Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

New insights on the activity of biochar supported nanoscale zerovalent iron composite and nanoscale zero valent iron under anaerobic or aerobic conditions

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Text S1 Introduction of chemical regents

Saw dust was obtained from a wood processing factory in Changsha suburb. All chemicals were purchased in analytical purity and used as received: $FeSO_4 \cdot 7H_2O$, NaCl, NaOH, HCl, $NaBH_4$, were used in experiments. All solutions were prepared with ultrapure (DI) water from a Milli-Q water system. Deoxygenation ultrapure water was prepared by sparging with N_2 for 2 h and then kept under seal in a refrigerator for following washing.

Text S2 Preparation of biochar, nZVI/biochar and nZVI

To prepare pristine saw dust derived biochars, crushed saw dust of 0.5-1.0 mm size was oven dried at 80 ^oC, and then pyrolyzed at 600 ^oC for one hour in a tube furnace under continuously flowing N_2 gases. The biochars were rinsed with tap water for 1 h and DI water for 10 min, and oven dried overnight at 80 ^oC. The nZVI/biochar composites were synthesized according to methods proposed by Gao *et al* and Chen *et al*. with modification[1, 2]. The reduction reaction took place by the following equations:

$$2Fe^{3+} + BH_4^- + H_2O \rightarrow 2Fe^0 + BO_2^2 \ + 2H_2 + H^+ \qquad (1)$$

Briefly, 2.5 g biochar was added into 300 mL DI water and suspension was sonicated for 1 h. $FeSO_4 \cdot 7H_2O$ of 2.474 g was dissolved in DI water and transferred to the biochar suspension dropwise, followed by 1 h sonication with continuously N_2. 5 g $NaBH_4$ was dissolved in 80 mL DI water, and the solution was added drop wisely to reduce Fe^{2+} to nZVI at around 90 ^oC. The reaction continued for 4 h and cooled down to room temperature under N_2. The suspension was filtered by a vacuum filter, and rinsed with DI water followed by ethanol. The resulting nZVI/biochar was dried in vacuum oven at 50 ^{o}C for 24 h, and nZVI was prepared by following same procedure but without biochar.

Text S3 Preliminary experiments

Preliminary experiments were performed in sealed glass conical flasks containing 250 mL of an unbuffered aqueous PNP. PNP removal was initiated by adding biochar, nZVI/biochar or nZVI. The reaction was designed in triplicates and continuously mixed using an orbital shaker at 200 rpm at 25 ± 2 °C. Then, aliquots of the aqueous solutions were withdrawn by a syringe at intervals and finally filtered by a 0.45 μm membrane to separate the solid from the liquid.

Text S4 Analysis procedures

The residual concentration of PNP was determined by high performance liquid chromatography (HPLC) (Agilent 1200, USA) equipped with a ZORBAX SB–C18 reversed phase column. The mobile phase of HPLC consisted of a mixture of 1% aqueous acetic acid and methanol (v/v = 3:7) with a total flow rate of 1.0 mL/min, and the wavelength was set at 315 nm [3]. The two main intermediates (p-aminophenol and p-benzoquinone) was analyzed by HPLC consisted of a mixture of 1% aqueous acetic acid and methanol (v/v = 1:4) with a total flow rate of 0.8 mL/min, and the wavelength was set at 280 nm. The concentration of iron speciation (Fe^{2+} and Fe^{3+}) were all determined by determined by UV–vis spectroscopy (SHIMADZU 2550). TOC of the sample were measured by TOC analyzer (Shimazu, Japan). Gas chromatography–mass spectrometry (GC–MS) (SHIMADZU, Japan) analytic methods were modified from those in our previous work [4].

Figure captions:

Fig. S1 XRD patterns of nZVI/biochar.

Fig. S2 The efficiency of PNP degradation for nZVI/biochar or nZVI systems with various pH values under different aeration conditions with initial PNP concentration of 100 mg/L, temperature at 25 ± 2 °C and contact time of 180 min. nZVI/biochar purging with N_2 (A) and air aeration (B), nZVI purging with N_2 (C) and air aeration (D).

Fig. S3 Effects of initial PNP concentration and contact time on the PNP degradation rate by nZVI/biochar purging with N_2 (A) and air aeration (B), nZVI purging with N_2 (C) and air aeration (D).

Fig. S4 Linear fitting using the pseudo-first-order model about PNP degradation for S-NZVI or NZVI systems with various initial PNP concentration under different aeration conditions, nZVI/biochar purging with N_2 (A) and air aeration (B), nZVI purging with N_2 (C) and air aeration (D).

Fig. S5 The pseudo-first-order kinetic plot for the degradation of PNP at different temperature, Reaction conditions: 100 mg/L PNP removed on nZVI/biochar purging with N_2 (A) and air aeration (B), nZVI purging with N_2 (C) and air aeration (D).

Fig. S6 Arrhenius plot of reaction rate constant. Reaction conditions: 100 mg/L PNP removed on nZVI/biochar purging with N_2 (A) and air aeration (B), nZVI purging with N_2 (C) and air aeration (D).

Fig. S7 Proposed reaction pathway for degradation of PNP with nZVI/biochar

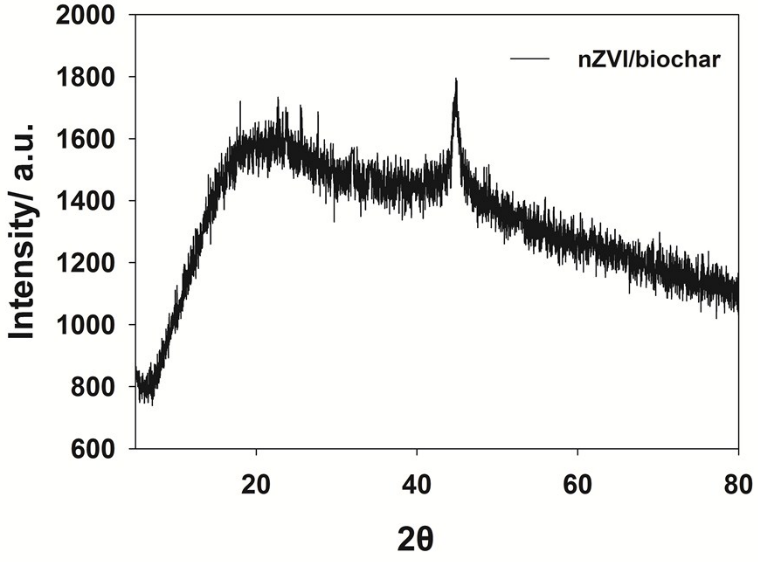
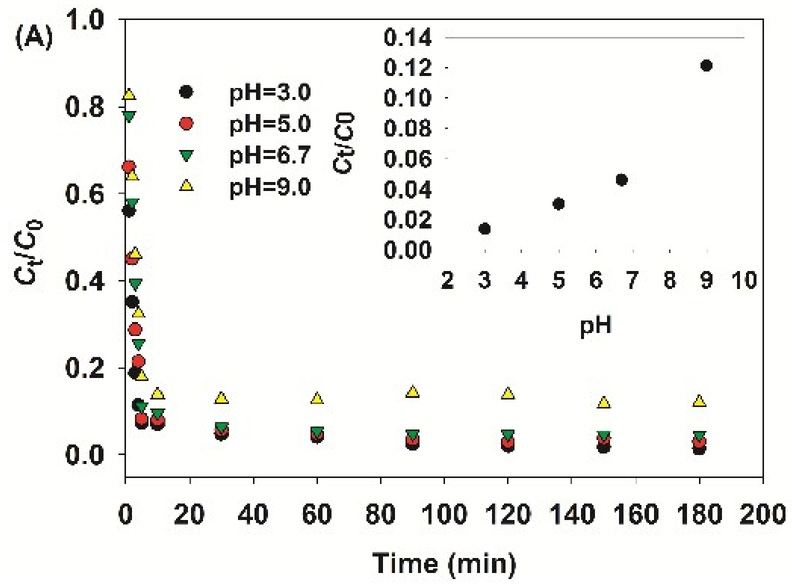
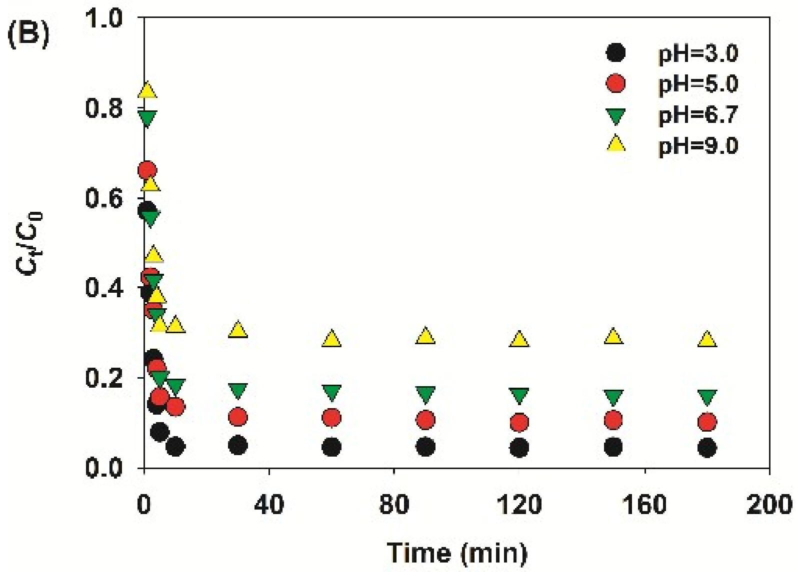

nZVI/biochar
Intensity/ a.u.
2θ
2000
1800
1600
1400
1200
1000
800
600
20
40
60
80

Fig. S1


(A)
1.0
0.8
0.6
0.4
0.2
0.0
C_t/C_0
● pH=3.0
● pH=5.0
▼ pH=6.7
△ pH=9.0
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Ct/C0
2 3 4 5 6 7 8 9 10
pH
0 20 40 60 80 100 120 140 160 180 200
Time (min)


(B)
1.0
0.8
0.6
0.4
0.2
0.0
C_t/C_0
● pH=3.0
● pH=5.0
▼ pH=6.7
▲ pH=9.0
0 40 80 120 160 200
Time (min)

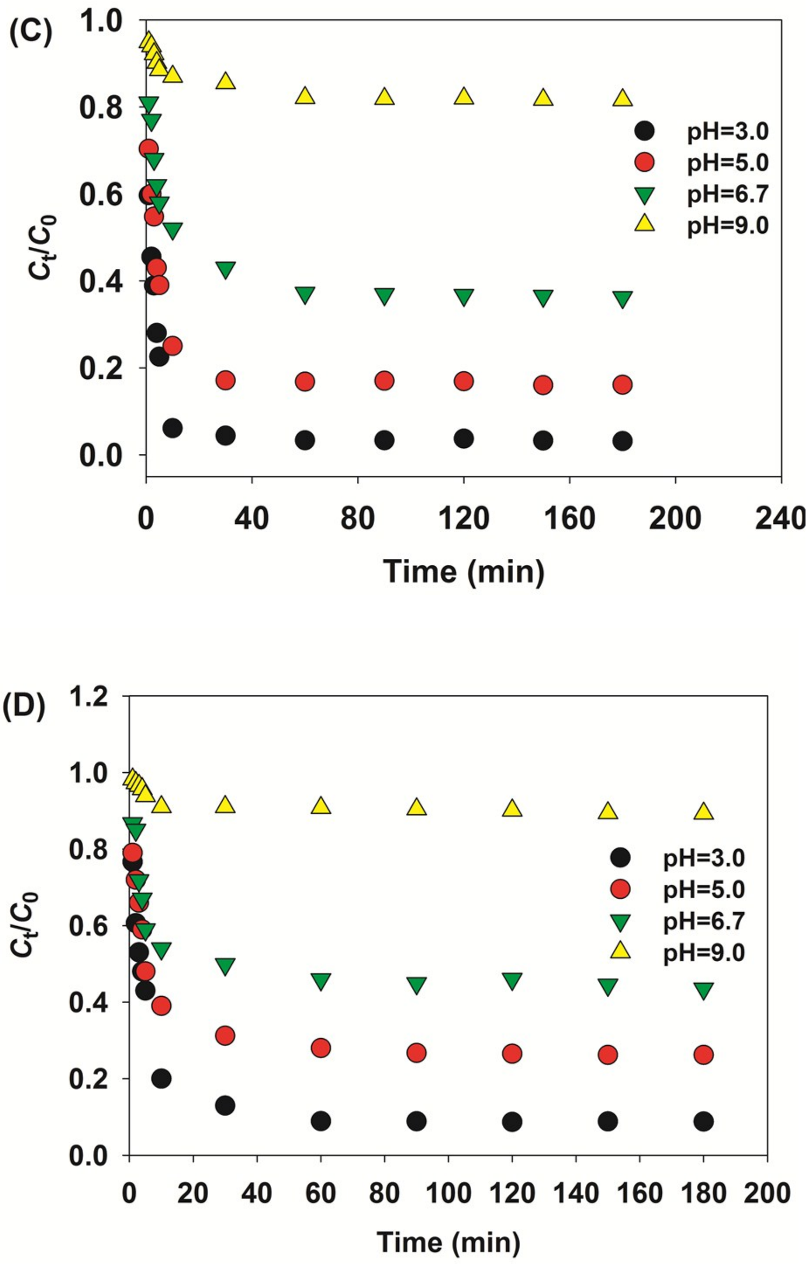
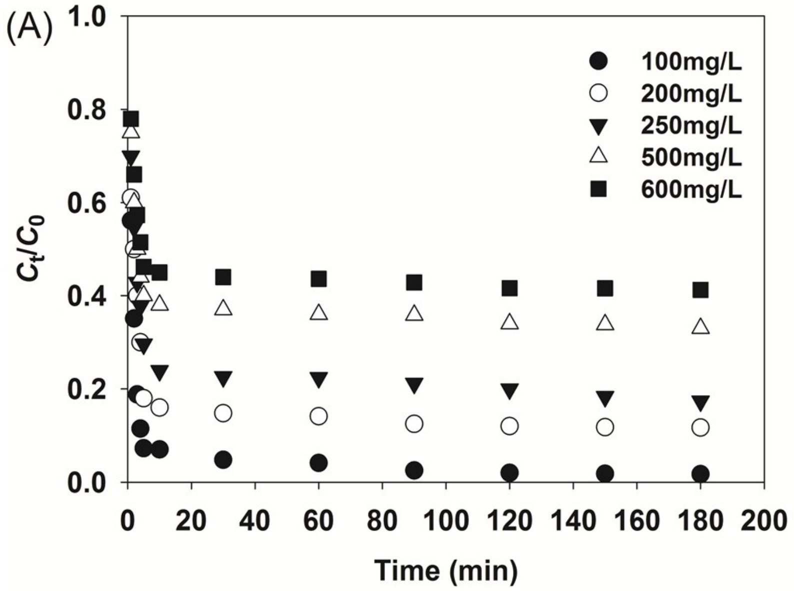
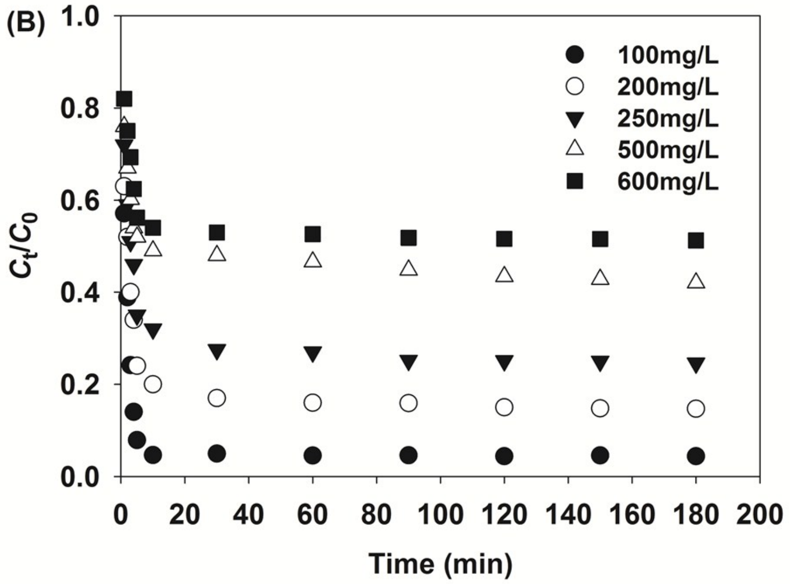

(C)
C_t/C_0
1.0
0.8
0.6
0.4
0.2
0.0
0
40
80
120
160
200
240
Time (min)
● pH=3.0
● pH=5.0
▼ pH=6.7
△ pH=9.0
(D)
C_t/C_0
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100
120
140
160
180
200
Time (min)
● pH=3.0
● pH=5.0
▼ pH=6.7
△ pH=9.0

Fig. S2


(A)
Ct/C0
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100
120
140
160
180
200
Time (min)
● 100mg/L
○ 200mg/L
▼ 250mg/L
△ 500mg/L
■ 600mg/L


(B)
Ct/C0
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100
120
140
160
180
200
Time (min)
● 100mg/L
○ 200mg/L
▼ 250mg/L
△ 500mg/L
■ 600mg/L

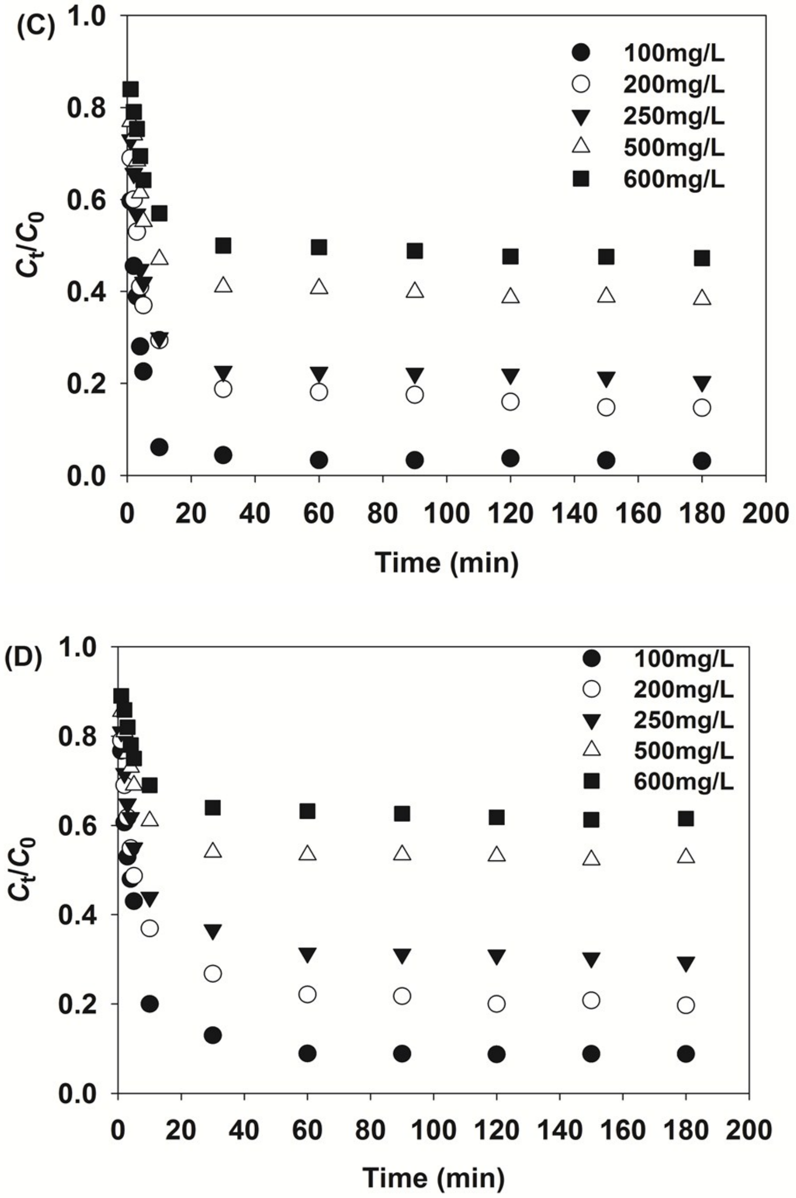
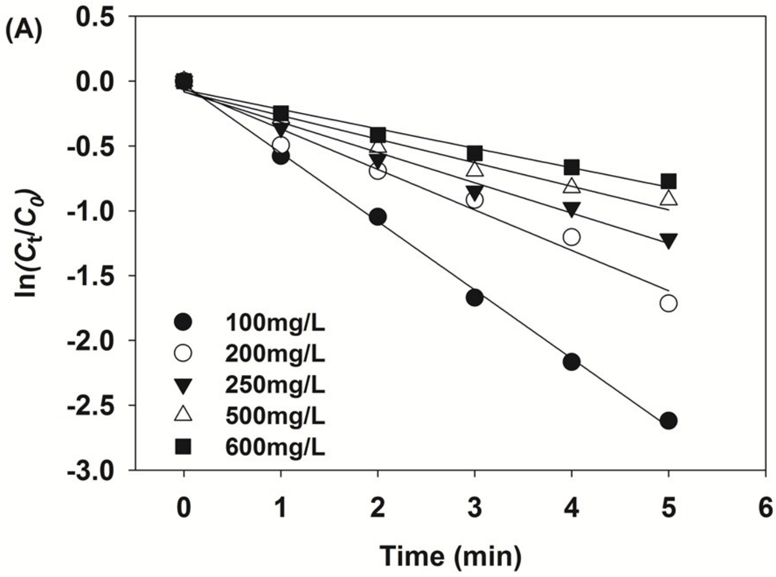
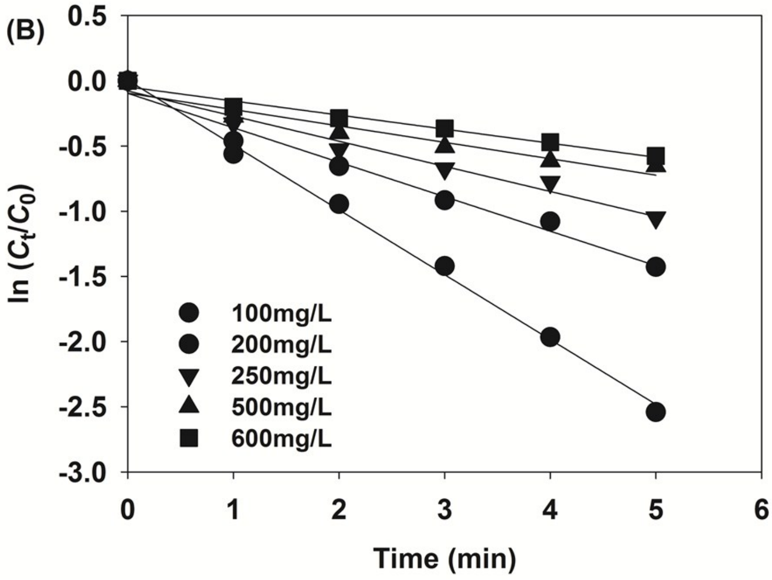
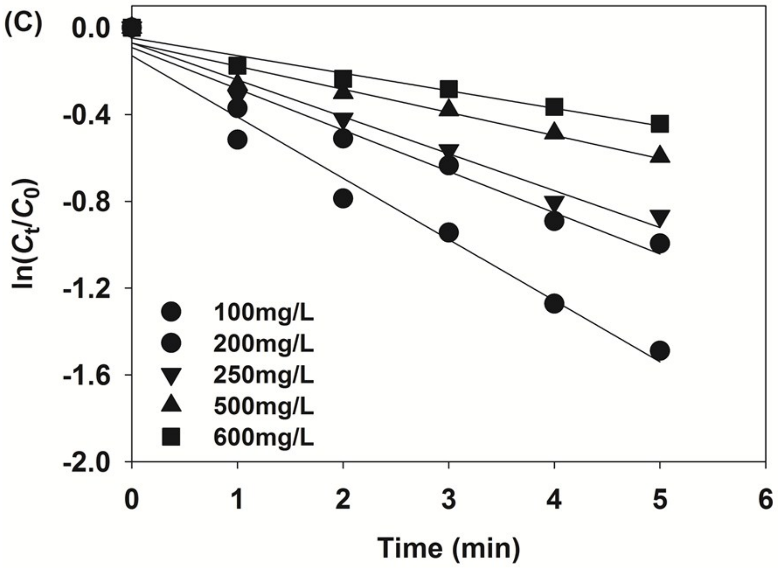

(C)
1.0
0.8
0.6
0.4
0.2
0.0
C_t/C_0
0
20
40
60
80
100
120
140
160
180
200
Time (min)
100mg/L
200mg/L
250mg/L
500mg/L
600mg/L
(D)
1.0
0.8
0.6
0.4
0.2
0.0
C_t/C_0
0
20
40
60
80
100
120
140
160
180
200
Time (min)
100mg/L
200mg/L
250mg/L
500mg/L
600mg/L

Fig. S3


(A)
ln(C_t/C_0)
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
0
1
2
3
4
5
6
Time (min)
● 100mg/L
○ 200mg/L
▼ 250mg/L
△ 500mg/L
■ 600mg/L


(B)
ln (C_t/C_0)
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
0
1
2
3
4
5
6
Time (min)
● 100mg/L
● 200mg/L
▼ 250mg/L
▲ 500mg/L
■ 600mg/L


(C)
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
ln(C_t/C_0)
0
1
2
3
4
5
6
Time (min)
● 100mg/L
● 200mg/L
▼ 250mg/L
▲ 500mg/L
■ 600mg/L

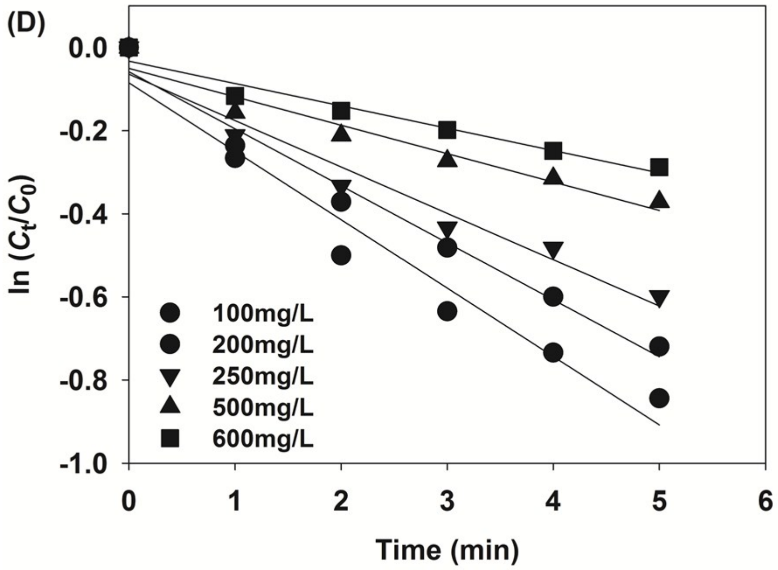
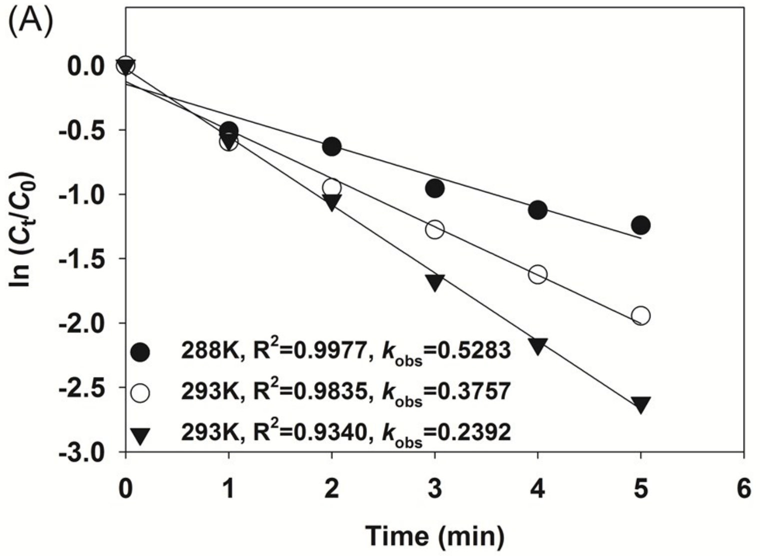
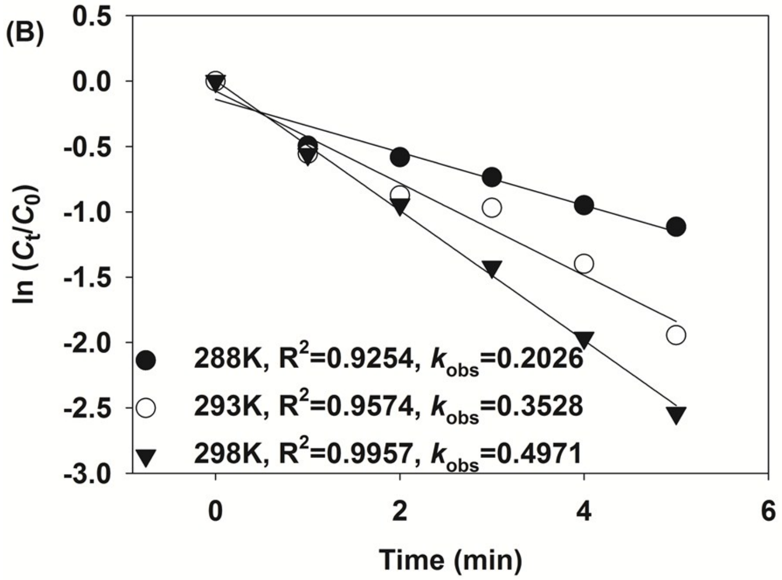

(D)
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
ln (C_t/C_0)
0
1
2
3
4
5
6
Time (min)
● 100mg/L
● 200mg/L
▼ 250mg/L
▲ 500mg/L
■ 600mg/L

Fig. S4


(A)
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
ln (C_t/C_0)
288K, R^2=0.9977, k_{obs}=0.5283
293K, R^2=0.9835, k_{obs}=0.3757
293K, R^2=0.9340, k_{obs}=0.2392
0
1
2
3
4
5
6
Time (min)


(B)
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
ln (C_t/C_0)
288K, R^2=0.9254, k_{obs}=0.2026
293K, R^2=0.9574, k_{obs}=0.3528
298K, R^2=0.9957, k_{obs}=0.4971
0
2
4
6
Time (min)

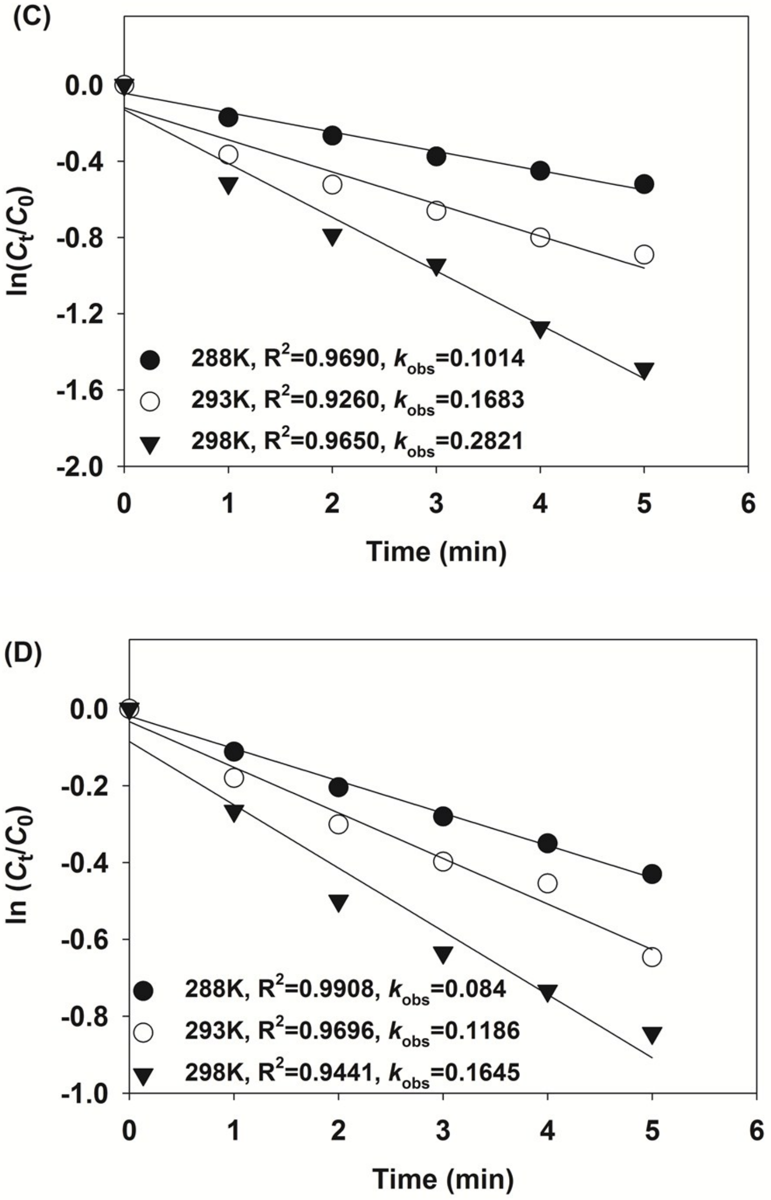
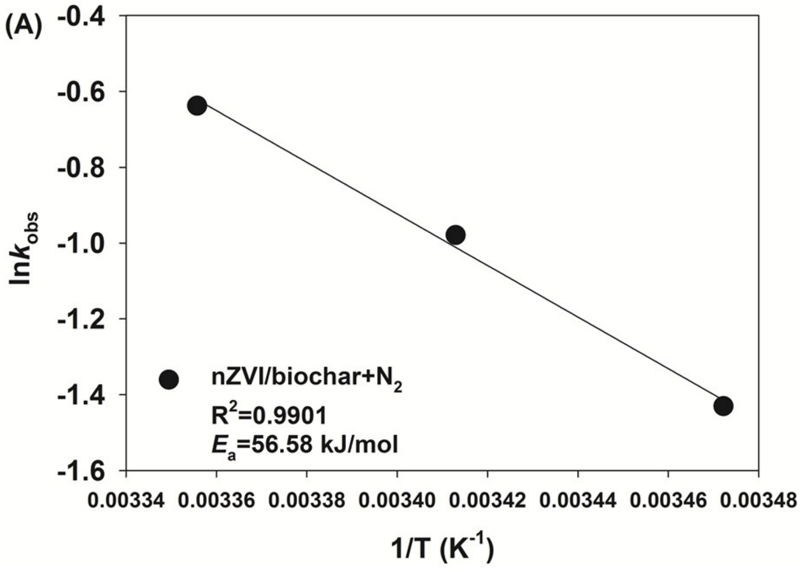
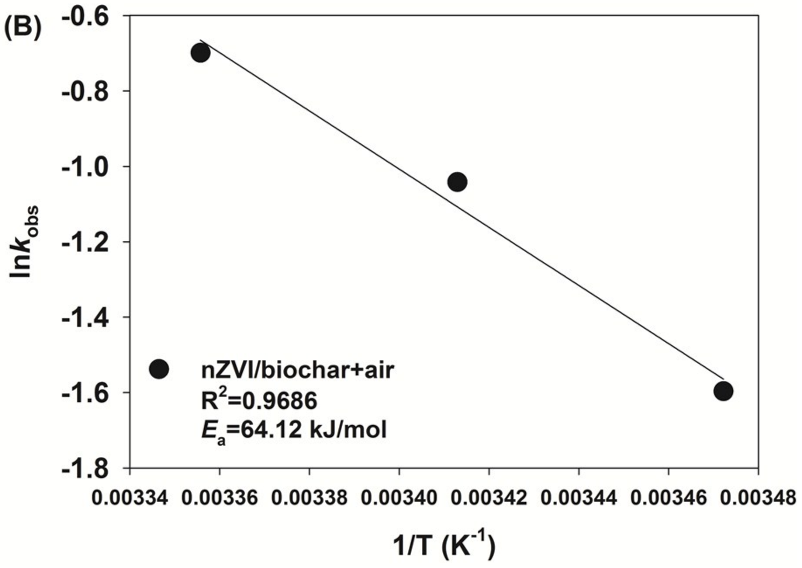
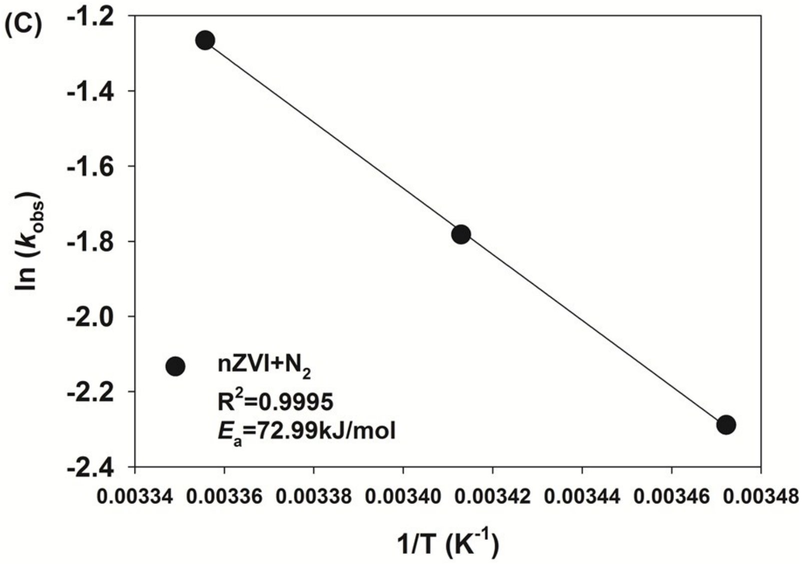

(C)
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
ln(C_t/C_0)
0
1
2
3
4
5
6
Time (min)
● 288K, R^2=0.9690, k_{obs}=0.1014
○ 293K, R^2=0.9260, k_{obs}=0.1683
▼ 298K, R^2=0.9650, k_{obs}=0.2821
(D)
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
ln (C_t/C_0)
0
1
2
3
4
5
6
Time (min)
● 288K, R^2=0.9908, k_{obs}=0.084
○ 293K, R^2=0.9696, k_{obs}=0.1186
▼ 298K, R^2=0.9441, k_{obs}=0.1645

Fig. S5


(A)
lnk_obs
1/T (K^-1)
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
0.00334
0.00336
0.00338
0.00340
0.00342
0.00344
0.00346
0.00348
nZVI/biochar+N₂
R²=0.9901
Ea=56.58 kJ/mol


(B)
lnk_obs
1/T (K^-1)
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
0.00334
0.00336
0.00338
0.00340
0.00342
0.00344
0.00346
0.00348
nZVI/biochar+air
R²=0.9686
Ea=64.12 kJ/mol


(C)
-1.2
-1.4
-1.6
-1.8
-2.0
-2.2
-2.4
ln (k_{obs})
0.00334
0.00336
0.00338
0.00340
0.00342
0.00344
0.00346
0.00348
1/T (K^{-1})
nZVI+N_2
R^2=0.9995
E_a=72.99kJ/mol

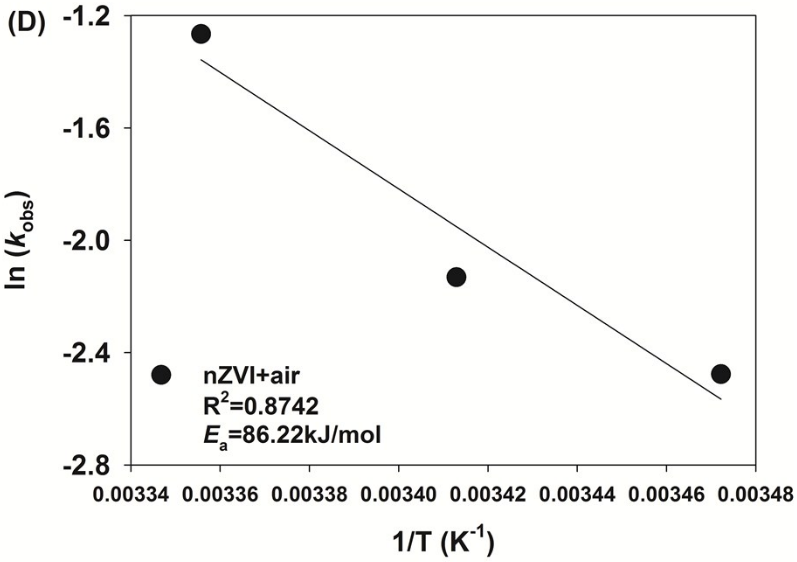

(D)
-1.2
-1.6
-2.0
-2.4
-2.8
ln (k_{obs})
0.00334
0.00336
0.00338
0.00340
0.00342
0.00344
0.00346
0.00348
1/T (K^{-1})
nZVI+air
R^2=0.8742
E_a=86.22kJ/mol

Fig. S6

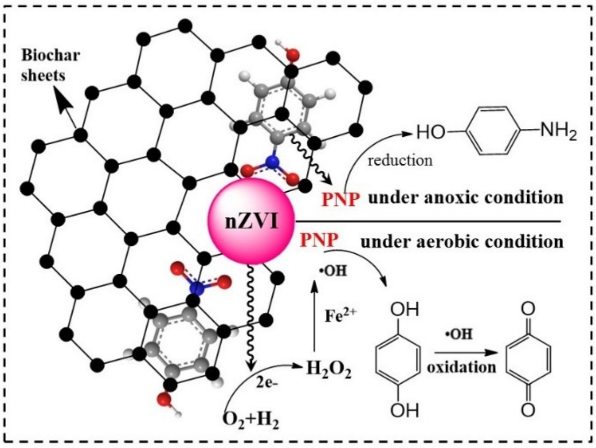

Biochar sheets
nZVI
HO
NH2
reduction
PNP under anoxic condition
PNP under aerobic condition
•OH
Fe2+
2e-
H2O2
O2+H2
OH
OH
•OH
oxidation
O
O

Fig. S7

Table S1 Pseudo-first-order model parameters for PNP removal in nZVI/biochar or nZVI systems under different aeration and solution pH conditions

Samples	Condition	Solution pH	Apparent rate constant (k_{obs})	Correlation coefficients (R^2)
nZVI/biochar	Purging with N_2	3.0	0.5283	0.9977
		5.0	0.4652	0.9573
		6.7	0.4196	0.9391
		9.0	0.3360	0.9543
	Air aeration	3.0	0.4971	0.9957
		5.0	0.3642	0.9908
		6.7	0.3092	0.9798
		9.0	0.2409	0.9928
nZVI	Purging with N_2	3.0	0.2821	0.9650
		5.0	0.1793	0.9517
		6.7	0.1043	0.9556
		9.0	0.0224	0.9380
	Air aeration	3.0	0.1645	0.9441
		5.0	0.1324	0.9629
		6.7	0.1023	0.9721
		9.0	0.0115	0.9670

Table S2 Pseudo-first-order model parameters for PNP removal in nZVI/biochar or nZVI systems under different aeration and PNP concentration conditions with pH=3.0.

Samples	Condition	Solution concentration	Apparent rate constant (k_{obs})	Correlation coefficients (R^2)
nZVI/biochar	Purging with N_2	100	0.5283	0.9977
		200	0.3122	0.9680
		250	0.2337	0.9761
		500	0.1818	0.9551
		600	0.1499	0.9649
	Air aeration	100	0.4971	0.9957
		200	0.2642	0.9732
		250	0.1925	0.9642
		500	0.1258	0.9108
		600	0.1079	0.9707
nZVI	Purging with N_2	100	0.2821	0.9650
		200	0.1902	0.9571
		250	0.1701	0.9606
		500	0.1064	0.9609
		600	0.0894	0.9820
	Air aeration	100	0.1645	0.9441
		200	0.1371	0.9794
		250	0.1116	0.9448

	500	0.0683	0.9484
	600	0.0537	0.9104

References

1. S. Wang, B. Gao, Y. Li, A. E. Creamer and H. Feng, *Journal of Hazardous Materials*, 2016.
2. J. Yan, H. Lu, W. Gao, X. Song and M. Chen, *Bioresource Technology*, 2014, **175**, 269-274.
3. T. Wang, G. Qu, Q. Sun, D. Liang and S. Hu, *Water Research*, 2015, **84**, 18-24.
4. L. Tang, J. Tang, G. Zeng, G. Yang, X. Xie, Y. Zhou, Y. Pang, Y. Fang, J. Wang and W. Xiong, *Applied Surface Science*, 2015, **333**, 220-228.