Electronic Supplementary Information

Facile room temperature synthesis of $NiFe_2O_4$-based magnetic covalent organic framework for the extraction of tetracycline residues in environment water samples prior to HPLC

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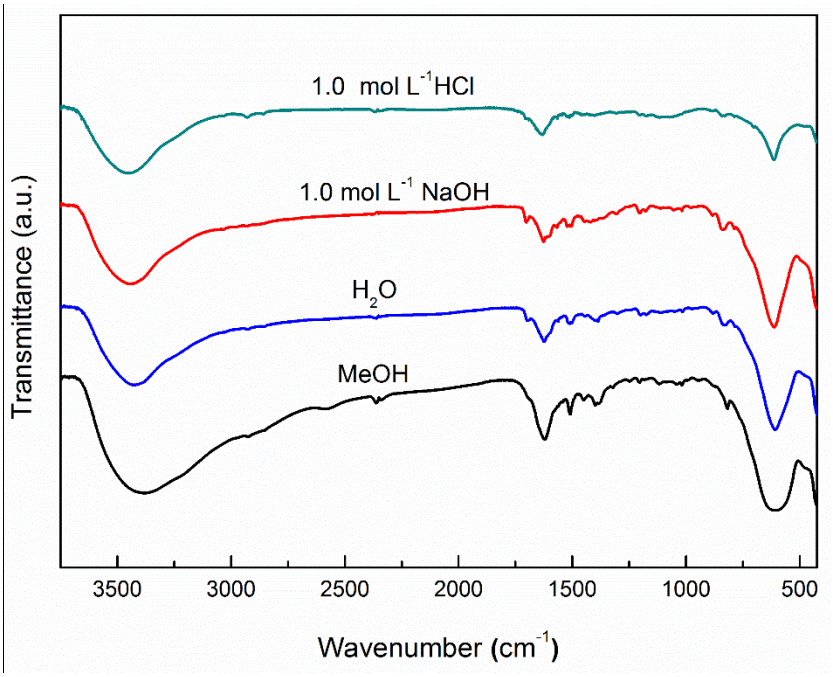


Fig.S1 FT-IR spectra of $NiFe_2O_4$@TAPB-TPA treated with different solvents for 48 h.

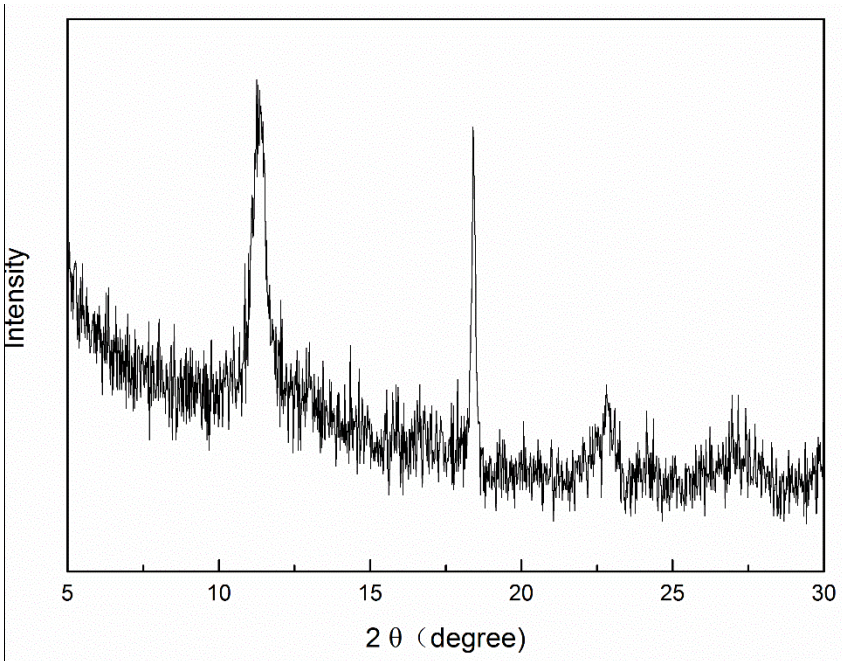


Fig.S2 Small-angle XRD patterns of $NiFe_2O_4$@TAPB-TPA.

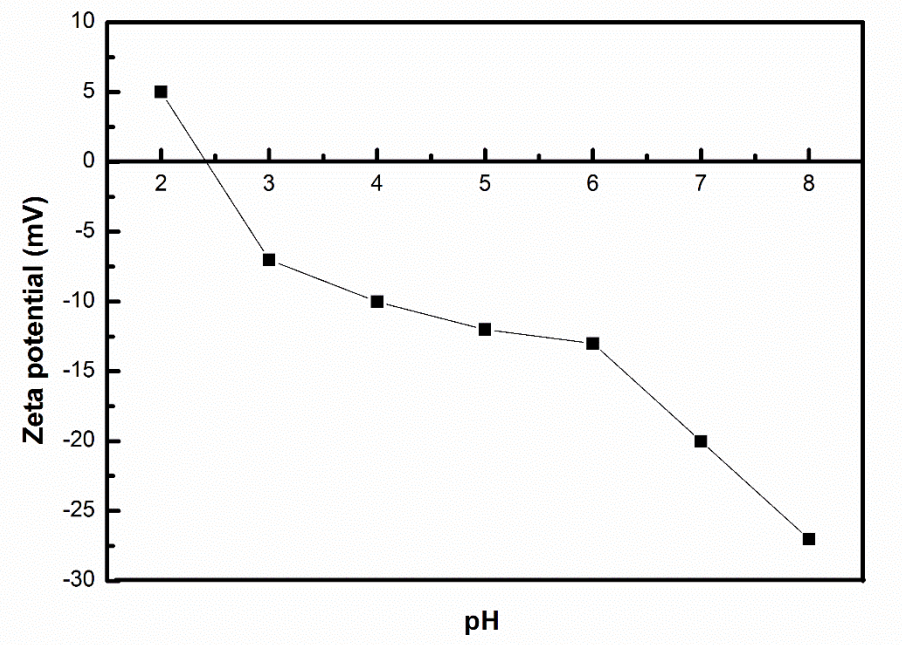


Fig.S3 Zeta potential of $NiFe_2O_4$@TAPB-TPA.

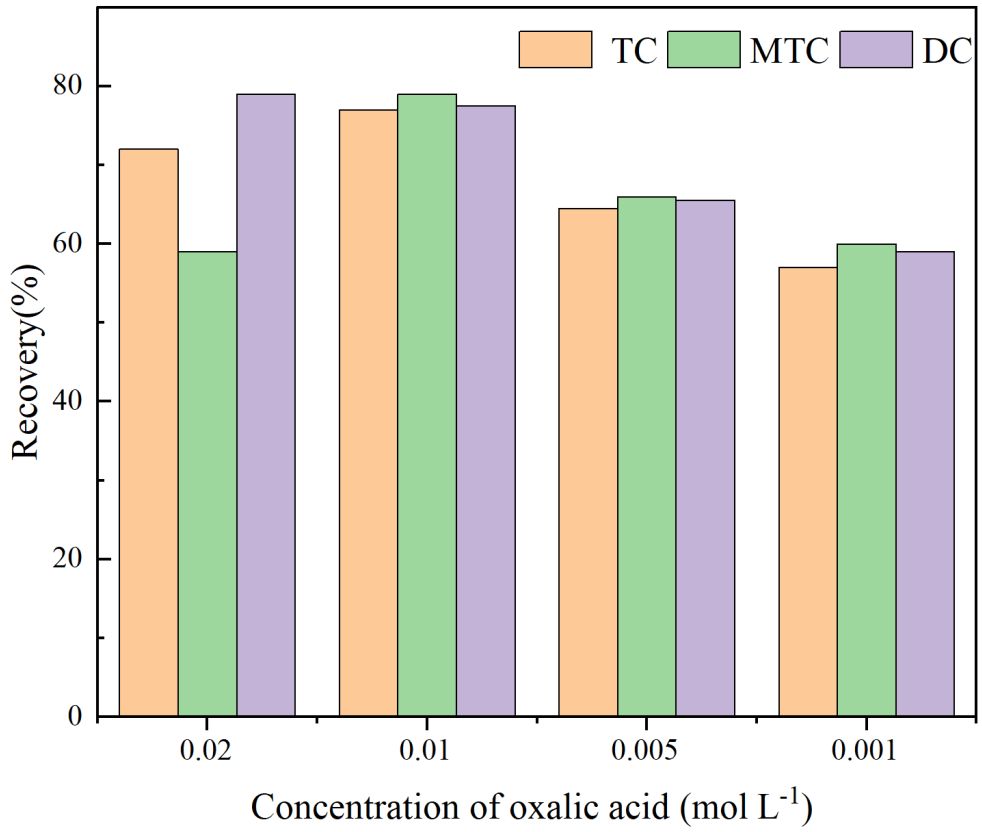


Fig.S4 Effect of oxalic acid concentration on the extraction recovery. The ratio of MeOH, ACN and oxalic acid was 1:2:7 (v:v:v); other conditions were the same as those in Fig. 4C.

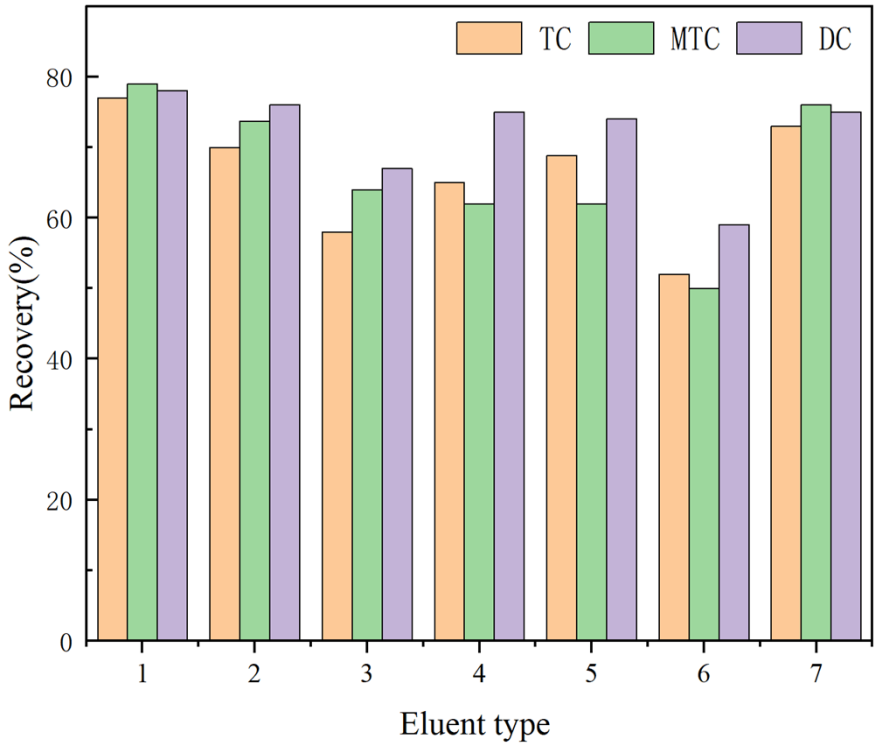
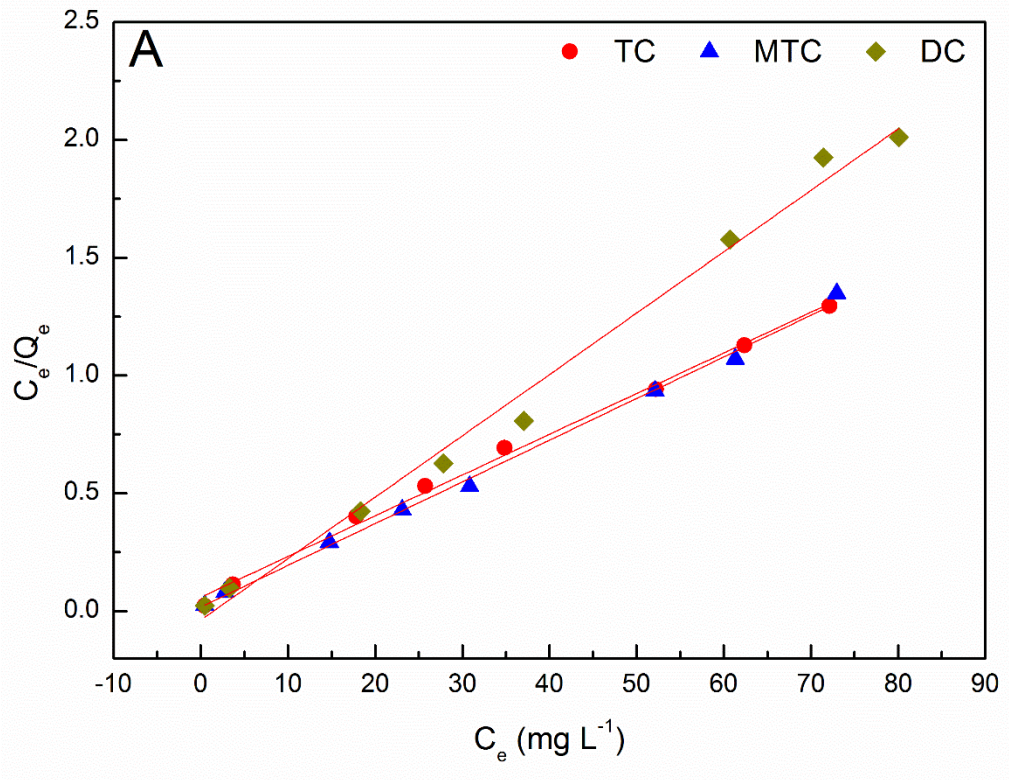
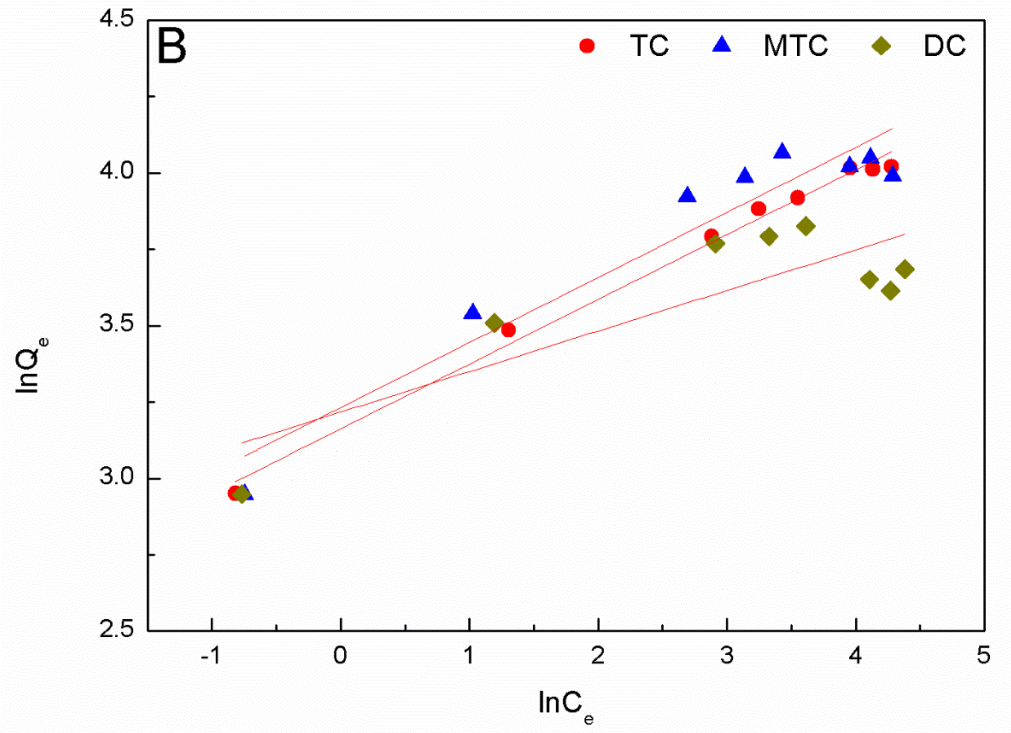


Fig. S5 Effect of eluent type on extraction recovery. Types of eluent were consisted of MeOH, ACN and oxalic acid (0.01 mol L^{-1}) at different ratio (v:v:v) : (1) 1:2:7; (2) 2:1:7; (3) 2.5:0.5:7; (4) 1:3:6; (5)2:2:6; (6) 3:2:5; (7) 1:1:8.


A
TC
MTC
DC
2.5
2.0
1.5
1.0
0.5
0.0
C_e/Q_e
-10
0
10
20
30
40
50
60
70
80
90
C_e (mg L^{-1})


B
TC
MTC
DC
4.5
4.0
3.5
3.0
2.5
lnQ_e
-1
0
1
2
3
4
5
lnC_e

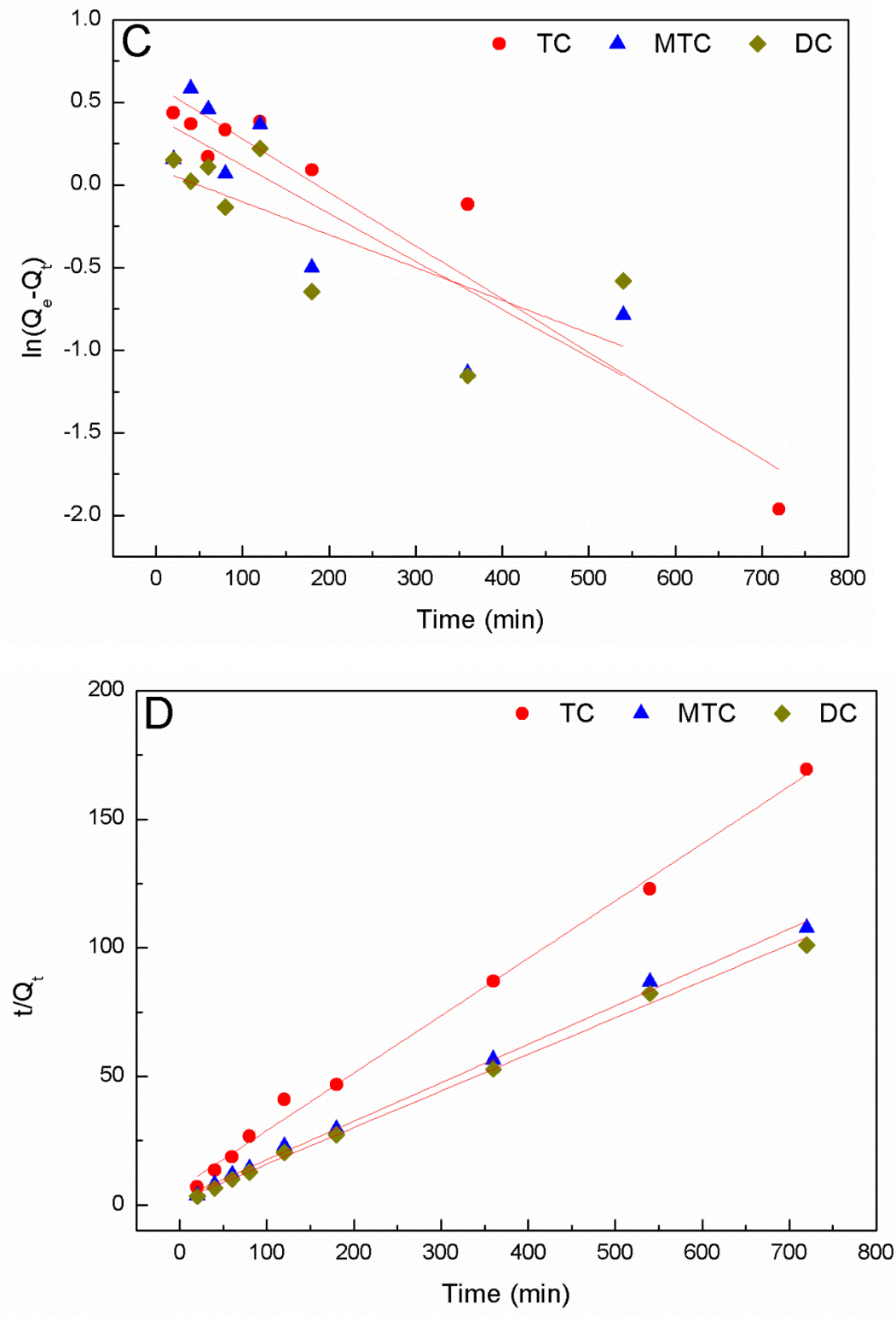


Fig.S 6 Adsorption isotherms and adsorption kinetics of TCs on $NiFe_2O_4$@TAPB-TPA. (A) Langmuir isotherm model curves; (B) Freundlich isotherm model curves; (C) Pseudo-first order model curves; and (D) Pseudo-second order model curves.

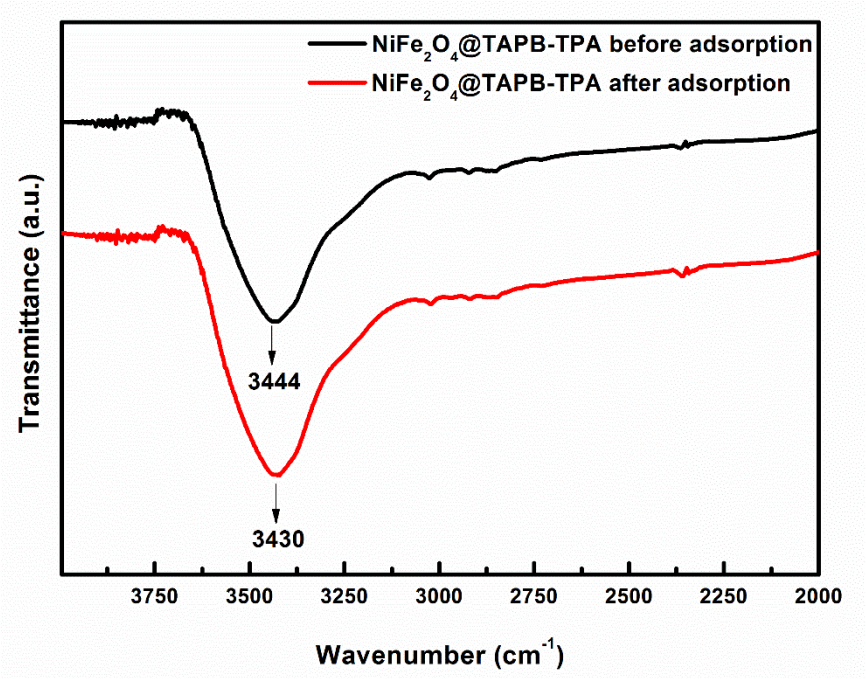


Fig.S7 The FT-IR spectra of $NiFe_2O_4$@TAPB-TPA before and after adsorption.

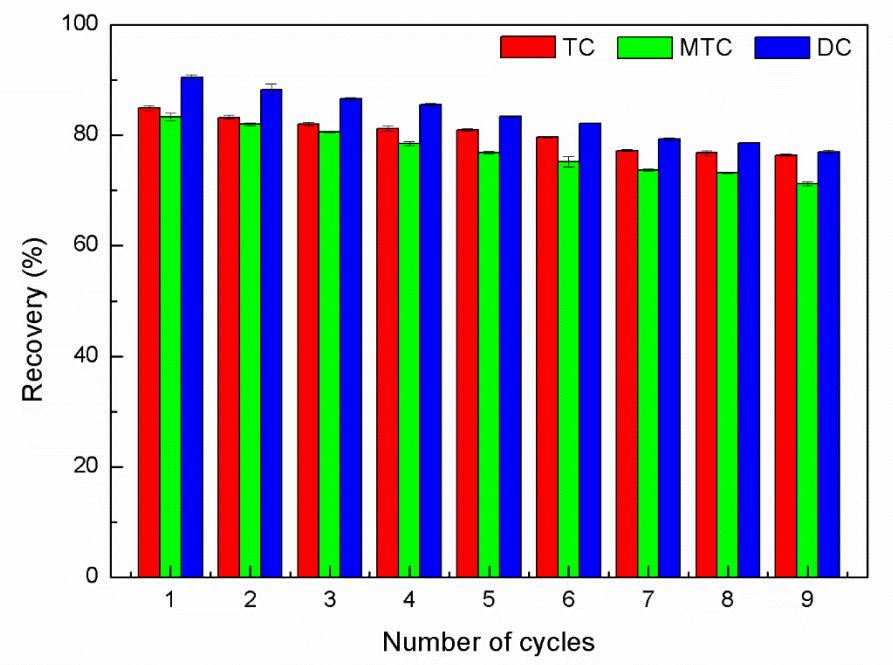
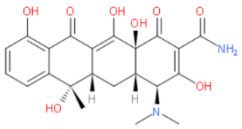
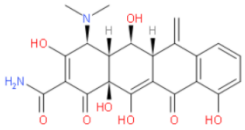
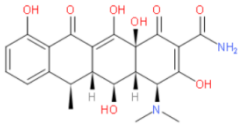


Fig.S8 Reusability of the $NiFe_2O_4$@TAPB-TPA as adsorbent.

Tables

Table S1 Some physical-chemical parameters of TCs.

Analytes	Abbreviation	Structure	Molecular weight	log_{Kow}[a]
Tetracycline	TC		444.45	-1.47
Methacycline	MTC		442.42	0.26
Doxycycline	DC		444.43	0.35

[a]: log_{Kow}: n-octanol/water partition coefficients, an indicator for hydrophobicity. Data taken from RSC Publishing Home: http://www.chemspider.com

Table S2 Results of isothermal models for the adsorption of $NiFe_2O_4$@TAPB-TPA towards TCs.

Analytes	Langmuir			Freundlich		
	K_L (L mg^{-1})	Q_{max} (mg g^{-1})	R^2	K_F	n	R^2
TC	0.97	57.87	0.9956	23.63	4.72	0.9901
MTC	3.25	56.53	0.9969	25.34	4.70	0.9061
DC	1.02	38.39	0.9905	24.96	7.54	0.6627

Table S3 Results of kinetic models for adsorption of $NiFe_2O_4$@TAPB-TPA towards TCs.

TCs	$Q_{e,\ exp}$ (mg g^{-1})	Pseudo-first-order model			Pseudo-second-order model		
		K_1 (min^{-1})	Q_e (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	Q_e (mg g^{-1})	R^2
TC	4.39	3.23×10^{-3}	1.82	0.9046	7.44×10^{-3}	4.48	0.9951
MTC	6.68	2.90×10^{-3}	1.51	0.6581	8.35×10^{-2}	6.69	0.9972
DC	7.12	1.99×10^{-3}	1.10	0.4768	1.20×10^{-2}	7.03	0.9960

Table S4 Comparison of proposed method with reported methods for TCs analysis.

Sorbent	Method	Mass of sorbent (mg)	Linear range (μg L^{-1})	LODs (μg L^{-1})	Recovery (%)	RSD (%)	Ref
PAN@COF-SCU1[1]	PT-SPE[5]-HPLC	10	4-70	0.6-3.0	82.7-117.5	1.2-9.5	48
RACNTs[2]	SPE[6]-HPLC	10	50-200	7.5-13.2	46.9-69.6	4.0-17.6	49
CTP_{CC-TP}[3]	SPE-HPLC	60	26.6–1500	8.0-16.8	81.3–98.7	3.9-7.7	50
SCAU-1 and SNW-1	SPE-UPLC[7]	60	1-500	8.0-16.8	88.4-93.4	2.5-4.8	51
Oasis HLB[4]	SPE-HPLC	200	50-500	17.2-21.0	83.3–111.8	3.5-16.2	52
$NiFe_2O_4$@TAPB-TPA	MSPE-HPLC	4	1-500	0.09-0.26	91.6-102.7	0.7-4.2	This work

[1] polyacrylonitrile@COFs- SCU1, SCU stands for Sichuan University

[2] restricted access carbon nanotubes

[3] microporous covalent triazine-terphenyl polymer

[4] Commercial adsorbent

[5] Pipette tip solid phase extraction

[6] Solid phase extraction

[7] Ultra-performance liquid chromatography