Supporting Information for

Alginate Polymer Caged C_{18} Functionalized Magnetic Titanate Nanotubes for Fast and Efficient Extraction of Phthalate Esters from Water Samples with Complex Matrix

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Characterization of Adsorbents. Transmission electron micrograph (TEM) images of adsorbents were recorded on a H7500 transmission electron micrograph (Hitachi, Japan) operating at 120 kV. Scanning electron micrograph (SEM) images were performed on an S-3000N electron microscope equipped with an energy-dispersive X-ray spectroscopy (EDAX) (Hitachi, Japan). An X-ray powder diffractometer (Rigaku III/B max) was used to analyze the crystalline structures of adsorbents. The radiation source was Cu Kα, the applied current was 30 mA, and the voltage was 40 kV. During the analysis, the sample was scanned from 5 to 100^{o} at a speed of 0.4^{o}/min. The specific surface areas of adsorbents were determined by the BET method with N_2 gas (ASAP2000V3.01A; Micromeritics, Norcross, GA). A Nicolet Avatar 360 spectrometer was used for the FTIR determination of samples. Magnetic property of the adsorbents was analyzed using a vibrating sample magnetometer (VSM, LDJ9600).

HPLC Analysis. Phthalate esters were separated and quantified by using a high-performance liquid chromatography (HPLC) system (DIONEX, USA). The HPLC equipment include a DIONEX P680 HPLC pump, an on-line connected degasser Solvent Rack SOR-100, a thermostated column compartment TCC-100, a DIONEX RF 2000 fluorescence detector (FLD), and a PDA-100 photodiode array detector. The separations were conducted on a Diamonsil® C_{18} column (250×4.6 mm; particle size, 5 μm). Gradient separations were carried out using water-acetonitrile (50:50) and acetonitrile as the A and B solvents respectively, and the flow rate was 1 mL min^{-1}. The linear gradient profile was as following: B maintained at 40% in the

first 15 min, then changed to 100% within 10 min, and held for 10 min, after that, the mobile phase was returned to the initial conditions in 3 min. Phthalate esters were quantified by UV detector and the wavelengths were set at 226 nm.

Sample Collection. River water sample was collected from North moat of Beijing, whose water storage was affected greatly by the urban stormwater runoff. A wastewater sample was taken from the effluent discharge gate of the biggest municipal wastewater treatment plant in Beijing (Chaoyang District, Beijing). A tap water was sampled from our laboratory and rain water was collected at 10 June, 2009 in Haidian District (Beijing). All samples were filtered through 0.22 μm filters (Shanghai Institute of Pharmaceutical Industry, China) to remove the suspended solids and stored at 4 °C until use.

Table S1 Saturation Magnetization, Remanence, Coercivity of Fe_3O_4-TNs with Different Fe_3O_4/TNs Ratio and C_{18} Functionalized Fe_3O_4 (0.5) with or without Alginate Coat

Sample	saturation magnetization （emu/g）	remanence （emu/g）	coercivity （Oe）
Fe_3O_4(0.4)	7.176	0.8718	36
Fe_3O_4(0.6)	19.85	3.967	54
Fe_3O_4(0.5)	10.99	1.376	16
Fe_3O_4(0.5)-C_{18}	9.745	1.016	18
ALG@Fe_3O_4(0.5)-C_{18}	7.299	0.7471	10

Table S2 Recoveries of Analytes in the Presence of 100 mg L^{-1} of Biphthalate Acid or n-Decanoic Acid at pH 3.0 and 9.5

Analytes	Recovery (%)			
	DPP	DBP	DCP	DOP
Biphthalate acid pH3.0	42.8	100	85.7	89.6
Biphthalate acid pH9.5	68.2	102	89.3	94.5
n-Decanoic acid, pH3.0	34.5	73.3	75.5	96.6
n-Decanoic acid, pH9.5	60.8	106	87.6	92.4

Table S3 Analytical Parameters of the Proposed Method

	Calibration Equation	R^2	Linear Range (ng L^{-1})	Detection Limits [a] (ng L^{-1})
DPP	y = 0.8609x - 0.047	0.998	60-10 000	24.4
DBP	y = 0.5039x + 0.1292	0.99	60-10 000	14.3
DCP	y = 1.0383x - 0.0313	0.999	60-10 000	35.9
DOP	y = 0.4106x + 0.0605	0.998	60-10 000	11.2

[a] The detection limits were calculated by using S/N=3

Table S4 Results of Determination and Recoveries of Real Water Samples Spiked with Target Analytes

Water sample	Spiked ($ng\ mL^{-1}$)	Detected ($ng\ mL^{-1}$) [a] ± R.S.D.[b] (Recovery %)			
		DPP	DBP	DCP	DOP
Tap water	0	nd [c]	0.55±10	nd	0.28±5.3
	0.2	0.19±7.3 (95.5%)	0.75±5.8 (100%)	0.21±4.0 (107%)	0.49±4.4 (101%)
	2.0	1.83±10.1 (91.4%)	2.48±10.9 (96.5%)	2.05±6.6 (103%)	2.25±5.2 (98.3%)
Rainwater	0	0.056±3.3	0.44±8.3	nd	0.75±11
	0.2	0.23±0.93 (87.2%)	0.65±2.5 (106%)	0.20±3.8 (102%)	0.94±6.3 (97.0%)
	2.0	1.82±4.2 (88.4%)	2.45±4.9 (101%)	1.93±0.32 (96.6%)	2.73±4.9 (99.2%)
Wastewater	0	0.034±2.5	0.25±3.0	nd	0.15±6.0
	0.2	0.21±8.2 (88.2%)	0.42±2.8 (86.5%)	0.22±3.2 (109%)	0.35±8.3 (101%)
	2.0	1.86±3.9 (91.5%)	2.34±5.9 (104%)	1.98±7.9 (99.1%)	2.23±5.2 (104%)
North Moat Water	0	nd	0.10±0.6	nd	0.064±8.5
	0.2	0.18±9.8 (92.2%)	0.29±6.8 (96.9%)	0.19±6.1 (95.3%)	0.25±3.1 (93.1%)
	2	1.69±6.0 (84.6%)	1.97±1.8 (93.4%)	2.02±2.6 (101%)	2.11±1.1 (102%)

[a]. Mean of three determinations, [b]. Standard deviation for three determinations. [c]. Not detected.

Figure S1 TEM images of (a) Fe_3O_4-TNs prepared without ferric and ferrous ions in solution in the alkali treatment process; (b) Fe_3O_4-TNs prepared without ion-exchange process; (c) Fe_3O_4 (0.6)-TNs; and (d) Fe_3O_4 (1)-TNs

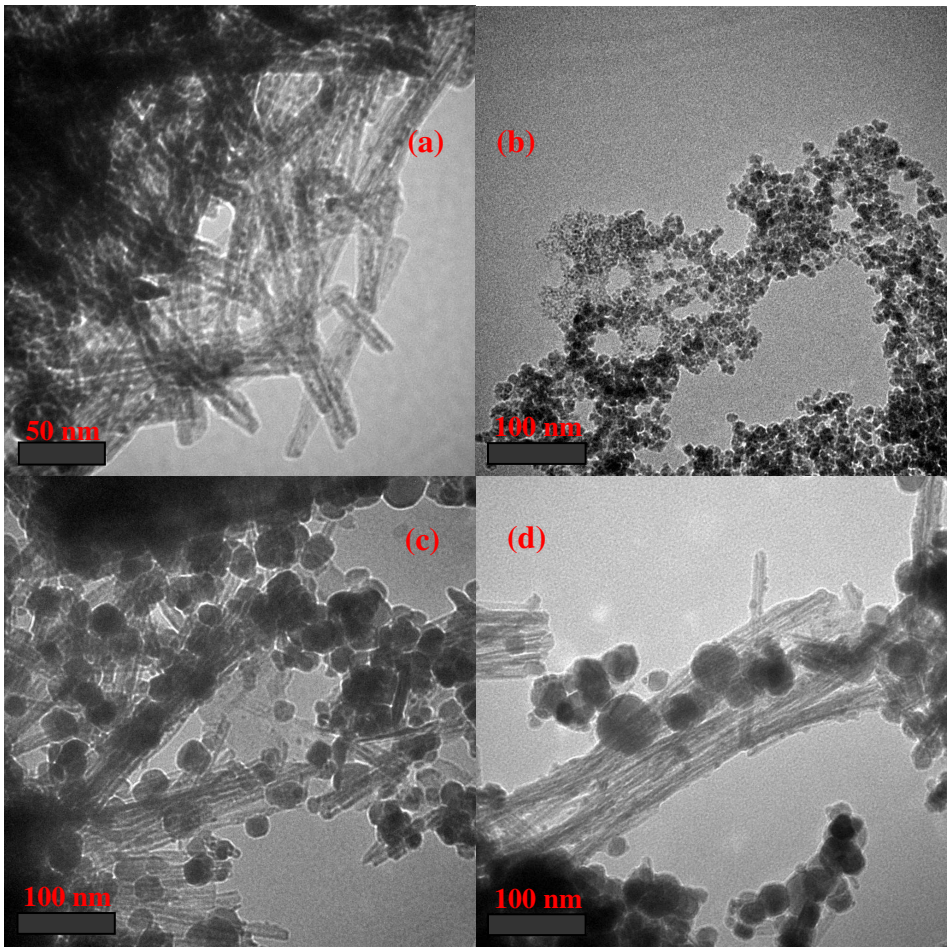


Figure S2. VSM magnetization curves of Fe_3O_4 (0.4), Fe_3O_4 (0.5), Fe_3O_4 (0.6), C_{18}-Fe_3O_4 (0.5)-TNs, and ALG@ C_{18}-Fe_3O_4 (0.5)-TNs

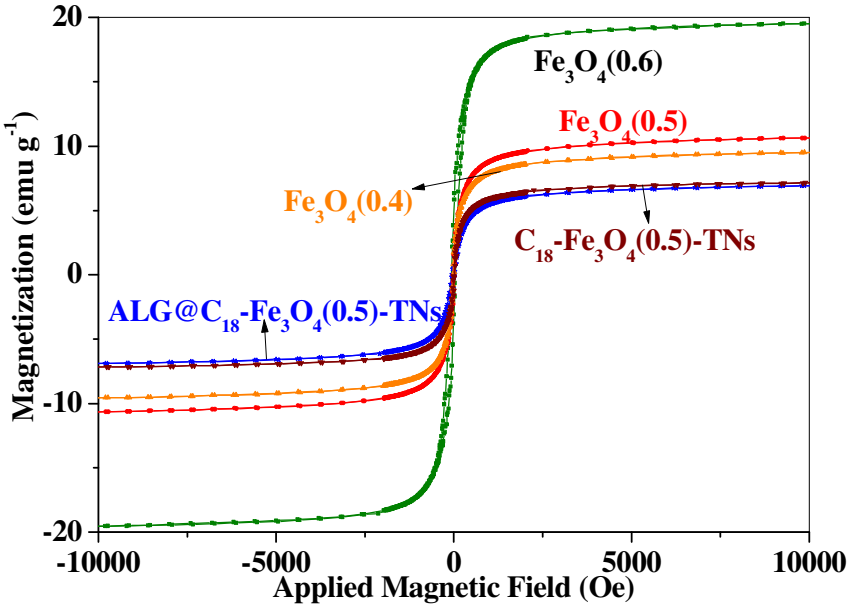
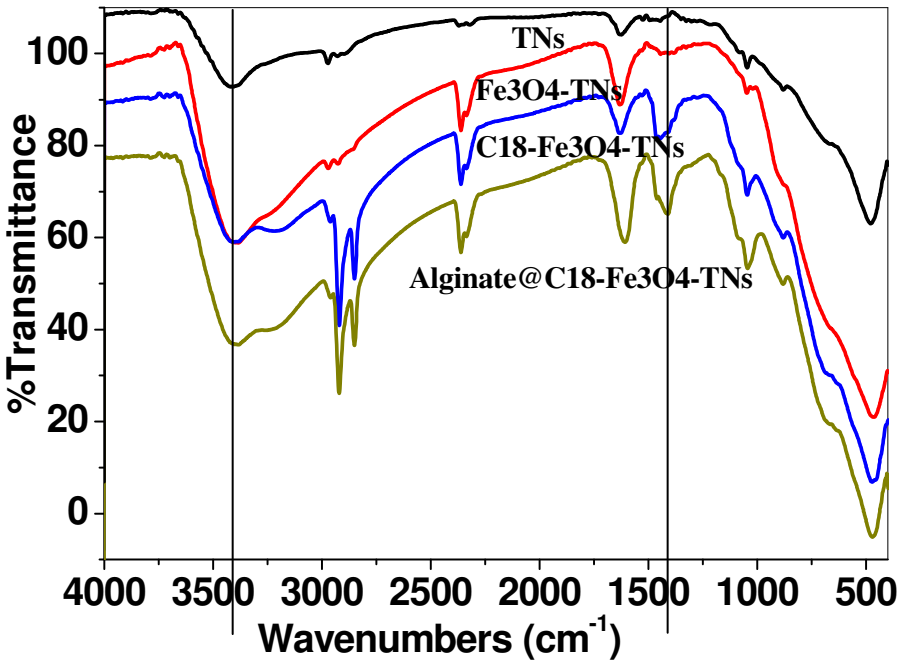


Figure S3 IR spectra of TNs, Fe_3O_4-TNs, C_{18}-Fe_3O_4-TNs, and ALG@C18-Fe_3O_4-TNa



The peaks at 1635 and 3420 cm^{-1} present in the FTIR spectrum of TNs were corresponding to the surface-adsorbed water and hydroxyl groups (1-4). In the spectrum of Fe_3O_4-TNs composite, the intensity of the two peaks increased obviously, resulting from the introduced Fe_3O_4. The peaks at 2973 and 2929 cm^{-1} were unchanged which attributed to stretching vibration or bending vibration of Ti–OH or Ti-O bonds of TNs (1, 3). After functionalization with C_{18}, O-H absorption at 3420 and 1620 cm^{-1} decreased, and the peaks for Ti-OH bonds were nearly overlapped by the new two peaks at 2920 and 2850 cm^{-1} which were ascribed to C-H bond (1, 3). A peak appeared in the range of 1450-1500 cm^{-1} for C_{18}-Fe_3O_4-TNs was caused by the bending vibration of $–CH_2$ species of C_{18} group (5). This indicated that the C_{18} chain

was successfully attached to the magnetic nanoparticles by replacing the hydroxyl groups on the surface. After encapsuled into barium alginate vesicles, O-H absorption increased again, and the adsorption peak for carboxylic group at 1413 cm^{-1} could be observed (6). The hydroxyl groups and carboxylic groups resulted from alginate, and this result indicated that alginate was successfully coated on the surface of C_{18}-Fe_3O_4-TNs adsorbents.

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Figure S4. Effect of humic acid concentration in neutral solution on the extraction efficiencies of phthalate esters