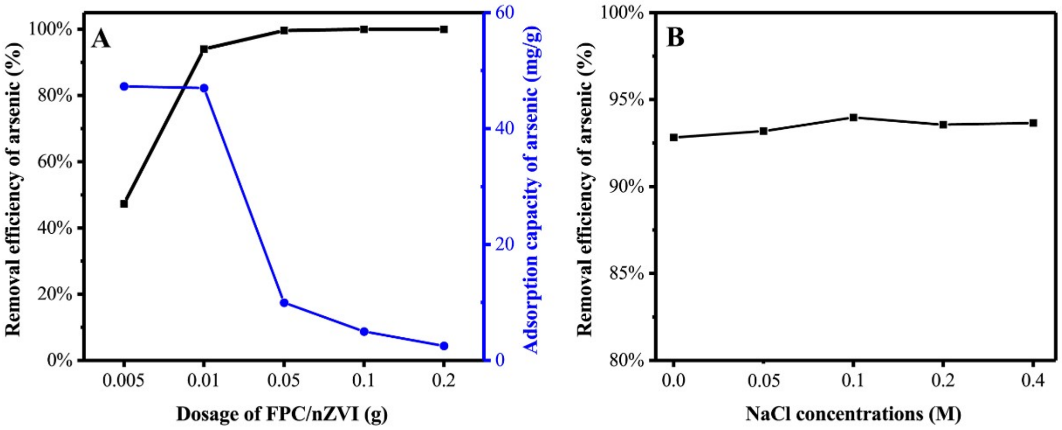


Fig. S1 The effect of dosages (A) and NaCl concentrations (B) on the removal of As(III) on FPC/nZVI. (Experimental conditions: 10 mL of 50 mg/L As(III), temperature 25 °C, reaction time 24 h and 200 rpm).

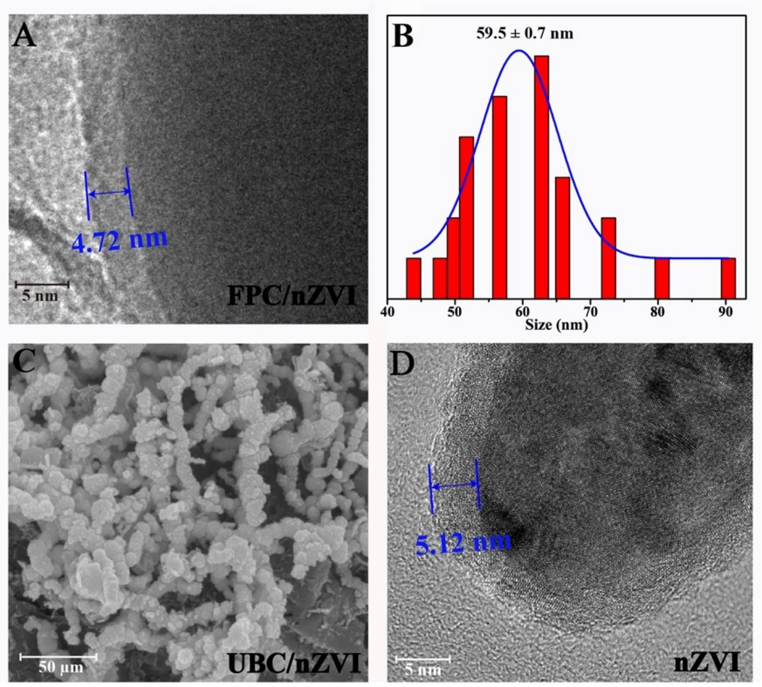
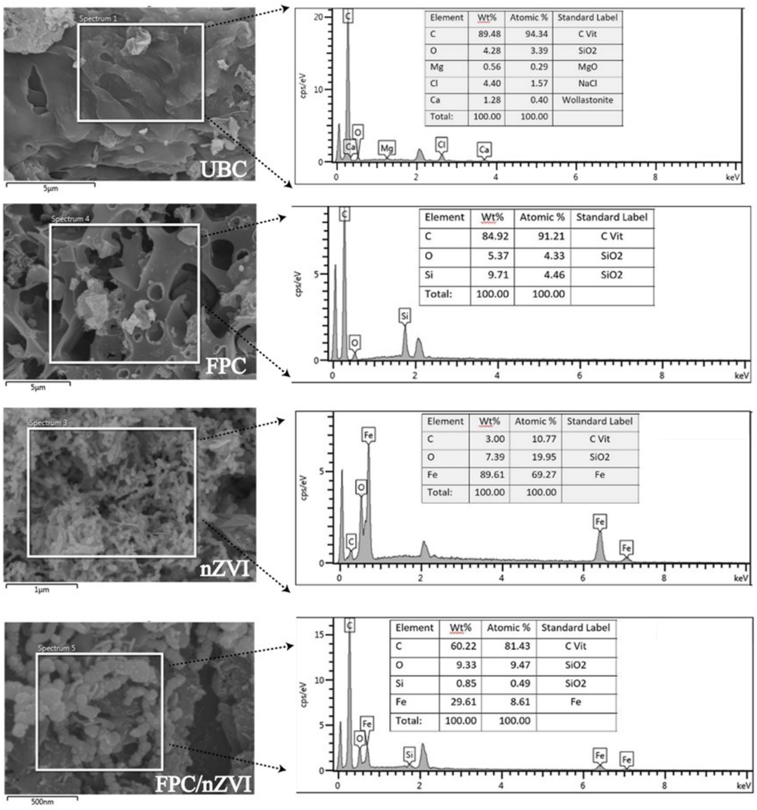


Fig. S2 The TEM images (A) and size distribution (B) of FPC/nZVI; (C) the SEM image of UBC/nZVI; (D) the TEM image of bare nZVI



Element	Wt%	Atomic %	Standard Label
C	89.48	94.34	C Vit
O	4.28	3.39	SiO2
Mg	0.56	0.29	MgO
Cl	4.40	1.57	NaCl
Ca	1.28	0.40	Wollastonite
Total:	100.00	100.00	

Element	Wt%	Atomic %	Standard Label
C	84.92	91.21	C Vit
O	5.37	4.33	SiO2
Si	9.71	4.46	SiO2
Total:	100.00	100.00	

Element	Wt%	Atomic %	Standard Label
C	3.00	10.77	C Vit
O	7.39	19.95	SiO2
Fe	89.61	69.27	Fe
Total:	100.00	100.00	

Element	Wt%	Atomic %	Standard Label
C	60.22	81.43	C Vit
O	9.33	9.47	SiO2
Si	0.85	0.49	SiO2
Fe	29.61	8.61	Fe
Total:	100.00	100.00	

Fig. S3 The EDX spectrum of UBC, FPC, nZVI and FPC/nZVI.

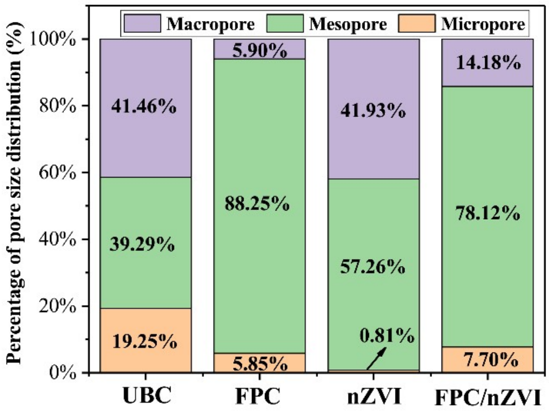


Fig. S4 Percentage of pore size distribution including macropore, mesopore and micropore.

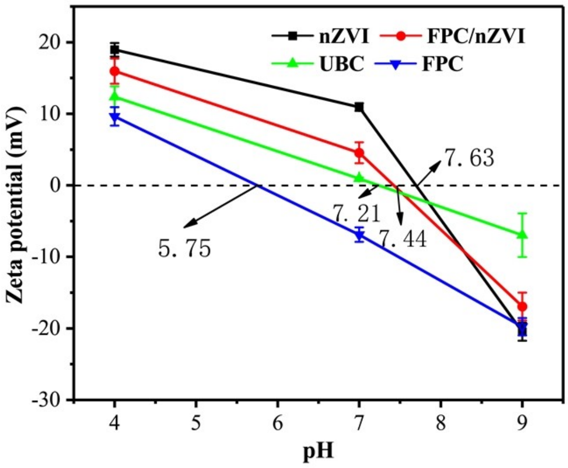


Fig. S5. The zeta potential values of UBC, FPC, nZVI and FPC/nZVI in 50 mg/L As(III) solution with different pH.

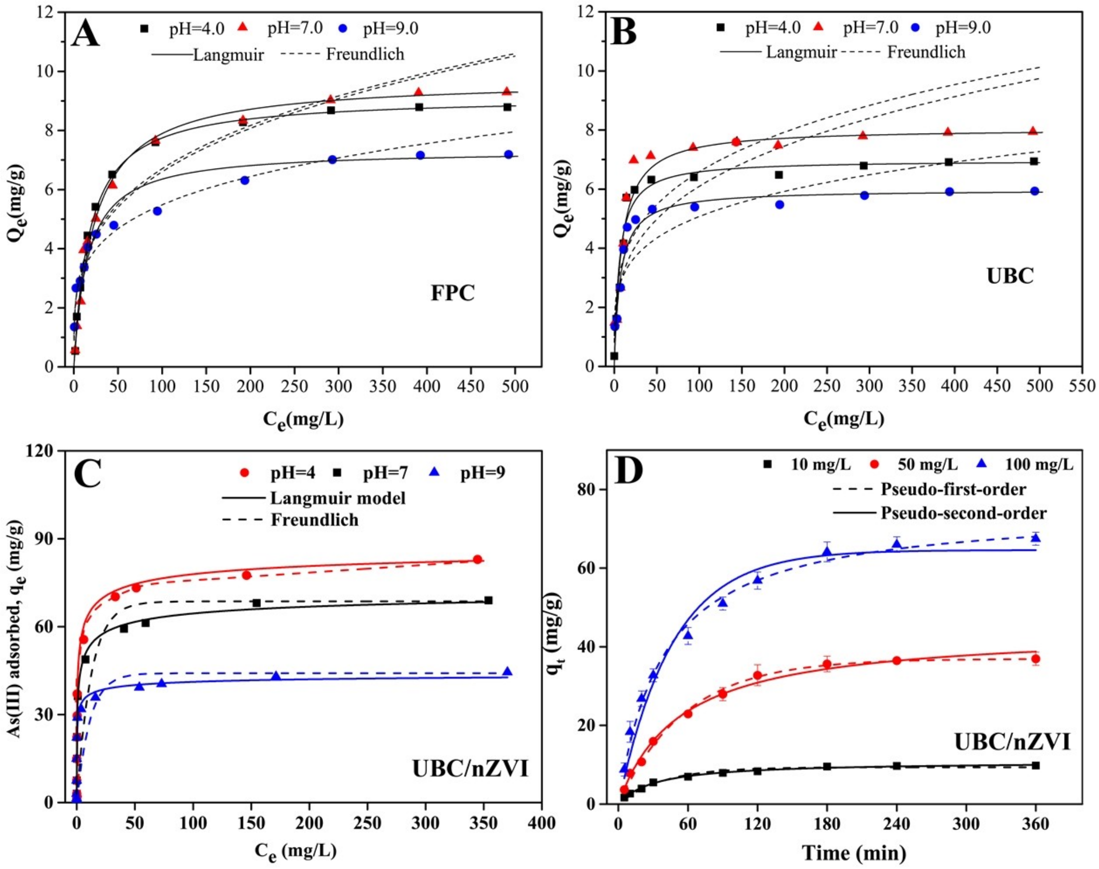


Fig. S6 Adsorption isotherms of As(III) on FPC (A), UBC (B) and UBC/nZVI at different pH (pH = 4.0, 7.0 and 9.0), experimental conditions:1 g/L of adsorbent dosage, the initial concentrations of As(III) range from 1 to 500 mg/L and temperature 25 ℃. Effect of contact time on As(III) removal with UBC/nZVI (D) at pH=7.0 (adsorbents concentration was 1.0 g/L; the initial As(III) concentrations ranged from 10 to 100 mg/L).

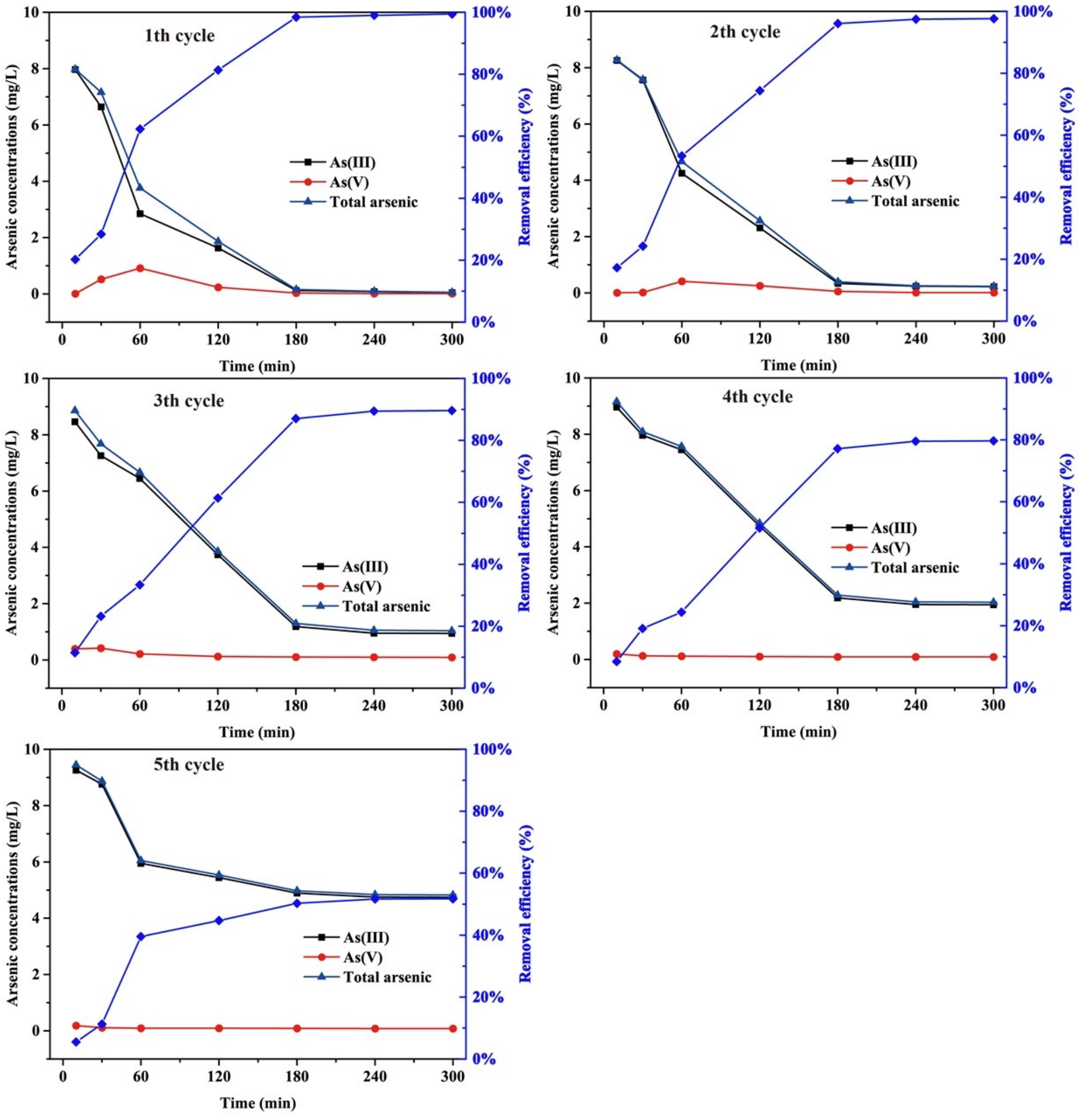


Fig. S7. The variations of different arsenic species and removal efficiency of total arsenic by FPC/nZVI at different regeneration cycles. (Initial As (III) concentration 10 mg/L, pH 7.0, temperature 298 K).

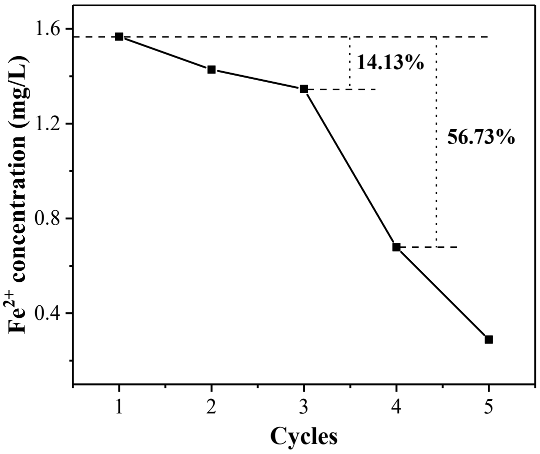


Fig. S8. Variations of Fe^{2+} concentration in solution for each cycle of the As(III) removal by FPC/nZVI (50 mL of As(III) (10 mg/L) for each cycle, 0.5 g of FPC/nZVI, pH=7.0 and T=298K).

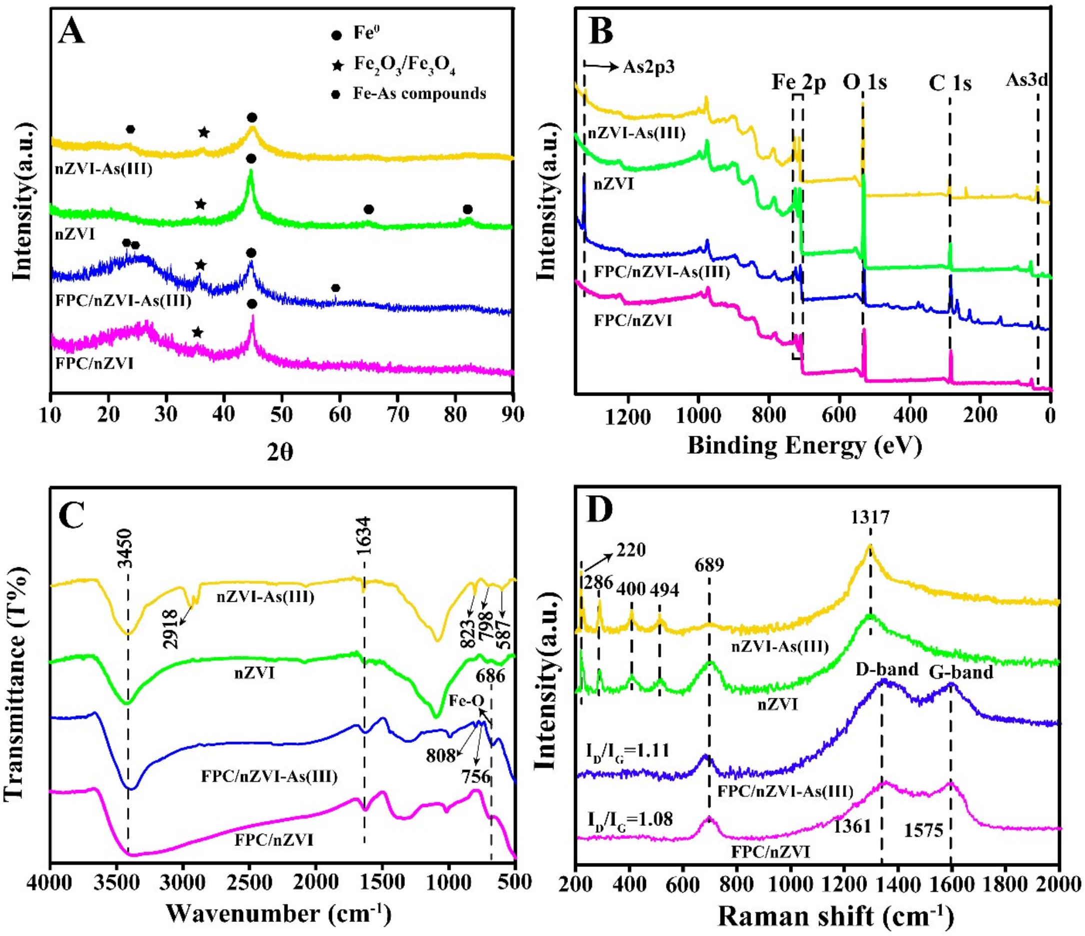


Fig. S9. XRD patterns (A), XPS (B), FTIR (C) and Raman (D) spectra of nZVI and FPC/nZVI before and after As(III) adsorption.

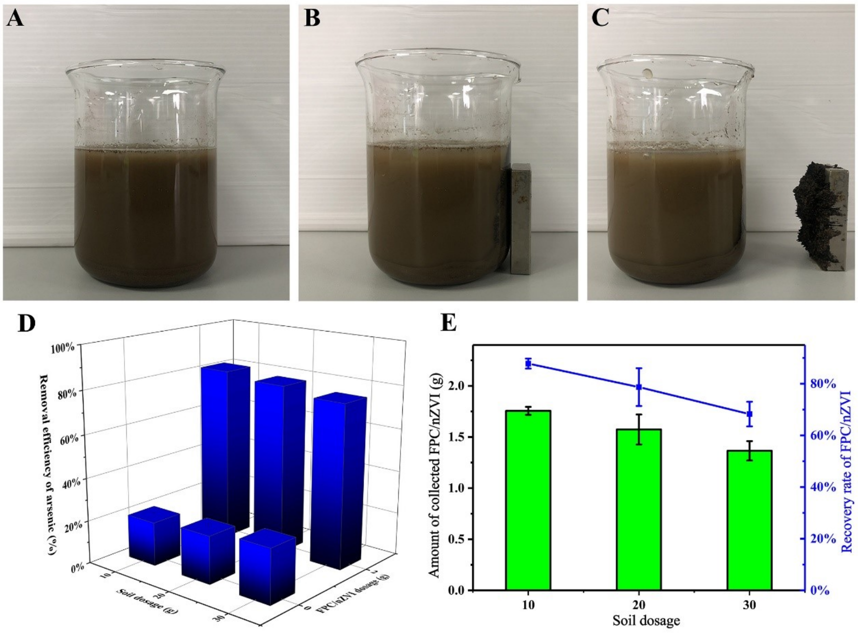


Fig. S10. (A-C) Digital images showing the removal process of As(III) from soil suspension using FPC/nZVI assisted by a magnetic; (D) Removal efficiency of arsenic from soil suspension (10, 20 and 30 g of soil mixed with 50 mL of As(III) solution (50 mg/L) using two dosages of FPC/nZVI (0 and 2 g); (E) Amount and recovery rate of FPC/nZVI collected by a magnet.

Table S1 The specific surface area and pore parameters of UBC, FPC, nZVI and FPC/nZVI (S_{BET} was calculated by the Brunner−Emmet−Teller method.

Samples	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{maco} (cm^3/g)	Average pore diameter (nm)
UBC	805.2	0.509	0.098	0.200	0.211	3.852
FPC	1696.6	1.744	0.102	1.539	0.103	3.598
nZVI	37.8	0.124	0.001	0.071	0.052	13.944
FPC/nZVI	1124.7	1.051	0.081	0.821	0.149	3.493

Table S2 Langmuir and Freundlich adsorption isotherm parameters for As(III) by U-BC, FPC, nZVI and FPC/nZVI

Adsorbents	pH	Langmuir model: $Q_e = \frac{K_L * Q_{max} * C_e}{1 + K_L * C_e}$			Freundlich model: $Q_e = K_f * C_e^{\frac{1}{n}}$		
		K_L	Q_{max} (mg/g)	R^2	K_f	$1/n$	R^2
UBC	4.0	0.168	6.978	0.999	1.593	0.291	0.891
	7.0	0.116	8.052	0.999	1.926	0.267	0.795
	9.0	0.139	5.981	0.997	1.673	0.258	0.798
FPC	4.0	0.066	9.074	0.999	1.743	0.289	0.922
	7.0	0.054	9.606	0.998	1.807	0.285	0.941
	9.0	0.064	7.342	0.965	1.892	0.231	0.955
nZVI	4.0	0.00432	40.173	0.989	41.180	0.329	0.981
	7.0	0.04843	36.312	0.995	34.539	0.307	0.988
	9.0	0.04169	28.205	0.997	28.025	0.294	0.995
FPC/nZVI	4.0	0.00293	92.245	0.991	100.677	0.213	0.995
	7.0	0.00126	130.036	0.988	143.074	0.198	0.994
	9.0	0.00249	79.855	0.984	85.134	0.188	0.990
UBC/nZVI	4.0	0.00736	90.320	0.955	40.443	0.256	0.952
	7.0	0.00684	82.142	0.944	35.697	0.123	0.932
	9.0	0.00953	49.654	0.983	23.401	0.107	0.978

Table S3 Pseudo-first-order and Pseudo-second-order kinetic model parameters for As(III) sorption onto nZVI and FPC/nZVI

Adsorbents	C_0 (mg/L)	q_e experimental (mg/g)	Pseudo 1st order kinetics			Pseudo 2nd order kinetics		
			q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (min/g/mg)	R^2
nZVI	10	9.97	7.53	0.021	0.966	9.93	9.10×10^{-3}	0.994
	50	19.57	8.92	0.014	0.952	20.58	2.58×10^{-3}	0.998
	100	24.04	12.95	0.009	0.928	25.13	1.53×10^{-3}	0.998
FPC/nZVI	10	9.98	9.98	0.061	0.999	10.44	7.76×10^{-3}	0.984
	50	48.89	46.01	0.046	0.992	52.79	9.32×10^{-4}	0.989
	100	86.69	84.60	0.044	0.996	94.13	5.81×10^{-4}	0.988
UBC/nZVI	10	9.989	10.02	0.0253	0.993	11.236	2.03×10^{-3}	0.975
	50	43.526	45.59	0.0157	0.996	59.308	1.98×10^{-4}	0.989
	100	72.326	76.95	0.0138	0.974	100.17	1.00×10^{-4}	0.952

Table S4 Comparison of As(III) adsorption capacities of various nZVI doped composites in the references.

Adsorbents	Range of As(III) concentrations (mg/L)	pH	Isotherm model	Q_{max} (mg/g)	Kinetics model	References
nZVI/Montmorillonit	2-200	7.0	Freundlich	59.9	PSO	[2]
S-nZVI	10-50	7.0	Langmuir	89.29	PSO	[3]
nZVI/Chitosan	0.01–25	6.0	Freundlich	1.67		[4]
nZVI/GO	1–20	6.0	Langmuir	18.51	PSO	[5]
nZVI/Coffee ground	10–50	7.0	Freundlich	52.20	PFO	[6]
nZVI/Zeolite	0.5–10	6.0	Langmuir	11.52	PSO	[7]
FPC/nZVI	1-500	7.0	Freundlich	130.04	PFO	This study

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