A core-shell magnetic mesoporous silica sorbent for organic targets with high extraction performance and anti-interference ability

Supplementary Information

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Contents

Experimental Section

Chemicals.

Fluoranthene (FluA), pyrene (Pyr), benzo(a)anthracene (BaA), benzo[b]fluoranthene (BaF), benzo(a)pyrene (BaP), and benzo[g,h,i]perylene (BghiP) were obtained from AccuStandard (New Haven, CT). Standard stock solutions (100 μg L^{-1}) containing these compounds were prepared in acetonitrile and stored at 4 ^{o}C. LC-grade acetonitrile were supplied by Fisher Scientific (Fair Lawn, NJ). Tetraethyl orthosilicate (TEOS) was obtained from Acros Organics (Morris Plains, NJ). Ammonia aqueous solution (25 %, w/w) was from Alfa Aesar (Ward Hill, MA). Octadecyltriethoxysilane was obtained from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). Humic acid were obtained from Sigma-Aldrich (St. Louis, MO). Bovine serum albumin (BSA) was from Beijing Xinjingke Biotechnology Co. Ltd. (Beijing, China). Cetyltrimethylammonium Bromide (CTAB), $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, toluene, anhydrous ethanol, sodium hydroxide, trisodium citrate and concentrated hydrochloric acid (37 %, W/W) were guarantee-grade reagents from Beijing Chemicals Co. Ltd. (Beijing, China). All reagents were used without further purification. Ultrapure water was prepared in the laboratory using a Milli-Q SP reagent water system from Millipore (Milford, MA).

Synthesis of $Fe_3O_4/SiO_2/SiO_2$-C_{18} magnetic microsphere.

The preparation of $Fe_3O_4/SiO_2/SiO_2$-C_{18} magnetic microsphere is illustrated in Scheme 1. First, Fe_3O_4 MNPs were synthesized by the co-precipitation of 5.2 g $FeCl_3 \cdot 6H_2O$ and 2.0 g $FeCl_2 \cdot 4H_2O$ with 25 mL of concentrated ammonia aqueous (25 %) at 90 °C.[1] The obtained magnetic nanoparticles were then washed with 200 mL of deionized water four times and redispersed in 200 mL of trisodium citrate solution (0.5 M) by ultrasonic. The mixture was stirred for 12 h at 60 °C, and the magnetic nanoparticles was washed with 50 mL of anhydrous ethanol and redispersed in 80 mL of deionized water to obtain a magnetic fluid of about 30 mg mL^{-1}.

Second, the trisodium citrate modified Fe_3O_4 MNPs were embeded in silica microsphere to gain the monodispersed Fe_3O_4/SiO_2 magnetic silica microsphere through Stöber method with some modification.[2] Briefly, 4.0 mL of the above mentioned magnetic fluid was homogeneously dispersed in a mixture of ethanol (320 mL), deioned water (80 mL) and $NH_3 \cdot H_2O$ solution (4.0 mL, 25 %). Then, 1.5 mL of TEOS was introduced to the mixture after ultrasonic vibration for 30 min. After being stirred at ambient temperature for 12 h, the Fe_3O_4/SiO_2 magnetic silica microsphere were recovered from the reaction system with a magnet, washed with ethanol and water for several times, and dispersed in 10 mL of anhydrous ethanol.

Third, mesoporous silica shell was fabricated on the surface of the Fe_3O_4/SiO_2 magnetic silica microsphere through surfactant-templating approach[3] with a minor modification. In brief, 3.0 mL of as-prepared Fe_3O_4/SiO_2 suspension was added into the mixture containing CTAB (0.5 g), ethanol (180 mL), deioned water (240 mL) and concentrated $NH_3 \cdot H_2O$ solution (3.0 mL). The suspension was homogenized by ultrasonic irradiation for 30 min, and then 0.3 mL of TEOS was added dropwise under vigorous stirring. The $Fe_3O_4/SiO_2/SiO_2$ magnetic mesoporous silica microsphere was isolated from the reaction mixture after stirring for 8h. The obtained magnetic microsphere was rinsed several times with ethanol/concentrated hydrochloric acid (95/5, V/V) under ultrasonication to remove the template CTAB, and then washed with anhydrous ethanol and anhydrous toluene successively, and redispersed in anhydrous toluene to get a suspension of 0.015 g mL^{-1}.

Finally, functionalization of the mesoporous silica shell with octadecyl groups were performed according to previous reported methods:[4] 80 mL of the above mentioned $Fe_3O_4/SiO_2/SiO_2$ suspension (0.015 g mL^{-1}) and 0.8 mL of octadecyltriethoxysilane were mixed under ultrasonic radiation for 30 min. The mixture was then put into a sealed autoclave and heated at 120 °C for 12 h in a furnace. The $Fe_3O_4/SiO_2/SiO_2$-C_{18} magnetic mesoporous silica microsphere was obtained after washing and drying.

Characterizations of $Fe_3O_4/SiO_2/SiO_2$-C_{18} magnetic microsphere.

The size and structure of Fe_3O_4/SiO_2, $Fe_3O_4/SiO_2/SiO_2$ and $Fe_3O_4/SiO_2/SiO_2$-C_{18} magnetic microsphere were determined by H-7500 transmission electronic microscopy (Hitachi, Tokyo, Japan) operating at 80 kV; the vibrating sample magnetization (VSM) curves of various magnetic particles were analyzed by using an LDJ9600 vibrating sample magnetometer (LDJ Electronics, Troy, MI). The successful coating of silica shell and functionalization with the octadecyl groups were confirmed by the infrared (IR) spectra of naked Fe_3O_4 MNPs, Fe_3O_4/SiO_2, $Fe_3O_4/SiO_2/SiO_2$ and $Fe_3O_4/SiO_2/SiO_2$-C_{18}

magnetic microspheres, which were taken in KBr pressed pellets on a NEXUS 670 infrared Fourier transform spectrometer (Nicolet Thermo, Waltham, MA). Low-angle X-ray diffraction measurements were performed on $Fe_3O_4/SiO_2/SiO_2$ and $Fe_3O_4/SiO_2/SiO_2$-C_{18} magnetic mesoporous silica microspheres with a PANalytical X'pert Pro diffractometer (PANalytical, Almelo, the Netherlands), using a monochromatized X-ray beam with nickel-filtered Cu Kα radiation with 0.4° min^{-1} scan rate. A continuous scan mode was used to collect 2θ data from 0.7° to 6.0°. Wide-angle XRD were also measured from 10.0° to 80° with 4° min^{-1} scan rate. Nitrogen sorption isotherms were measured at 77 K with a Quadrasorb™ SI Four Station Surface Area Analyzer and Pore Size Analyzer (Quantachrome Instruments, Boynton Beach, FL). Before measurements, the samples were degassed in a vacuum at 300°C for at least 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (SBET) using adsorption data in a relative pressure range from 0.05 to 1.0. By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms, and the total pore volumes (Vt) were estimated from the adsorbed amount at a relative pressure P/P_0 of 0.985.

Magnetic solid phase extraction proceduce.

The whole extraction procedure of the targets from water solutions with the $Fe_3O_4/SiO_2/SiO_2$-C_{18} magnetic sorbent is as follows. First, 30 mg of magnetic sorbent and 10 mL of NaCl (1.0 M) were mixed with 500 mL of ultra-pure water spiked with various targets (20 ng L^{-1}) by ultrasonic irradiation for 30 sec to get a homogeneous suspension. The suspension was allowed to stand for 15 min to achieve equilibrium. Second, a strong Nd-Fe-B magnet (150 mm × 100 mm × 20 mm) was deposited at the bottom of the vessel to isolate the sorbent from the suspension. After about 20 min, the suspension became limpid and the supernatant was decanted. Next, the targets were desorbed from the isolated sorbent with 12 mL of acetonitrile (3 mL every time and washed four times). Ultrasonic irradiation for 30 sec during each elution was carried out to desorb most of the targets from sorbent. The eluate was concentrated with a stream of nitrogen at 55 ^{o}C to less than 0.5 mL and diluted to 0.5 mL with acetonitrile. Finally, 20 μL of this solution was analyzed by HPLC-FLD system.

Liquid Chromatography - Fluorescence Spectrometry Analysis.

The HPLC apparatus was a Dionex HPLC system (Sunnyvale, CA) composed of a P680 pump, a DIONEX RF 2000 fluorescence detector and Chromeleon 6.70 software. PAHs were separated on a Diamonsil® C_{18} column (5 μm particle diameter, 4.6 mm i.d. × 250 mm length, Dikma Tech.). Gradient separation was carried out using water-acetonitrile (50:50) and acetonitrile as A and B solvents, respectively, and the flow rate was 1 mL min^{-1}. The linear gradient profile was as follows: B maintained at 80% in the first 15 min, and then linear gradient to 100% in 2 min and maintained for 3 min, after that, mobile phase was returned to initial conditions in 2 min. The PAHs were determined by using a fluorescence detector, and the time-programmed excitation/emission wavelengths were as following: 0 min, 252/370 nm; 7 min, 280/460 nm; 8 min, 270/390 nm; 11 min, 260/432 nm; 13.5 min, 290/410 nm; 22 min, 252/370 nm.

Following a similar enrichment and analysis procedure, the influences of pH, ionic strength, amounts of sorbent, humic acid and protein on extraction of PAHs were investigated in terms of the recoveries of the target compounds under a variety of experimental conditions.

References

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[2] Y. H. Deng, C. C. Wang, J. H. Hu, W. L. Yang, S. K. Fu, *Colloids Surf., A.*, 2005, **262**, 87.

[3] Y. H. Deng, D. W. Qi, C. H. Deng, X. M. Zhang, D. Y. Zhao, *J. Am. Chem. Soc.*, 2008, **130**, 28.

[4] Y. L. Liu, L. Jia, *Microchem. J.*, 2008, **89**, 72.

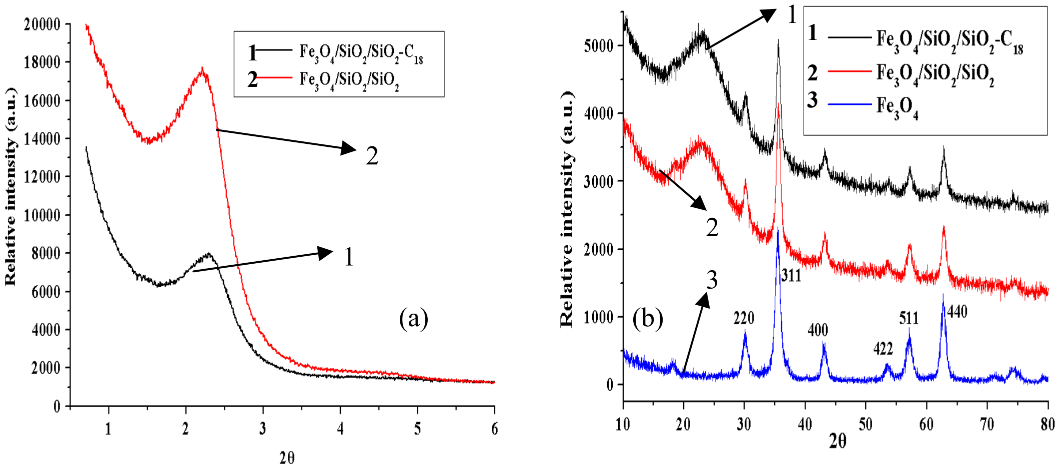

Figure S1. Low-angle (a) and wide-angle (b) XRD patterns of the synthesized $Fe_3O_4/SiO_2/SiO_2$ and $Fe_3O_4/SiO_2/SiO_2$-C_{18} microspheres.

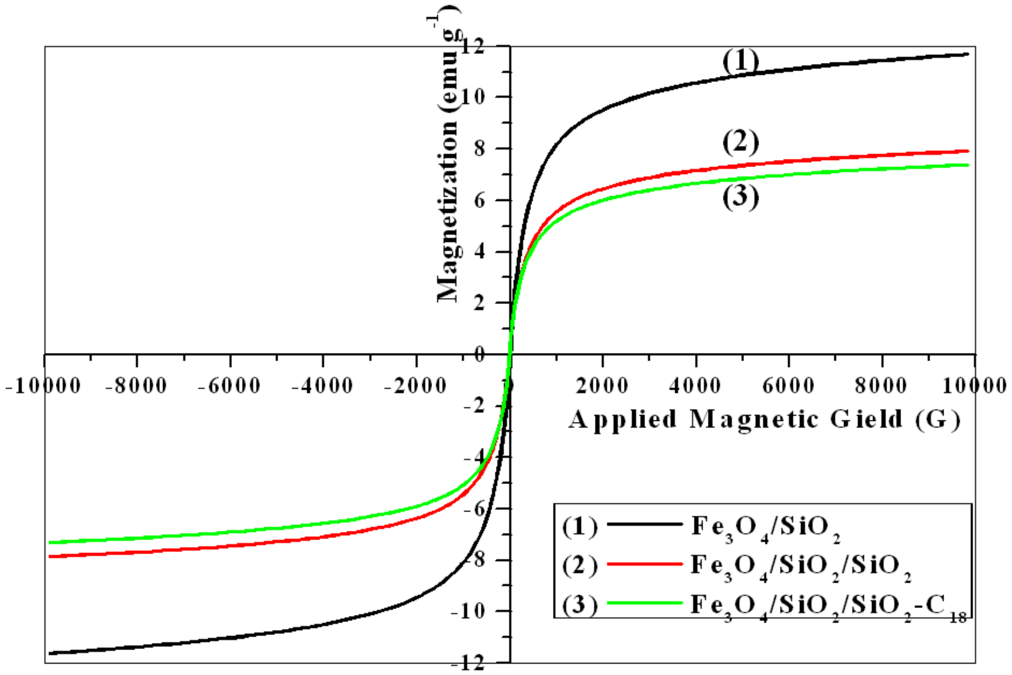

Figure S2a. VSM curves of Fe_3O_4/SiO_2, $Fe_3O_4/SiO_2/SiO_2$ and $Fe_3O_4/SiO_2/SiO_2$-C_{18} microspheres.

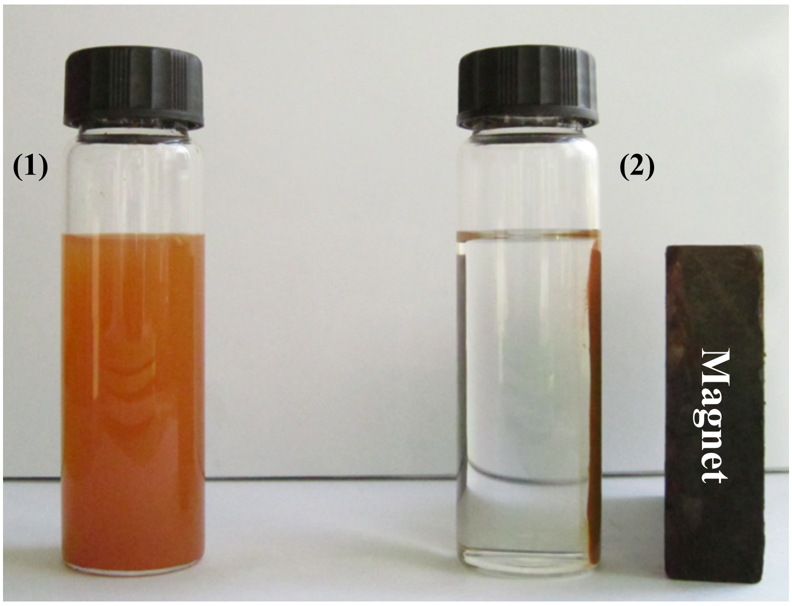

Figure S2b. Dispersion (1) and magnetic separation (2) of the sorbent.

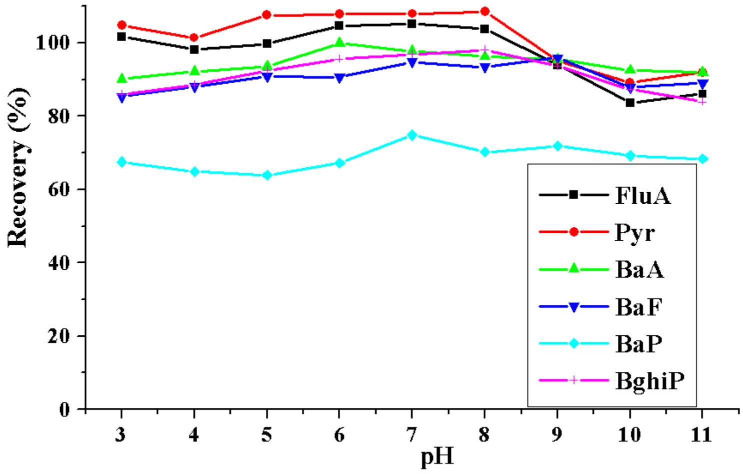

Figure S3. Effects of the pH on the extraction of PAHs.

Conditions: $Fe_3O_4/SiO_2/SiO_2\text{-}C_{18}$ sorbent, 30 mg; loading volume, 500 mL; spiked concentration of various targets, 20 ng L^{-1}; pH, 3-11; NaCl, 0.02 M; adsorption time, 15 min; eluent, 3 mL acetonitrile× 4 and concentrated the eluate to 0.5 mL.

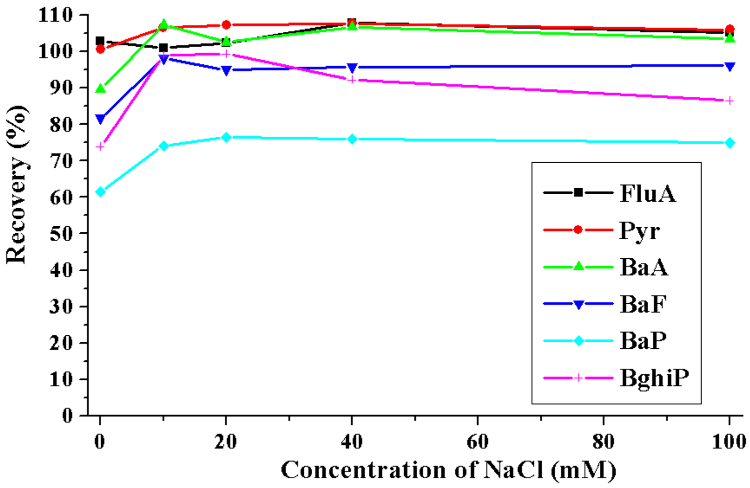

Figure S4. Effect of the ionic strength on the extraction of PAHs.

Conditions: $Fe_3O_4/SiO_2/SiO_2$-C_{18} sorbent, 30 mg; loading volume, 500 mL; spiked concentration of various targets, 20 ng L^{-1}; pH, natural; NaCl, 0-0.1 M; adsorption time, 15 min; eluent, 3 mL acetonitrile× 4 and concentrated the eluate to 0.5 mL.

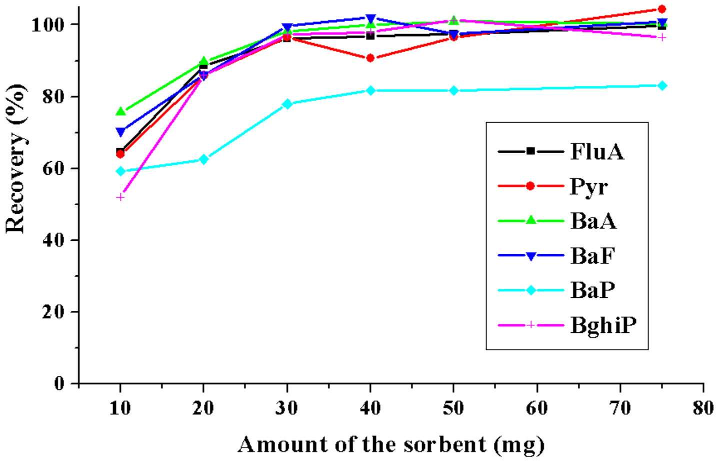

Figure S5. Effect of the sorbent amount on extraction of PAHs.

Conditions: $Fe_3O_4/SiO_2/SiO_2$-C_{18} sorbent, 10-75 mg; loading volume, 500 mL; spiked concentration of various targets, 20 ng L^{-1}; pH, natural; NaCl, 0.02 M; adsorption time, 15 min; eluent, 3 mL acetonitrile× 4 and concentrated the eluate to 0.5 mL.

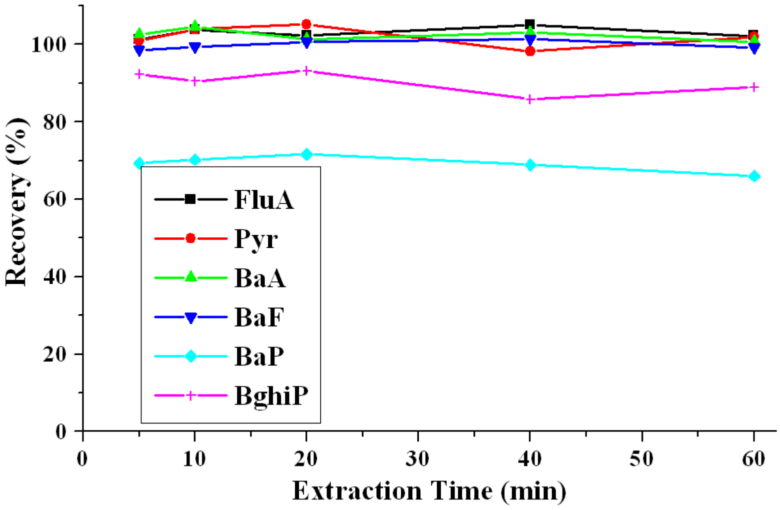

Figure S6. Effect of the equilibrium time on the recoveries of PAHs

Conditions: $Fe_3O_4/SiO_2/SiO_2$-C_{18} sorbent, 30 mg; loading volume, 500 mL; spiked concentration of various targets, 20 ng L^{-1}; pH, natural; NaCl, 0.02 M; adsorption time, 5 -60 min; eluent, 3 mL acetonitrile× 4 and concentrated the eluate to 0.5 mL.

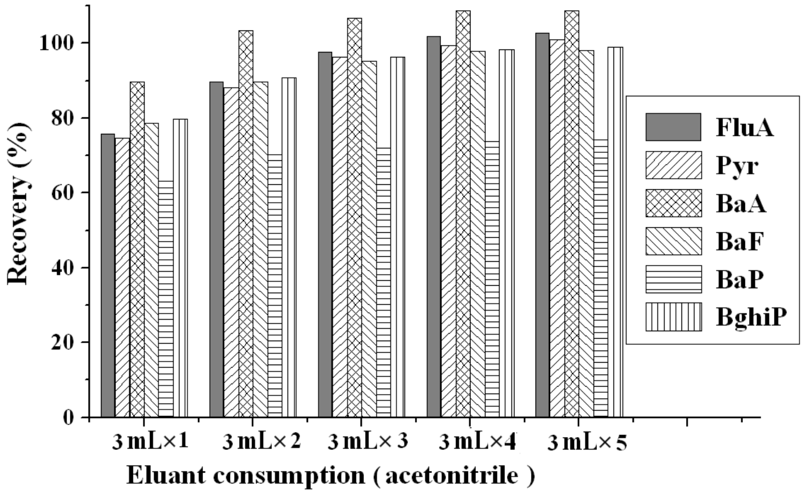

Figure S7. Effect of the desorption conditions on the recoveries of PAHs

Conditions: $Fe_3O_4/SiO_2/SiO_2$-C_{18} sorbent, 30 mg; loading volume, 500 mL; spiked concentration of various targets, 20 ng L^{-1}; pH, natural; NaCl, 0.02 M; adsorption time, 15 min; eluent, acetonitrile, 3 – 15 mL, and concentrated the eluate to 0.5 mL.

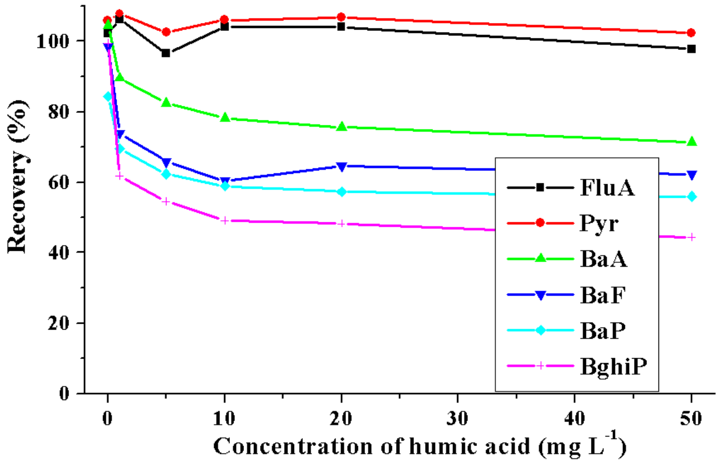

Figure S8. Effects of the concentration of humic acid on the extraction of PAHs.

Conditions: $Fe_3O_4/SiO_2/SiO_2$-C_{18} sorbent, 30 mg; loading volume, 500 mL; spiked concentration of various targets, 20 ng L^{-1}; pH, natural; NaCl, 0.02 M; concentration of humic acid, 0-50 mg L^{-1}; adsorption time, 15 min; eluent, 3 mL acetonitrile× 4 and concentrated the eluate to 0.5 mL.

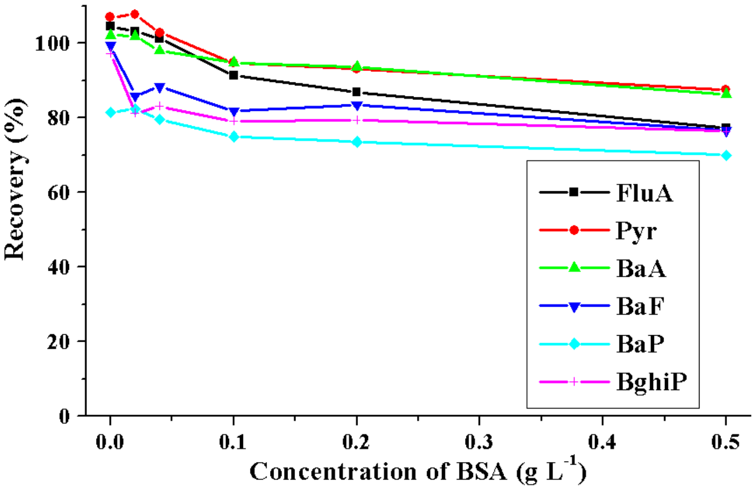

Figure S9. Effects of the concentration of BSA on the extraction of PAHs.

Conditions: $Fe_3O_4/SiO_2/SiO_2$-C_{18} sorbent, 30 mg; loading volume, 500 mL; spiked concentration of various targets, 20 ng L^{-1}; pH, natural; NaCl, 0.02 M; concentration of BSA, 0-0.5 g L^{-1}; adsorption time, 15 min; eluent, 3 mL acetonitrile× 4 and concentrated the eluate to 0.5 mL.