Electronic Supplementary Information

Part I: Synthesis of MagCNTs@mSiO$_2$

The magnetic CNTs (MagCNTs) were prepared via a modified hydrothermal method reported by Jia et al. [1] Briefly, multiwalled CNTs (400 mg, diameter 20~40 nm, Shenzhen Nanotech Port Co., Ltd.) were dispersed into 50 mL concerntrated nitric acid at 60°C with magnetic stirring for 7 hours. The pretreated CNTs were collected by washing with water for five times and then dired in vacuum at 50°C. Then the dried pretreated CNTs (150 mg) and $FeCl_3 \cdot 6H_2O$ (810 mg) were dispersed into 40 mL ethylene glycol solution with trisodium citrate (0.15 g), sodium acetate (3.6 g) and poly(ethylene glycol)-20000 (1.0 g) by ultrasonication and magnetic stirring for 3 hours. The mixture was sealed in the autoclave to be heated at 200°C for 10 hours. Finally the gained MagCNTs were washed and collected by magnetic separation-redispersion cycle.

According to a reported method [2], the mesoporous silica was coated on the MagCNTs as following: MagCNTs (30 mg) and CTAB (0.3 g) were well dispersed in 300 mL deioned water with NaOH (12 mg) by ultrasonication. After the mixture was heated at 60°C for half an hour, 1.5 mL tetraethyl orthosilicate (TEOS) ethanol solution (0.186 g mL^{-1}) was added in three batches with the aid of a mild shake. Then the mixture continued to be heated at 60°C for 12 hours to finish the coating process. Finally the products of MagCNTs@mSiO$_2$ were washed several times in warmed alcohol (60°C) and collected by magnetic separation-redispersion cycle.

Part II: Characterization

Transmission electron microscopy (TEM) images were taken on a JEOL 2011 microscope (Japan) operated at 200 kV. Scanning electronic microscope (SEM) images were recorded on a Philips XL30 electron microscope (Netherlands) operating at 20 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D4 X-ray diffractometer with Ni-filtered Cu K_R radiation (40 kV, 40 mA). Fourier transform infrared spectra (FT-IR) were collected on Nicolet Fourier spectrophotometer using KBr pellets (USA). Nitrogen sorption isotherms were measured at 77 K with a Micromeritcs Tristar 3000 analyzer (USA). The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. The pore size distribution was derived from the adsorption branches of isotherms by using the Barrett-Joyner-Halenda (BJH) model. The Raman spectra were recorded at room temperature on a LabRam-1B Raman spectrometer with a laser at an excitation wavelength of 632.8 nm.

Part III: Removal of MC-LR in water using MagCNTs@mSiO$_2$

MagCNTs@mSiO$_2$ (20 μg) was added to 200 μL MC-LR aqueous solution (50 μg L^{-1}). After the mixture was vibrated at room temperature for a certain time, the materials carrying MC-LR were removed quickly with the help of a magnet while the supernatant was ready for MALDI-TOF MS analysis. MALDI-TOF MS analysis used here was performed on positive ion mode on a 4700 Proteomics Analyzer (Applied Biosystems) with the Nd: YAG laser at 355 nm, a repetition rate of 200 Hz and acceleration voltage of 20 kV.

Caution! Microcystins are toxic substances that should be handled with appropriate safety equipment.

Part IV: Removal of gaseous benzene using MagCNTs@mSiO$_2$, MagCNTs and Fe$_3$O$_4$@mSiO$_2$

The scheme for this experiment was illustrated in Figure S7a. There is a GC-FID analysis instrument equipped with a glass sorbent tube of the thermal desorption unit. The benzene (0.2 μL) was directly injected into the glass tube, went through the tube and then was analyzed by the GC-FID. The materials (5 mg) that had been disc-formed under high pressure were fixed in the end of the tube. By this means, we assessed the capability of the materials. With no materials in the tube (Figure S7b), the area of the corresponding peak was 657463. When using Fe$_3$O$_4$@mSiO$_2$ (Figure S7c), MagCNTs (Figure S7d) or MagCNTs@mSiO$_2$ (Figure S7e) as the adsorbent in the tube, the peak areas were 652383, 590525 and 463268 respectively. The result shows that MagCNTs@mSiO$_2$ have the best adsorption ability while Fe$_3$O$_4$@mSiO$_2$ does hardly function in adsorption. This phenomenon confirmed that the CNTs made more contribution to the adsorption of benzene than the silica mesopores. Thus we conjecture that contaminants were first selectively sequestered by the silica mesopores and then adsorbed by π-π stacking interaction between the sidewalls of CNTs and aromatic groups.[3] The silica mesopore channels are the accesses that provide rapid mass transport to the sidewalls of CNTs. This bi-modal adsorption nature possibly made for the advantage of the MagCNTs@mSiO$_2$ over the MagCNTs.

Fe$_3$O$_4$@mSiO$_2$ composites used in the experiment were synthesized by coating mesoporous silica onto the Fe$_3$O$_4$ microspheres through the same method as MagCNTs@mSiO$_2$. The Fe$_3$O$_4$ microspheres were fabricated through the solvothermal reaction of $FeCl_3 \cdot 6H_2O$ (1.35 g) and sodium acetate (3.6 g) in 75 mL ethylene glycol at 200°C for 16 hours. The TEM image of the as-prepared Fe_3O_4@$mSiO_2$ was illustrated in Figure S7f. These composites have the similar mesoporous silica layer outside like the MagCNTs@$mSiO_2$.

References:

[1] B. P. Jia, L. Gao, J. Sun, *Carbon*, 2007, **45**, 1476
[2] K. L. Ding, B. J. Hu, Y. Xie, G. M. An, R. T. Tao, H. Y. Zhang, Z. M. Liu, *J. Mater. Chem.*, 2009, **19**, 3725
[3] A. Hirsch, *Angew. Chem. Int. Ed.*, 2004, **41**, 185

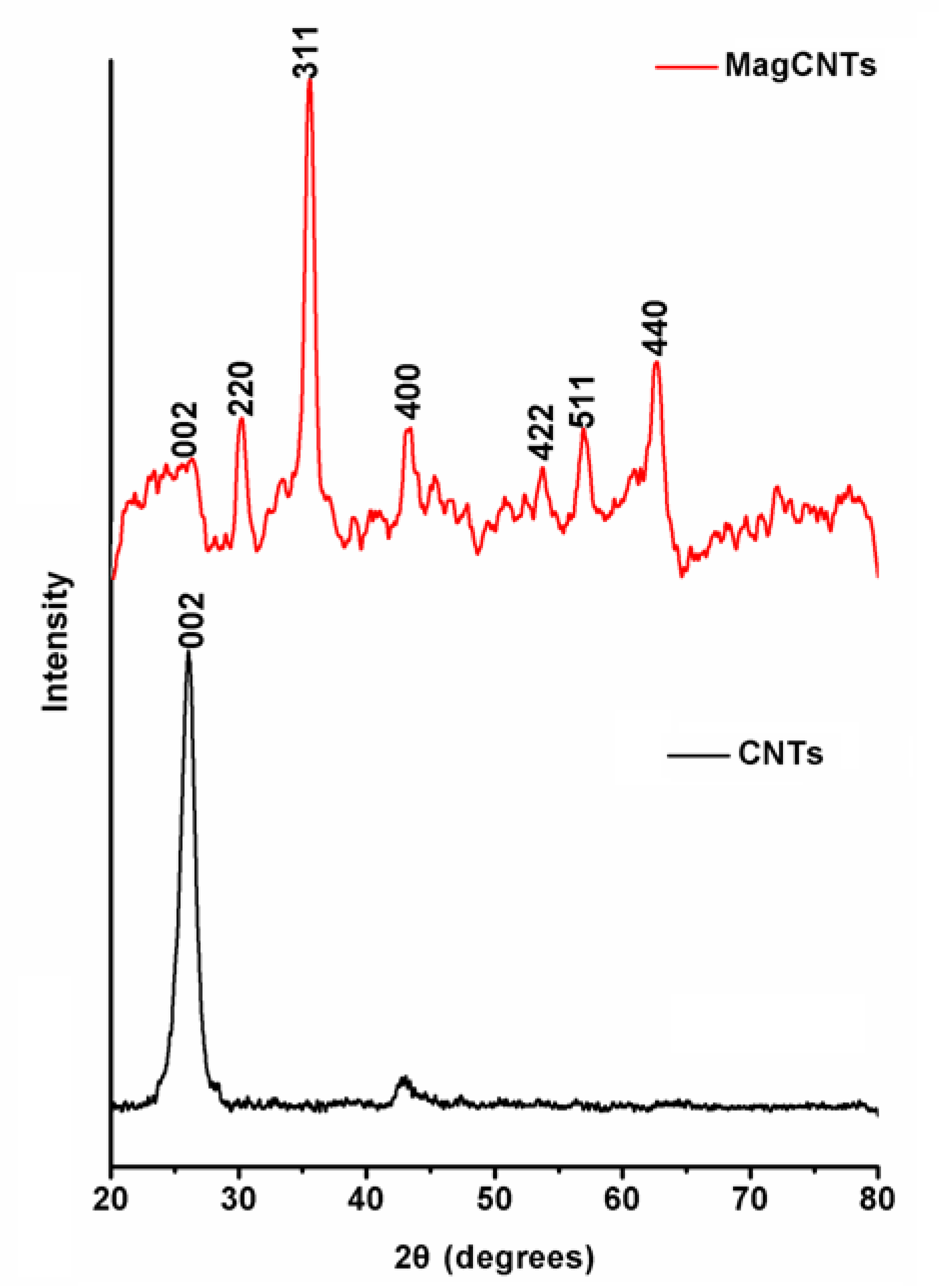

Figure S1 Wide angle XRD patterns of the CNTs and MagCNTs.

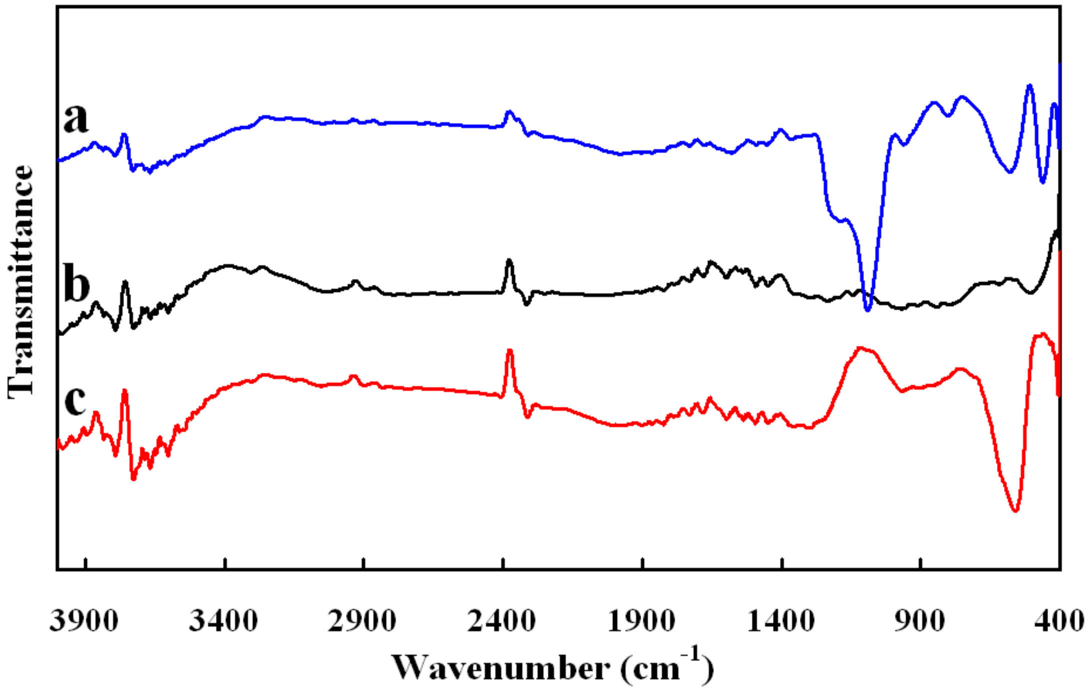

Figure S2 FT-IR spectra of (a) MagCNTs@mSiO$_2$, (b) CNTs and (c) MagCNTs. Typical bands assigned to the Fe-O stretching are visible at around 580 and 430 cm^{-1} for MagCNTs and MagCNTs@mSiO$_2$. The strong band around 1090 cm^{-1} in curve of MagCNTs@mSiO$_2$ is consistent with the Si-O-Si stretching vibration, which confirms that silica was well coated on the MagCNTs.

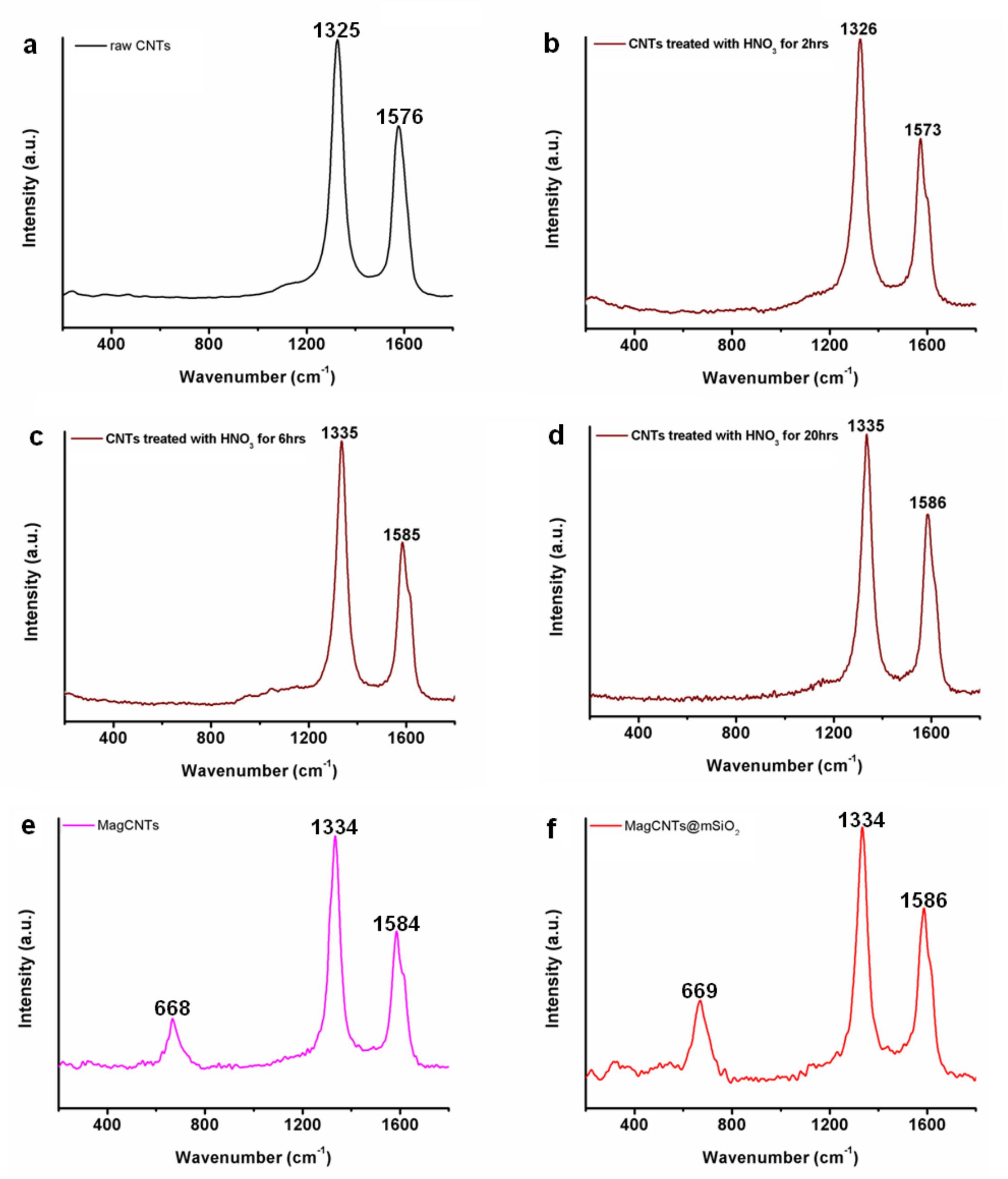

Figure S3 The Raman spectra of (a) raw CNTs, (b~d) CNTs treated with HNO_3 for 2 hours, 6 hours and 20 hours, (e) MagCNTs and (f) MagCNTs@mSiO_2.

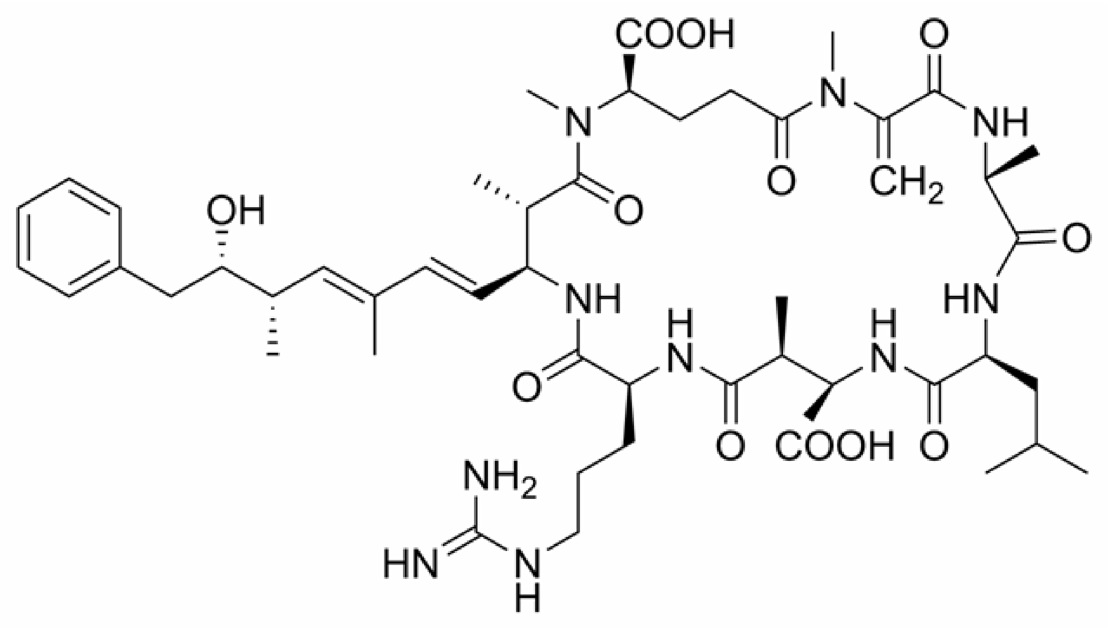

Figure S4 Chemical structure of microcystin-LR.

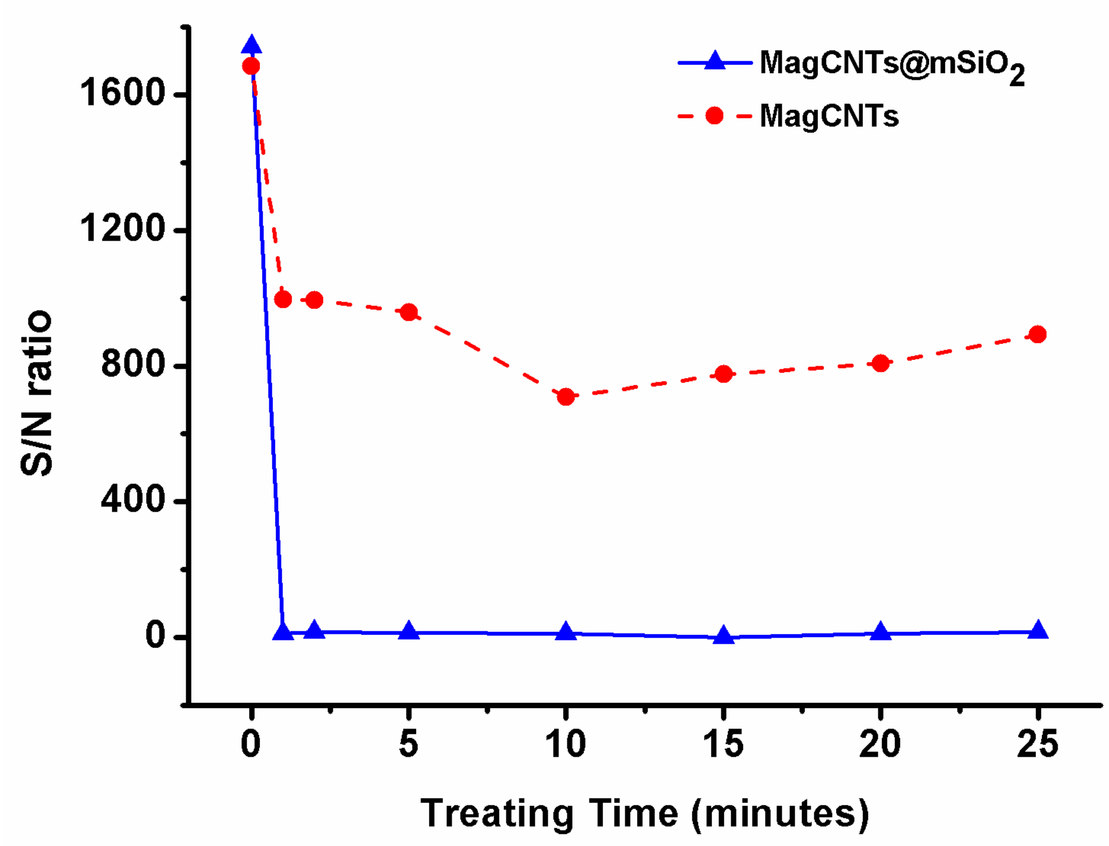

Figure S5 The adsorption kinetics of MC-LR with MagCNTs@mSiO$_2$ (blue solid line) and MagCNTs (red dash line). Y axis corresponds to the S/N ratios for the MC-LR remains after the treatment with different treating time. 20 µg of MagCNTs@mSiO$_2$ or MagCNTs was used in 200 µL of MC-LR solution (50µg L^{-1}).

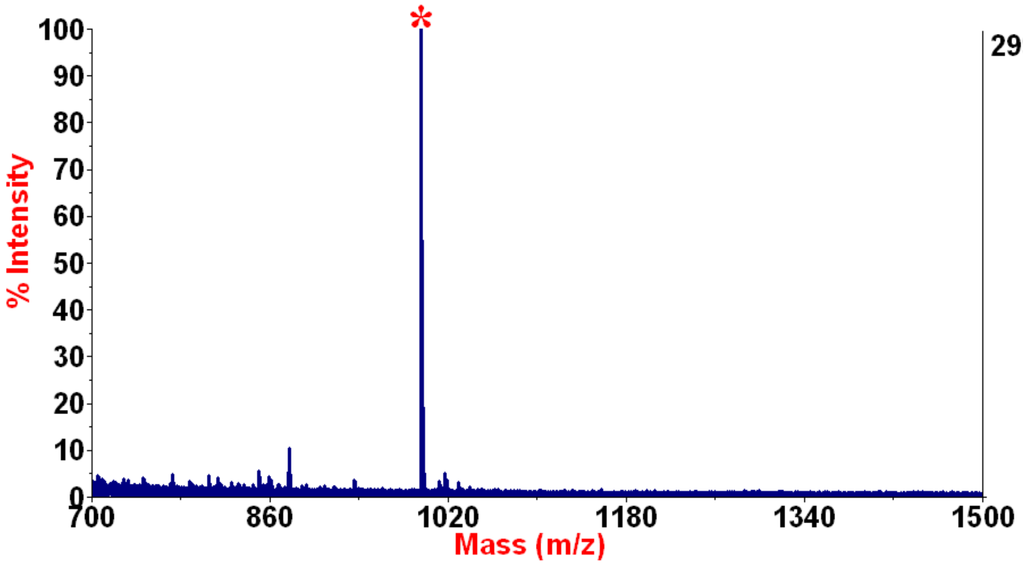

Figure S6 MALDI-TOF mass spectra of 50 μg L^{-1} MC-LR aqueous solution (200 μL) after the treatment with the 20 μg of MagCNTs for 1 minute. The peak of $[MC\text{-}LR + H]^+$ ion with the S/N ratio of 995.7 is marked by asterisks.

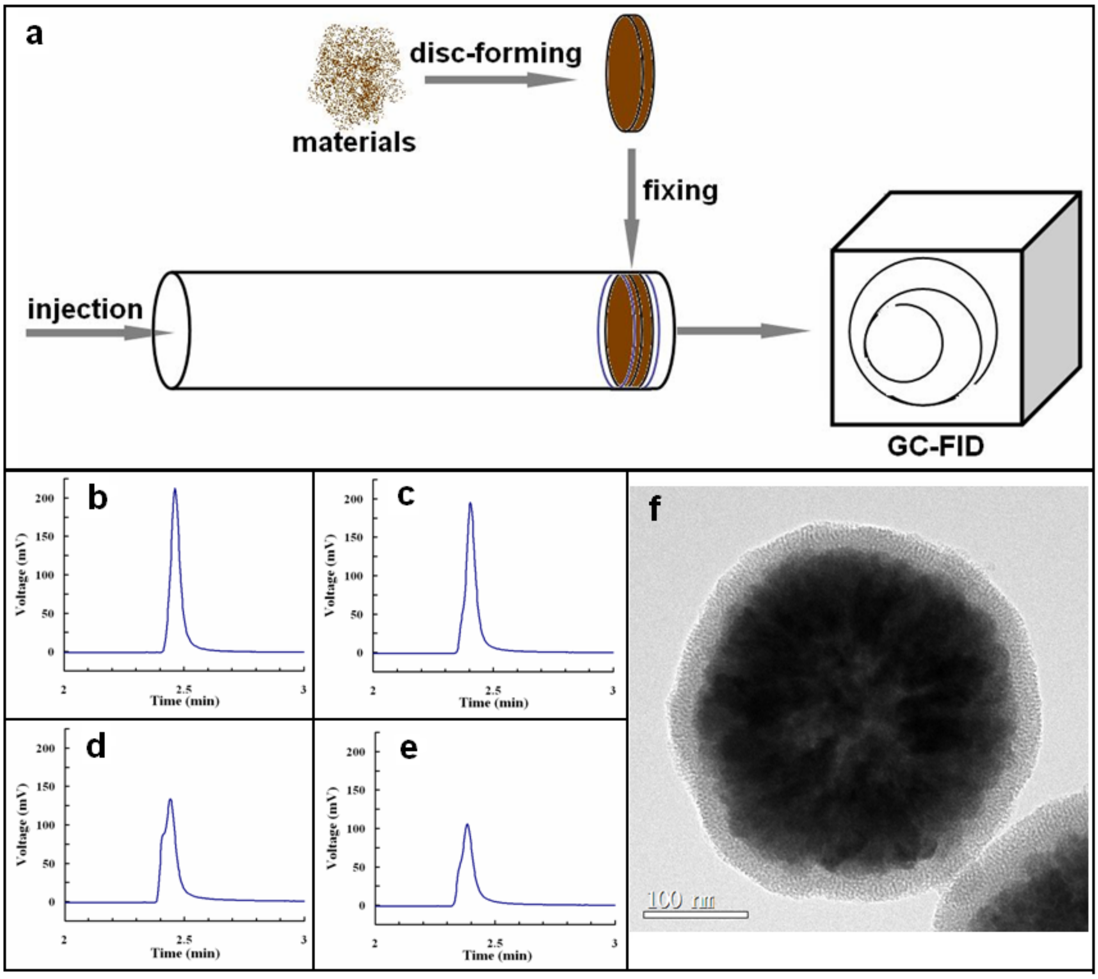

Figure S7 (a) The scheme of the experiment for adsorption of gaseous benzene. (b~e) GC-FID detection of the benzene with the adsorption by (b) no materials, (c) Fe_3O_4@mSiO_2, (d) MagCNTs and (e) MagCNTs@mSiO_2. (f) The TEM image of Fe_3O_4@mSiO_2.