Electronic Supplementary Material (ESI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2016

Electronic Supporting Information (ESI) for

Hydrophilic, hollow Fe₃O₄@PDA spheres with storing cavity for

efficient removal of polycyclic structured tetracycline

Bingqi Mao, Qingda An*, Zuoyi Xiao and Shangru Zhai*

Faculty of Light Industry and Chemical Engineering, Dalian Polytechnic University,

Dalian 116034, China

Prof. Dr. Shang-Ru Zhai,

Faculty of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian 116034, China Tel: (+86) 411-8632-2638 Fax: (+86) 411-8632-2638 E-mail: <u>zhaisr@dlpu.edu.cn</u>



Fig. S1 EDS analysis of (a) Fe₃O₄@PDA (50) HSs; (b) Fe₃O₄@PDA (100) HSs; (c)

Fe₃O₄@PDA (200) HSs.



Fig. S2 FT-IR spectra of (a) PS-COOH nanospheres; (b) PS@Fe₃O₄@PDA composites; (c) Fe₃O₄@PDA HSs; (d) pure TC; (e) TC loaded Fe₃O₄@PDA HSs.



Fig. S3 (a) XRD pattern of Fe₃O₄@PDA HSs; (b) Room temperature magnetization curve of Fe₃O₄@PDA HSs, The inset photographs: separation of Fe₃O₄@PDA HSs from aqueous dispersion using an external magnet.



Fig.S4 Molecular structure of TC on a planar view.



Fig. S5 Magnified TEM image of (a) $Fe_3O_4@PDA$ (50) HSs; (b) $Fe_3O_4@PDA$ (200) HSs and (c) $Fe_3O_4@PDA$ (200) HSs.



Fig. S6 Adsorption efficiency of Fe₃O₄@PDA HSs after repeated regeneration.

Isotherm model	Parameters	10 °C	25 °C	40 °C
Langmuir	$q_m (mg \cdot g^{-1})$	136	151	171
	$K_L (\times 10^3 \text{ L} \cdot \text{mg}^{-1})$	0.09	0.13	0.40
	R ²	0.93	0.89	0.84
Freundlich	$K_{F} \left(L \cdot g^{-1} \right)$	32.32	45.22	66.77
	n	3.45	4.00	4.43
	\mathbb{R}^2	0.97	0.96	0.94
Temkin	K_T (L·mol ⁻¹)	2.37	119.42	11.91
	\mathbf{B}_{T}	22.25	13.72	26.30
	R ²	0.96	0.77	0.93

 Table S1 The parameters derived from the Langmuir, Freundlich and Temkin.

_

 Table S2 Binding Energy and Relative Content of O in Fe₃O₄@PDA HSs.

Valance state	Sample	Proposed components	Binding energy	Relative content
			(eV)	(%)
O 1s	Fe ₃ O ₄ @PDA HSs	Fe-O	530.04	22.5
		H-O	531.5	46.9
		C-O	533.02	30.6
	TC-loaded HSs	Fe-O	530.5	44.6
		H-O	531.5	29.2
		C-0	532.4	26.2