

Facile synthesis of uniform magnetic graphitic carbon for an efficient adsorption of pentachlorophenol

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Experimental Section

Materials

FeCl₃·6H₂O, trisodium citrate, ethylene glycol, sodium acetate, tetraethyl orthosilicate (TEOS), ethanol, resorcinol, formaldehyde, concentrated ammonia solution (28 wt%), RhB, PCP, BPA were of analytical grade and purchased from Sigma-Aldrich (USA). All chemicals were used as received without further purification. Millipore water was used for all experiments.

Synthesis of Fe₃O₄ nanoparticles.

The water-dispersible Fe₃O₄ nanoparticles were synthesized *via* a solvothermal method reported previously.³¹ Briefly, FeCl₃·6H₂O (3.25 g), trisodium citrate (1.3 g), and sodium acetate (NaAc, 6.0 g) were dissolved in ethylene glycol (100 mL) with magnetic stirring. Afterwards, the obtained yellow solution was transferred and sealed into a Teflon-lined stainless-steel autoclave (100 mL in capacity). The autoclave was heated at 200 °C for 10 h, and then allowed to cool to room temperature. The black products were washed with deionized water and ethanol for 3 times, respectively.

Synthesis of core-shell $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanospheres.

The core-shell $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanospheres were prepared through a versatile Stöber sol-gel method. For a typical synthesis, an ethanol dispersion of the Fe_3O_4 magnetite particles obtained above (3.0 mL, 0.05 g/mL) was added to a three-neck round-bottom flask with ethanol (280 mL), deionized water (70 mL) and concentrated ammonia solution (4.0 mL, 28 wt%). The mixed solution was sonicated for 15 min. Then, 2.0 mL of TEOS was added dropwise in 10 min, and the reaction was allowed to proceed for 10 h at room temperature under continuous mechanical stirring. The resultant products (denoted as $\text{Fe}_3\text{O}_4@\text{SiO}_2$) were separated and collected with a magnet, followed by washing with deionized water and ethanol for 3 times, respectively.

Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{g-C}$

The uniform carbon shells were prepared via a modified Stöber method. Typically, the core-shell $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanospheres were dispersed in ethanol (20 mL), water (10 mL), and mixed with concentrated ammonia solution (0.50 mL, 28 wt%) under ultrasound for 15 min. Into the resultant dispersion, resorcinol (0.2 g) and formaldehyde (0.2 g) were added consecutively, and the mixed dispersion was mechanically stirred for 2 h at 45 °C. After polymerization, the magnetite $\text{Fe}_3\text{O}_4@\text{SiO}_2$ particles could be uniformly coated by a layer of RF resin, and the obtained core-shell $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{RF}$ microspheres were collected by a magnet and washed with deionized water and ethanol three times, respectively. Then, the sample was carbonized at 850 °C under the protection of N_2 for 3 h.

For comparison, $\text{Fe}_3\text{O}_4@\text{C-450}$ and $\text{Fe}_3\text{O}_4@\text{g-C}$ core-shell nanospheres were synthesized through directly coating the carbon shell on Fe_3O_4 cores and carbonized at 450 and 850 °C, respectively.

Materials characterization.

X-ray diffraction (XRD) patterns were recorded on a Bruker D8X-ray diffractometer with Ni-filtered Cu K α radiation (40 kV, 40 mA) and a scanning time of 1 min/degree. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a PHI-5000 VersaProbeTM ULVAC system (Japan) with Al K monochromatic radiation ($h\nu = 1486.6$ eV). Raman and FTIR spectra were recorded on a combined Raman FT-IR spectrometer (LabRam ARAMIS IR2) with the excitation of a 532 nm laser. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer (USA). Prior to measurements, the samples were degassed in a vacuum at 180 °C for 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas using adsorption data in the relative pressure range $P/P_0 = 0.04 - 0.3$. Transmission electron microscopy (TEM) was carried out on a JEOL 2011 microscope (Japan) operated at 200 kV. For TEM measurements, the sample was suspended in ethanol and supported on a holey carbon film on a Cu grid. The magnetization was measured using a Vibrating Sample Magnetometer (EV9 including auto-matic sample rotation, Microsense, Japan) under a magnetic field of 10 KOe and a temperature of 24 °C.

Adsorption test

The reactor consisted of a double-layered cylindrical container with a capacity of 1.25 L (Φ 10.0 \times 6 cm). The solution temperature was measured using a thermometer (Tecpel DTM-318) and maintained with a water jacket. Aqueous suspensions (100 mL) of PCP (5 mg L⁻¹) and adsorbent (50 mg L⁻¹) were used for the adsorption test. A mechanical stirrer was applied for mixing the solution and adsorbent with a speed of 300 rpm. At given time intervals, 0.5 mL of the suspension was removed using a 2-mL syringe and filtered by a membrane with a pore size of

~ 0.45 μm . The PCP concentration in the resultant filtrate was analyzed on a High-performance Liquid Chromatography (HPLC, Agilent 1260) with a ZORBAX Eclipse Plus C18 column (4.6 \times 100 mm, 5 μm) and a diode array UV detector (G4212B 1260 DAD, $\lambda = 222 \text{ nm}$). For carrying out the recycle test, the adsorbent was collected by applying a magnetic field (10000 Oe) after each cycle and washed 3 times by using ethanol and deionized water, respectively.

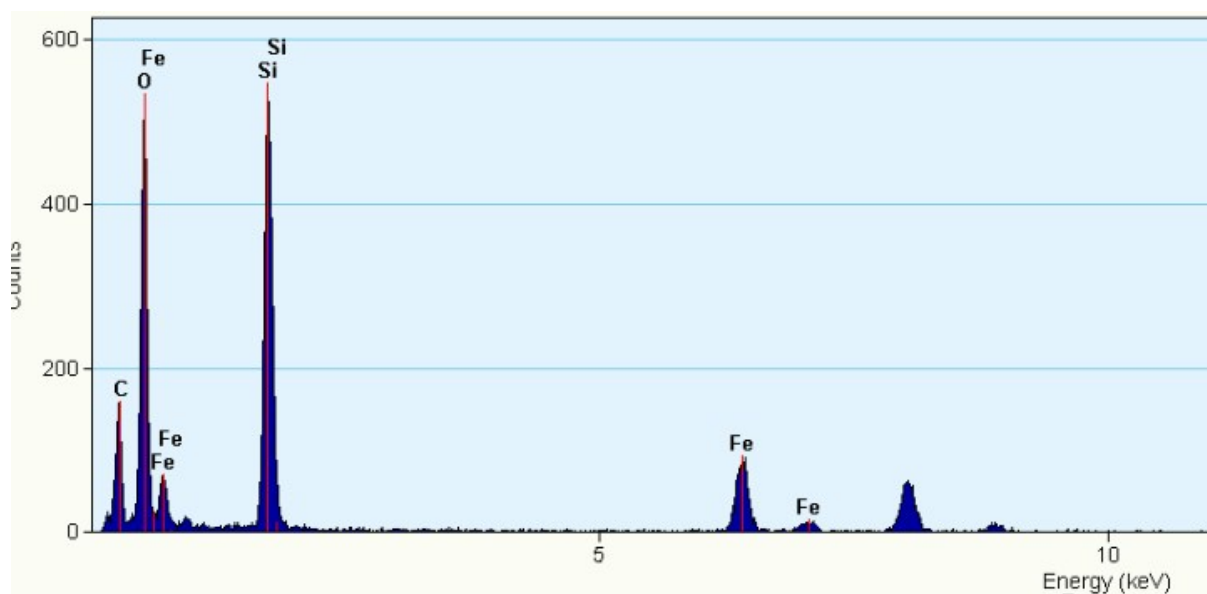


Fig. S1. EDX analysis of magnetic g-C

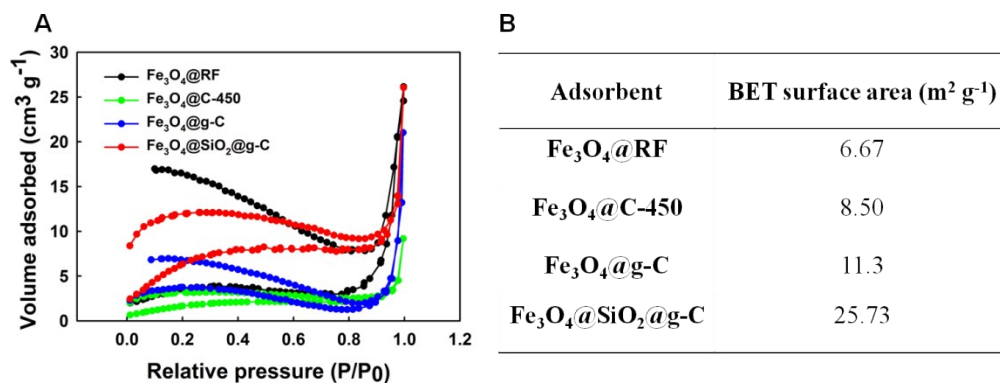


Fig. S2. N₂ sorption isothermals (A) and summary table for the BET surface areas calculated at relative pressure $0.05 < P/P_0 < 0.3$.

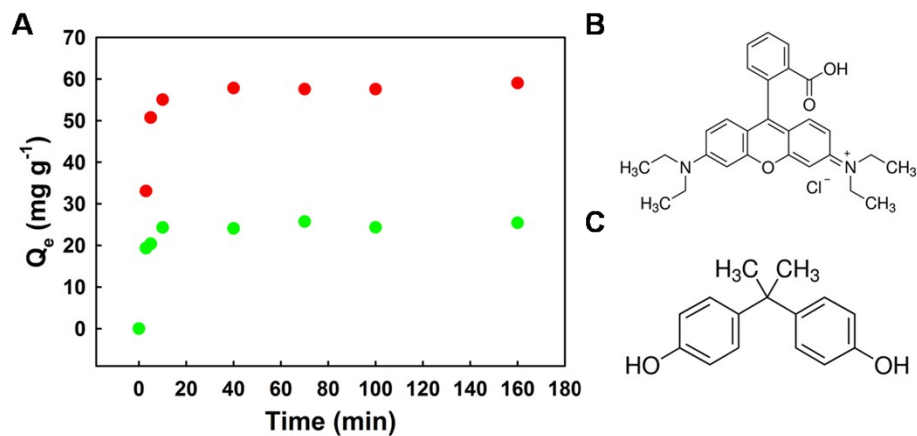


Fig. S3. The adsorption profiles for RhB and BPA pollutants (A) and the molecule structures of RhB (B) and BPA (C).

Table S1. The comparison of the adsorption capacity between the previous literature and this study for the adsorption of PCP.

Adsorbent	T (°C)	pH	Adsorption capacity (mg g ⁻¹)	BET surface area (m ² g ⁻¹)	Normalized adsorption capacity (mg m ⁻²)	Ref.
Magnetic biochar	25	7.0	48.0	67	0.72	[1]
Fe ₃ O ₄ @SiO ₂ -MWCNTs	25	6.8	35.3	-	-	[2]
Ni-ZVI magnetic biochar	25	3-9	40-50	167.86	0.24-0.30	[3]
Fe ₃ O ₄ /C	25	5	0.005	-	-	[4]
Fe ₃ O ₄ @SiO ₂ @g-C	15	6.8	58.0	25.73	2.30	This study

References

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