Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Data

for

Surface modification of magnetic nanoparticles via admicellar polymerization for selective removal of tetracycline from real water samples

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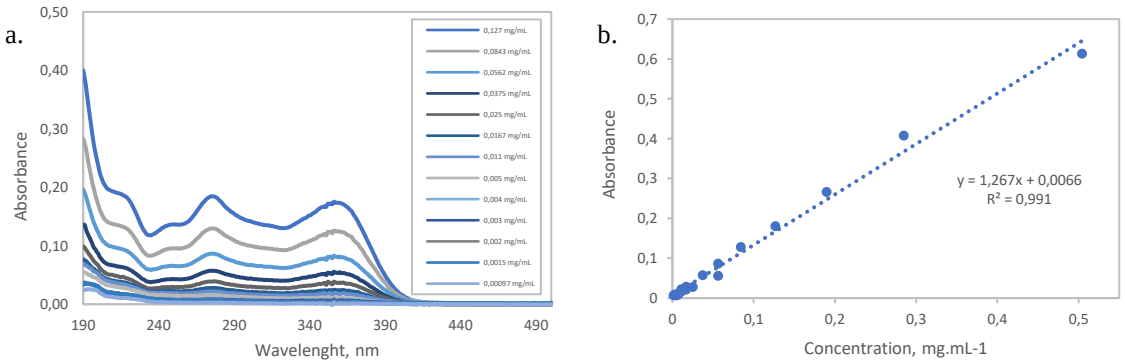

Figure S1. (a) The UV-Visible spectrum of tetracycline in the water at pH 7 and (b) the calibration curve.

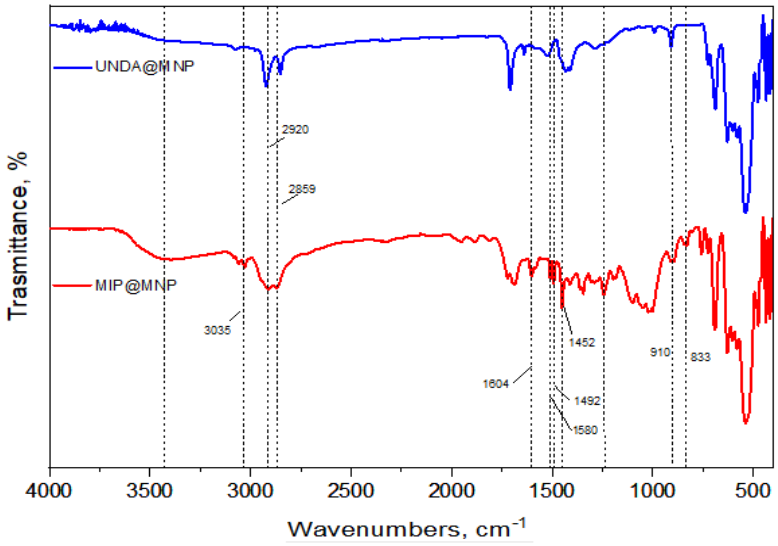

Figure S2. FTIR spectra of magnetic Fe_2O_3 nanoparticles (MNP), UNDA and MNP after modification with UNDA (UNDA@MNP).

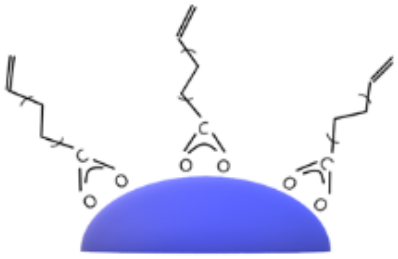

Figure S3. Chelating bidentate interaction between the carboxylate group of UNDA and the iron atom.

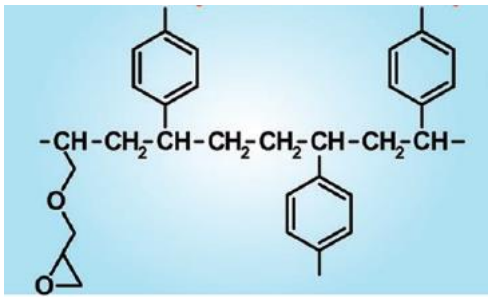

Figure S4. Chemical structure of STY-DVB-GMA.

The stability of the UNDA@MNP was checked by shacking at 70 ºC for 16 h.

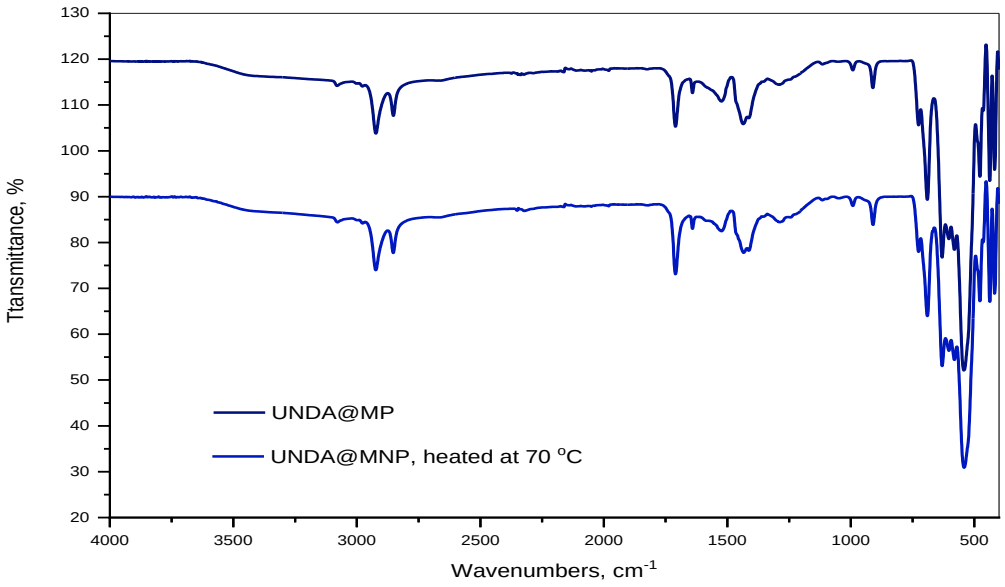

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Figure S5. FTIR spectra of UNDA@MNP before and after heated at 70 ºC.

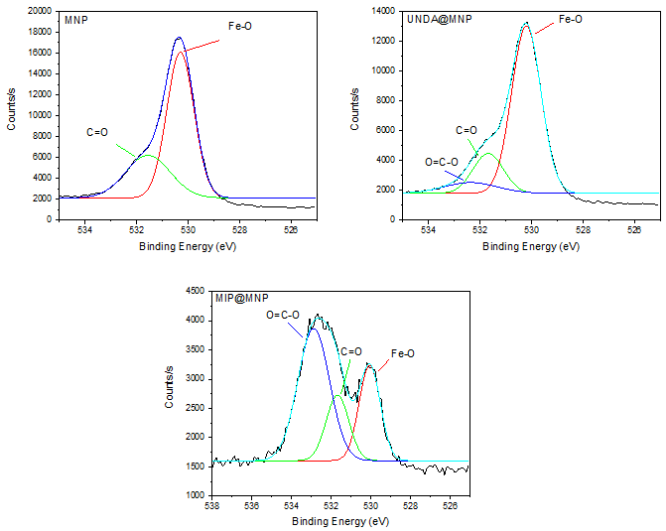


Figure S6. XPS O1s core level spectra of MNP, UNDA@MNP and MIP@MNP.

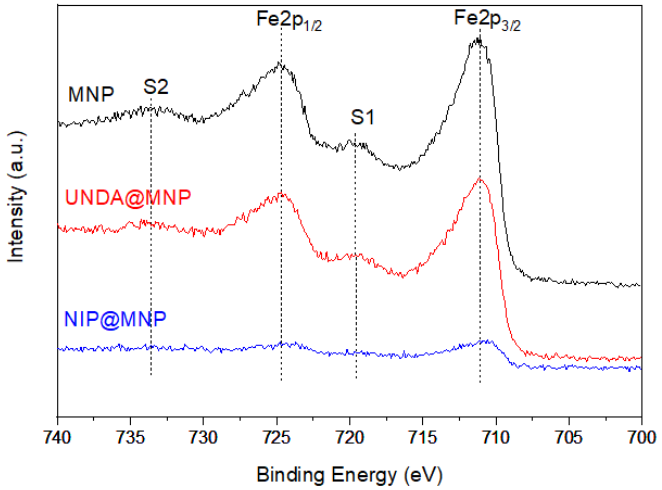


Figure S7. Fe2p core spectra of MNP before and after surface modification.

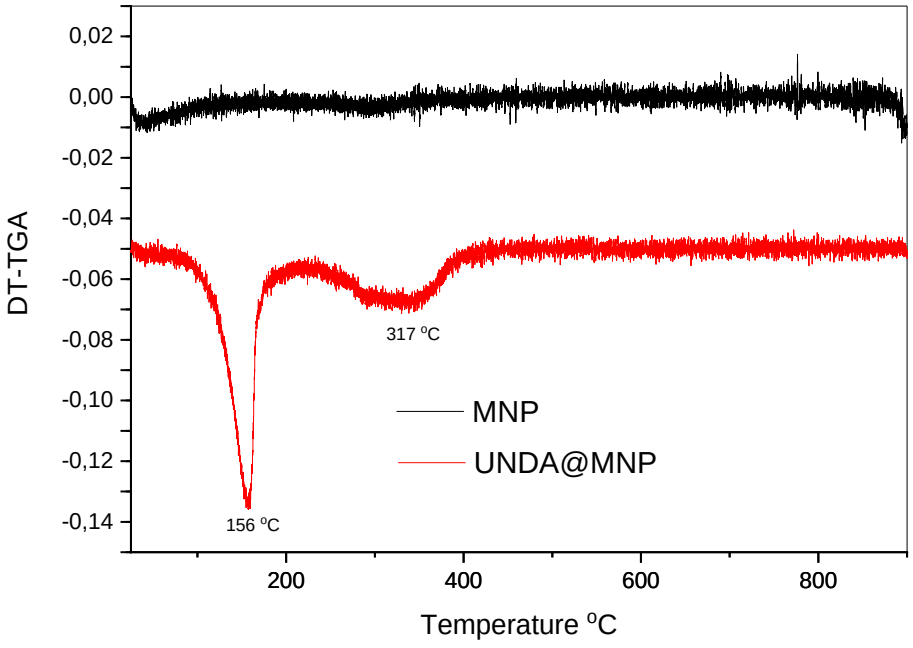


Figure S8. First derivation curve of MNP and UNDA@MNP.

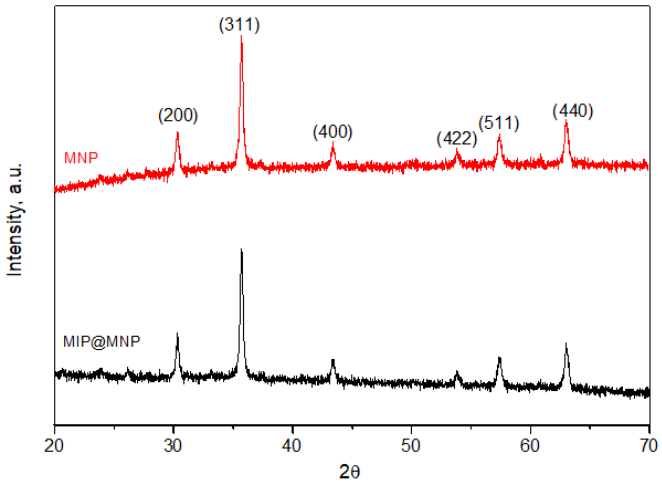


Figure S9. XRD pattern for Fe_2O_3 magnetic nanoparticles (MNP) and MIP modified Fe_2O_3 magnetic nanoparticles (MIP@MNP).

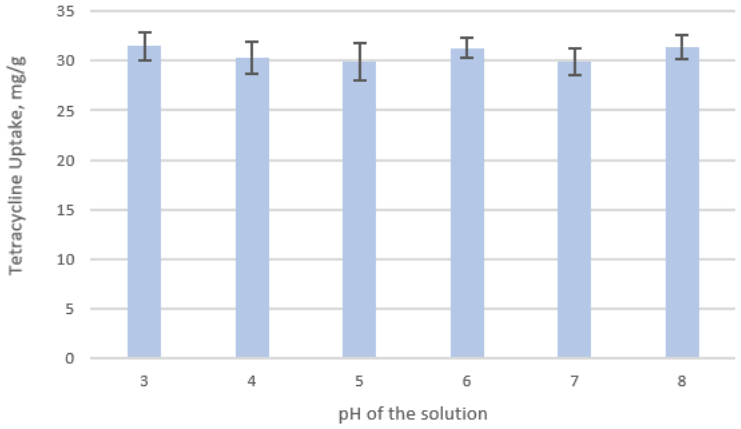


Figure S10. pH effect on the binding capacity of MIP@MNP (5.00 mg modified MIP@MNP in 0.050 mg.mL^{-1} tetracycline solutions with different pH values. The incubation time was 60 min, n= 3).

15 mg of MIP@MNP was put into solutions of 0.03 M KNO_3 adjusted at different pH values. The suspensions were shaken for 3 h in a shaker at 250 rpm until an equilibrium pH value was

reached. The changes in pH values (ΔpH) were determined. The pH_{pzc} was determined by using ΔpH vs initial pH curve (Figure S11) [1].

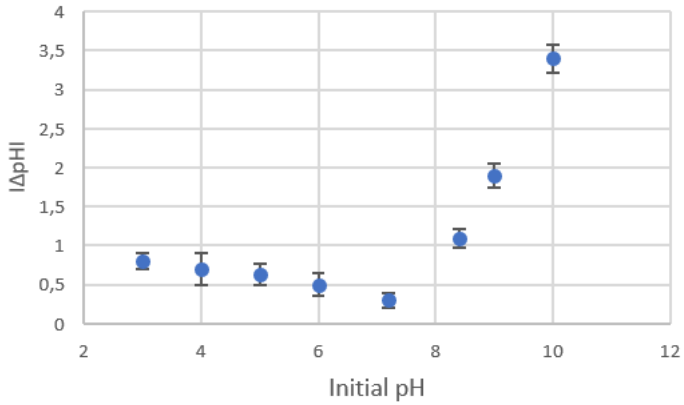


Figure S11. Experimental immersion technique curve for MIP@MNP.

[1] N. Fiol, I. Villaescusa, *Environ Chem Lett* 2009, **7**, 79–84.

Binding behaviours of MNP were investigated by employing binding isotherms. Bi-Langmuir and Freundlich models were used (Table S1). The obtained curves can be seen in Figure S6.

Table S1 Isotherm models and related parameters used in this work.

Isotherm	Equation	Parameters
Langmuir	$B = \frac{NKF}{1 + KF}$	B, amount of bound analyte on imprinted network F, free concentration of analyte in solution N, number of binding sites K, binding constant
Bi-Langmuir	$B = \frac{N_1 K_1 F_1}{1 + K_1 F_1} + \frac{N_2 K_2 F_2}{1 + K_2 F_2}$	
Scatchard Equation	$\frac{B}{F} = KN - KB$	
Freundlich	$B = aF^m$	a, adsorption constant m, heterogeneity index

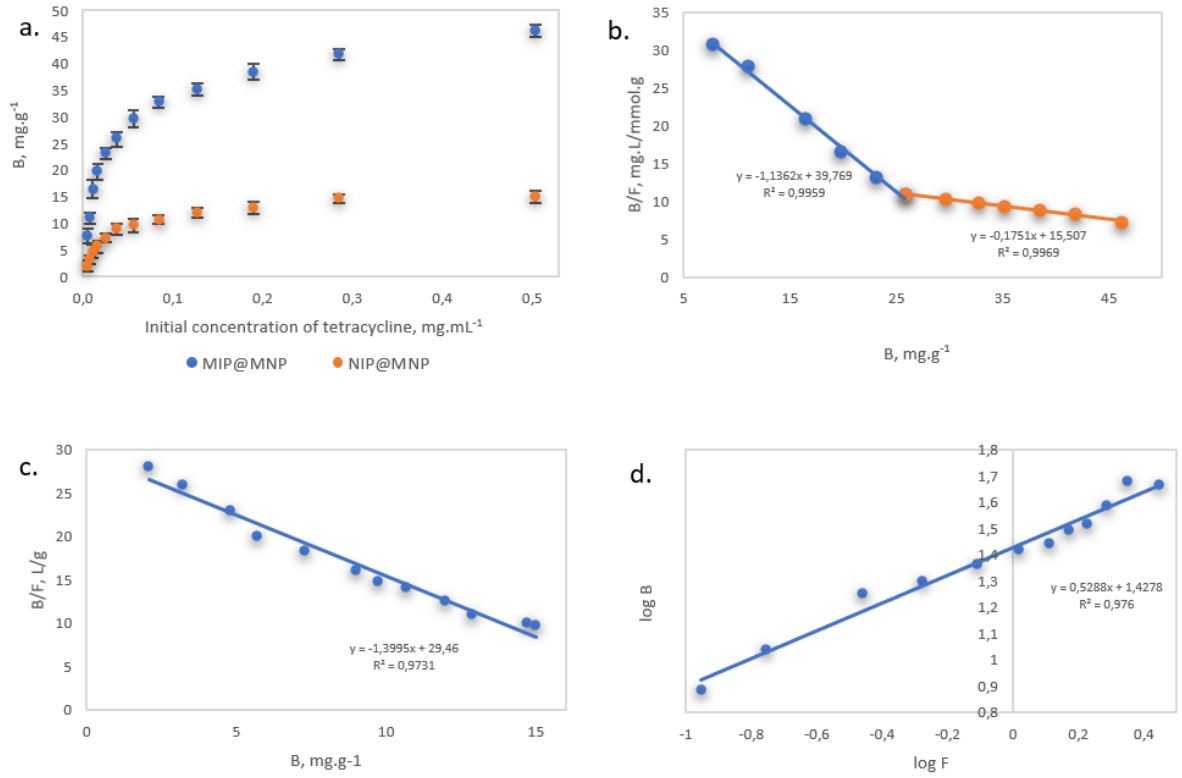


Figure S12. (a) The binding isotherms (b) Scatchard analysis plot of MIP@MNP and (c) NIP@MNP and (d) Freundlich plot of MIP@MNP (5.00 mg modified MNP, incubation time 35 min, pH: 7, n: 3).

Table S2 Lagergren's 1st order and pseudo 2nd order rate equations and related parameters.

Pseudo-First Order Kinetic Model	$\mathbf{\ln(q_e - q_t) = \ln(q_e) - k_1 t}$	q_e, amount of the adsorbed analyte at equilibrium q_t, amount of the adsorbed analyte at time t t, time k_1, pseudo-first order rate constant k_2, pseudo-second order rate constant
Pseudo-Second Order Kinetic Model	$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) t$	

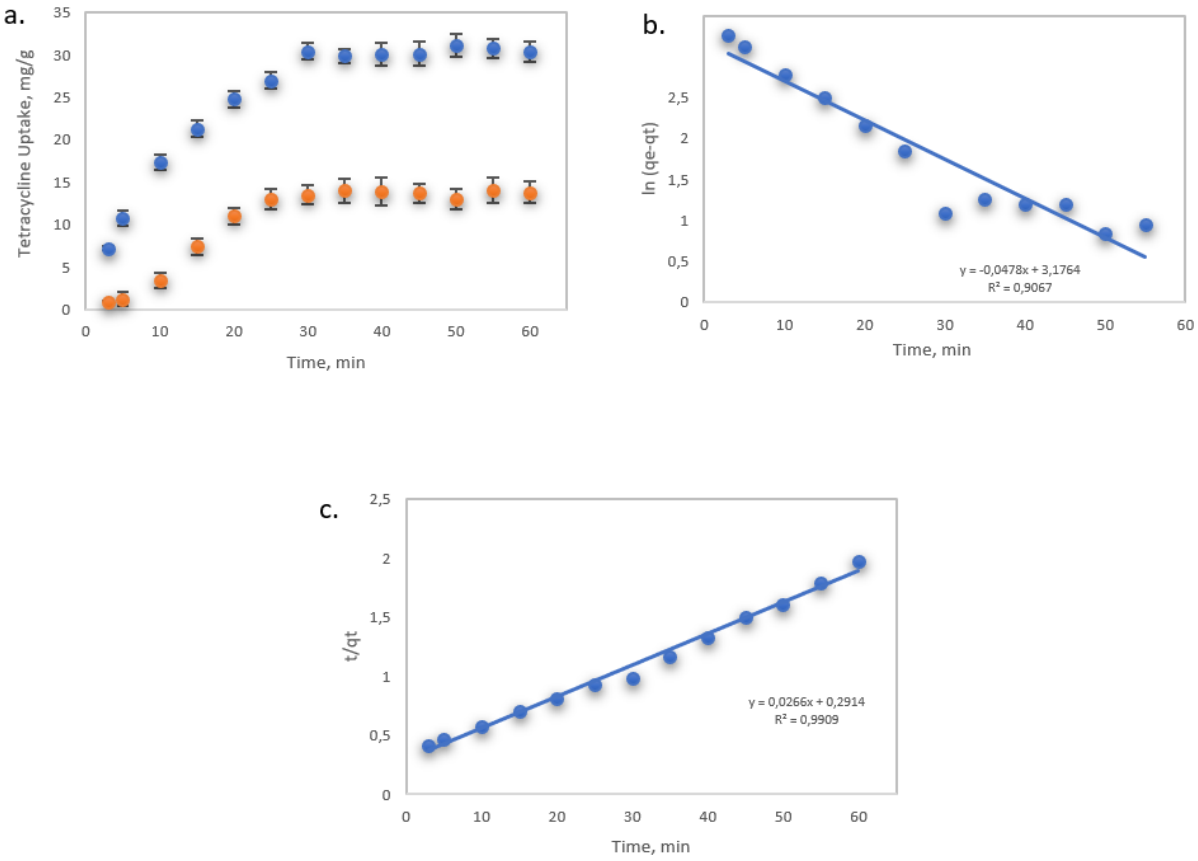


Figure S13. a) Change in adsorption of tetracycline with time, b) pseudo-1st-order and c) pseudo-2nd-order for MIP@MNP, respectively (amount of MIP@MNP: 5.00 mg, tetracycline concentration: 0.050 mg.mL^{-1}, pH: 7, n: 3).

Table S3 The rate constant, *k* and value of binding capacity at equilibrium, q_e for tetracycline binding onto MIP@MNP.

First-Order	k_1 (min^{-1})	0.0478
	q_e (mg g^{-1})	24.0
	R^2	0.9067
Pseudo Second-Order	k_2 (g mg^{-1} min^{-1})	0.0024
	q_e (mg g^{-1})	37.6
	R^2	0.9909

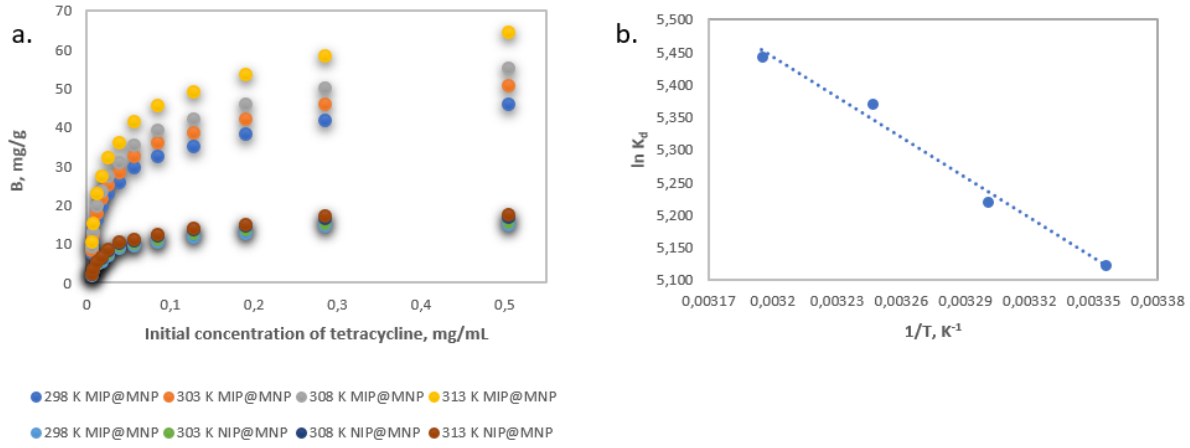


Figure S14. (a) Adsorption isotherms of tetracycline adsorption on MIP@MNP and NIP@MNP at different temperatures and (b) linear fitting curve of equilibrium constant (K_d) versus temperature (ln K_d versus 1/T) at 0.05 mg/mL of tetracycline concentration (pH: 7, incubation time: 35 min, n: 3).

Table S4 Thermodynamic parameters for adsorption of tetracycline on MIP@MNP.

Temperature (K)	K (L.g^{-1})	ln K	ΔG^0 (kJ.mol^{-1})	ΔH^0 (kJ.mol^{-1})	ΔS^0 (J.mol^{-1}K^{-1})
298	168	5.124	-12.70		
303	185	5.220	-13.15	17.16	100.2
308	215	5.371	-13.75		
313	231	5.442	-14.16		

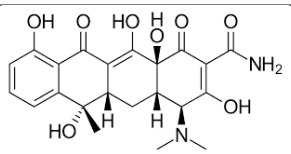
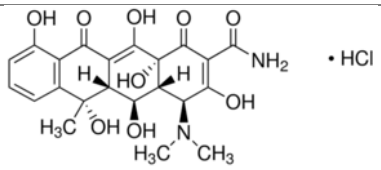
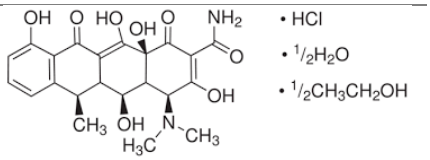
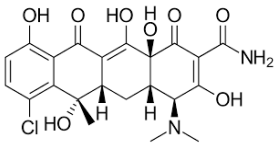
Tetracycline	
Oxytetracycline hydrochloride	
Doxycycline hyclate	
Chlorotetracycline	

Figure S15. Chemical structures of tetracycline (TC) and oxytetracycline hydrochloride (OTC), doxycycline hyclate (DO), chlorotetracycline (CTC).

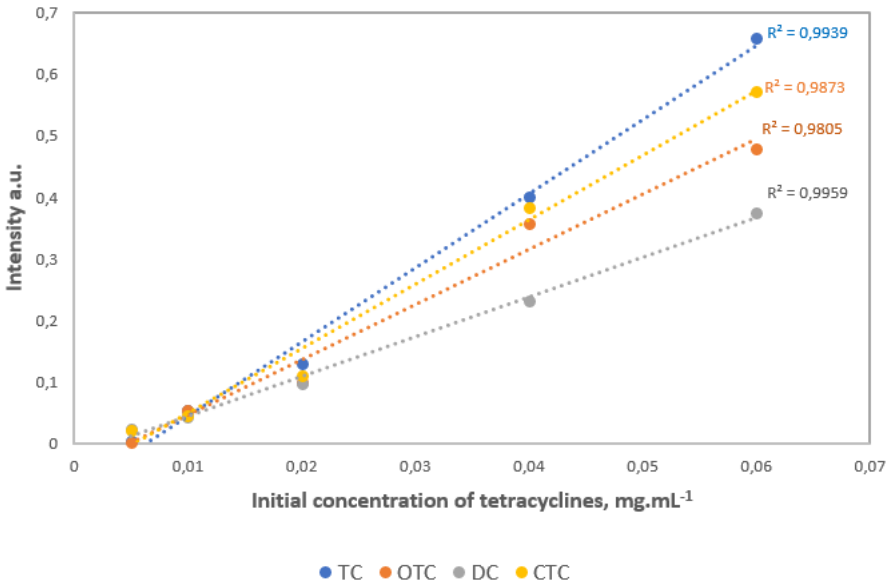


Figure S16. Calibration curves of tetracycline (TC) and oxytetracycline hydrochloride (OTC), doxycycline hyclate (DO), chlorotetracycline (CTC) obtained by HPLC.

Table S5 Equations and related parameters for dissociation constant (K_d), selectivity coefficient (k) and relative selectivity coefficient (k').

	Equation	Parameters
Dissociation Constant (K_d)	$K_d = \frac{(C_0 - C_f)}{C_f} x \frac{V}{m}$	C_0 Initial concentration of dye C_f Final concentration of dye V volume of the solution M mass of the dry polymer k_{MIM} Selectivity coefficient of imprinted membrane k_{NIM} Selectivity coefficient of non-imprinted membrane
Selectivity Coefficient (k)	$k = \frac{K_{d\,Tetracycline}}{K_{d\,Antibiotic}}$	
Relative Selectivity Coefficient (k')	$k' = \frac{k_{MIM}}{k_{NIM}}$	

Table S6 Dissociation constant (K_d), selectivity coefficient (k) and relative selectivity coefficient (k′) of MIM.

	$K_{D,\,MIP}$	$K_{D,\,NIP}$	k_{mip}	k_{nip}	k'
TC	14.9	4.4			
OTC	10.6	6.8	1.41	0.64	2.20
DC	11.2	7.4	1.33	0.59	2.24
CTC	6.05	4.9	2.45	0.89	2.76