Supplementary Information

Fabrication of Novel Rattle-Type Magnetic Mesoporous carbon Microspheres for Removal of Microcystins

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1 Synthesis of Fe_3O_4@nSiO_2@mSiO_2 microspheres

Synthesis of Magnetic Fe_3O_4 Nanoparticles

The water dispersible Fe_3O_4 particles were synthesized according to the method reported previously.[1] Typically, $FeCl_3$ (0.65 g, 4.0 mmol) and trisodium citrate (0.20 g, 0.68 mmol) were first dissolved in ethylene glycol (20 mL), afterward, NaAc (1.20 g) was added with stirring. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclave was heated at 200 ℃ and maintained for 10 h, and then allowed to cool to room temperature. The black products were washed with ethanol and deioned water for several times.

Synthesis of Fe_3O_4@nSiO_2@mSiO_2 Nanocomposites

The core–shell structured Fe_3O_4@nSiO_2@mSiO_2 nanoparticles were prepared according to the previously reported method with same modification.[2] In a typical procedure, as-prepared Fe_3O_4 (0.3 g) nanoparticles were well dispersed in a mixture of ethanol (120 mL), deionized water (35 mL), and concentrated ammonia aqueous solution (25 wt%, 3.5 mL). After mechanical stirring for 15 min at room temperature, 1.0 mL of tetraethyl orthosilicate (TEOS) was added dropwise in 2 min, and the reaction was allowed to proceed for 6 h under continuous mechanical stirring. The resultant core-shell Fe_3O_4@SiO_2 microsphere product was separated and collected with a magnet, followed by washing with ethanol and water several times. Then the Fe_3O_4@SiO_2 microspheres (0.1g) were redispersed in a mixed solution containing cetyltrimethylammonium bromide (CTAB) (0.36 g), deionized water (80 mL), concentrated ammonia aqueous solution (25 wt %, 2.5 mL), and ethanol (120 mL). The resulting solution was stirred for 30 min. TEOS (1.5 ml) was then added dropwise to the solution with stirring. After another stirring for 6 h, the products were collected and separated with a magnet, washed with ethanol and water several times. The structure directing agent (CTAB) was subsequently removed by a reflux method. Briefly, the as-prepared sample containing CTAB was dispersed in acetone and refluxed at 75 ℃ for 48 h. The extraction was repeated 3 times to ensure a complete removal of CTAB templates. Finally, the product was dried in vacuum at 60℃ for 12 h and denoted as Fe_3O_4@nSiO_2@mSiO_2.

2 Removal of MCs in water using RTMMCSs

Procedure

MC-RR, MC-LR and MC-LR were dissolved in Milli-Q water (pH =7.0) to make a stock solution with concentrations of 5 µg mL^{-1}. A 10µL suspension of magnetic mesoporous carbon microspheres (3 mg mL^{-1}), were added to 1 mL of 5 μg mL^{-1} microcystins solution in 1.5 mL comparison tube. The mixed solutions were then vibrated at room temperature for 5 min. After that, with the help of a magnet, the MCs absorbed by RTMMCSs were removed. The supernatant was analyzed by HPLC analysis. Separation and analysis were performed with an Agilent 1200 HPLC system detected at 238 nm. The Agilent ZORBAX Eclipse XDB-C18 Column (150 mm×4.6 mm, 5µm) was used for the separation of MCs. The mobile phase consisted of methanol-water with 0.1% trifluoroacetic acid (60:40). The flow rate was 1.0 mL·min^{-1}.

Determination of adsorption time and maximum load amount of MCs

Kinetic experiments to determine the amount of microcystins adsorbed as a function of contact time were conducted by incubating several same samples of 1 mL of 5 μg mL^{-1} microcystins solution with 30 ug of the RTMMCSs with shaking at room temperature in a comparison tube. At a given time, one sample was taken and separated with a magnet, followed by the collection of the supernatant for analysis.

In order to investigate the removal efficiency of microcystins using the RTMMCSs, various amounts of the RTMMCSs ranging from 0 to 0.1 mg were added into the aqueous solution of microcystins (1 ml, 5 μg mL^{-1}). After the incubation for 5 min, separation by a magnet, the supernate was applied for HPLC analysis. Removal efficiency was evaluated according to the analysis of HPLC.

The maximum load amount of MCs by RTMMCSs was determined by mixing 20 μg RTMMCSs with various final concentrations (0.01-10 μg ml^{-1}) solution of microcystins in water. After the incubation for 5 min, separation by a magnet, the supernate was applied for HPLC analysis. The adsorption amount for MCs of per microgramme of the RTMMCSs was calculated and the maximum load amount was evaluated when the absorption amount kept steady and no longer increased.

The reuse of the RTMMCSs

To test the reusability of the RTMMCSs, The RTMMCSs microspheres used for removing the MCs was collected and washed with methanol containing 0.1% TFA (1ml) for three times and water (1 mL) for once respectively. After washing, the RTMMCSs were reused for the removal of the MCs. The supernatant was analyzed by HPLC.

3 Characterization

The morphology and microstructure of the samples were investigated by SEM (S-4800), TEM (JEOL JEM-1011CX), HRTEM (JEOL JEM-2011CX). Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Dmax-2500 with Ni-filtered Cu KR radiation (18 kV). The S-4800 scanning electron microscope was used to acquire the EDX analysis results. The Raman spectra were obtained on a Via-Reflex with excitation from an argon ion laser (532 nm). Magnetization measurements were performed on a MPM5-XL-5 superconducting quantum interference device (SQUID) magnetometer at 300 K. Nitrogen-sorption isotherms and BET surface area were measured at 77 K with an ASAP 2020 Nitrogen System.

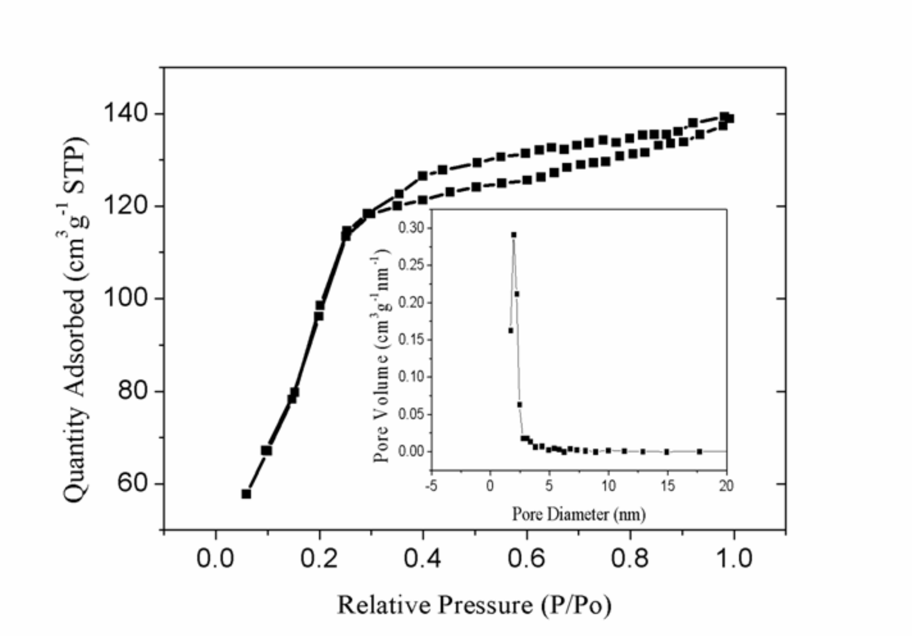

Fig. S1 Nitrogen adsorption/desorption isotherm of Fe_3O_4@nSiO_2@mSiO_2 spheres; the inset shows the pore-size distribution.

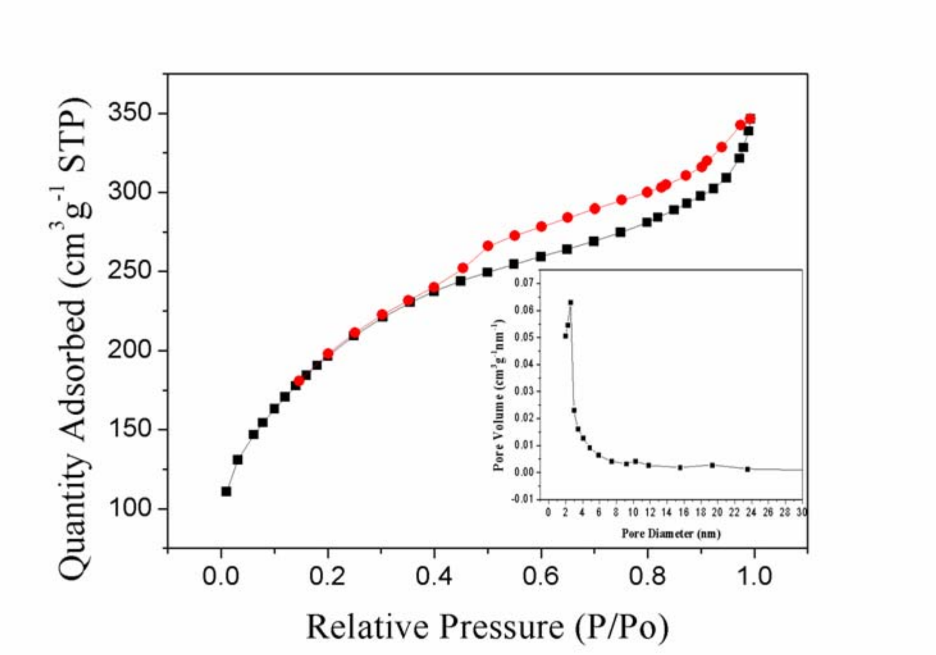

Fig. S2 Nitrogen adsorption/desorption isotherm of RTMMCSs; the inset shows the pore-size distribution.

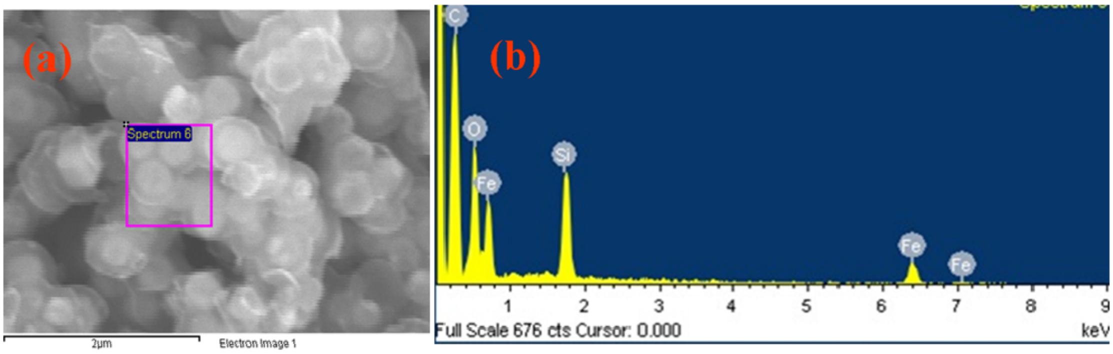

Fig. S3 (a) SEM image, and (b) EDX spectrum of RTMMCSs taken from the area marked with rectangle in (a).

Table S1 The element composition of the RTMMCSs.

Element	Weight (%)^a	Atomic (%)^b
C K	37.32	59.91
O K	18.27	22.02
Si K	8.03	5.51
Fe L	36.38	12.56
Totals	100.00	

^{a} The weight percentage of the element. ^{b} The atomic percentage of the element.

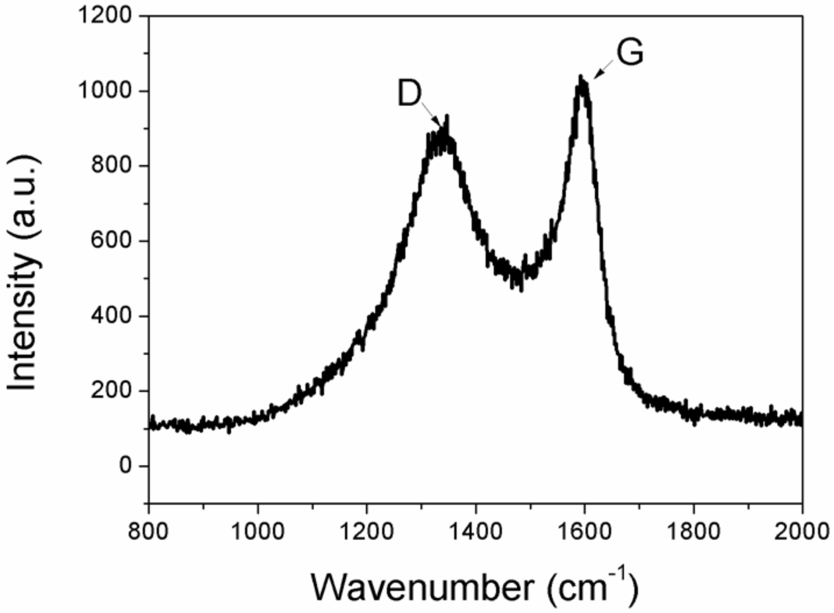

Fig. S4 Raman spectra of the as prepared RTMMCSs.

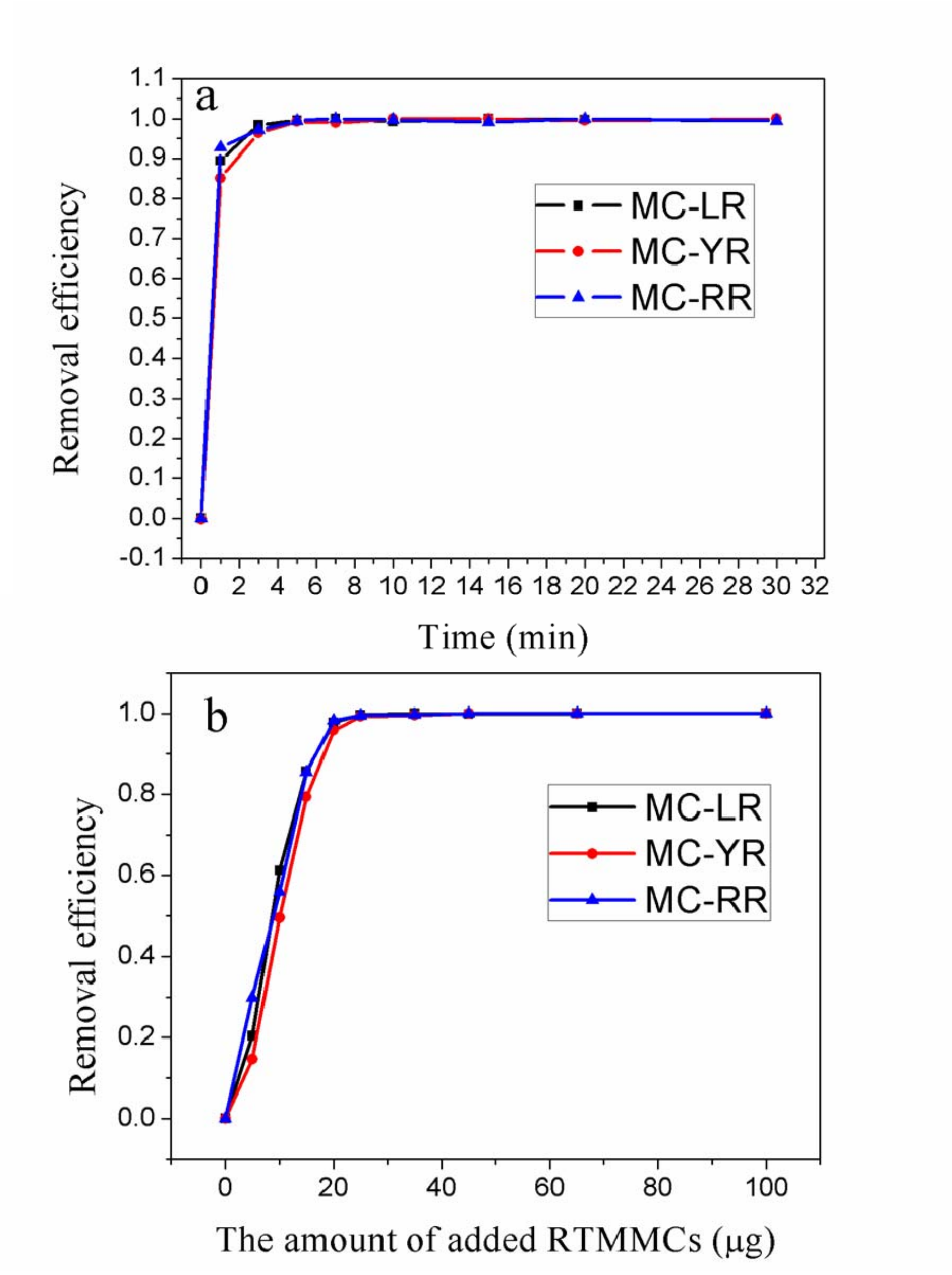

Fig. S5 The results of removal efficiency affected by the time of adsorption (a), and the affection of the amount of the RTMMCSs (b).

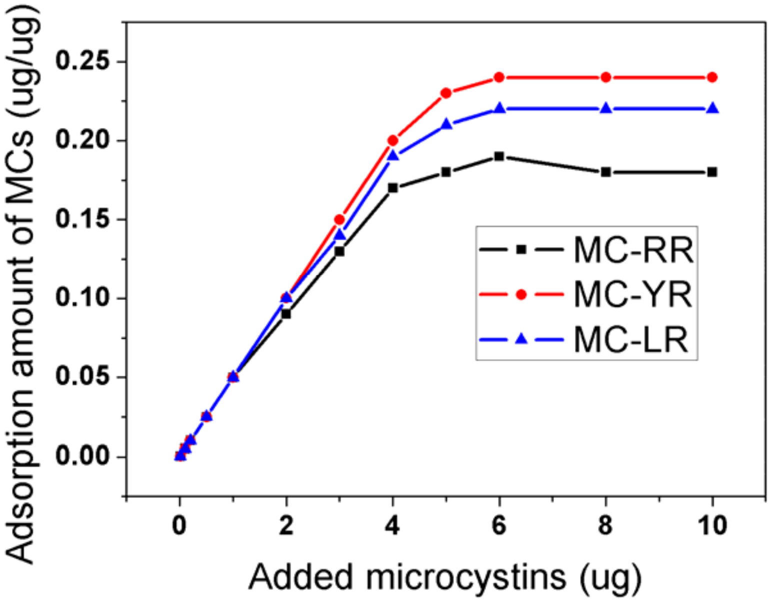

Fig. S6 The adsorption amount of MCs affected by the amount of added MCs

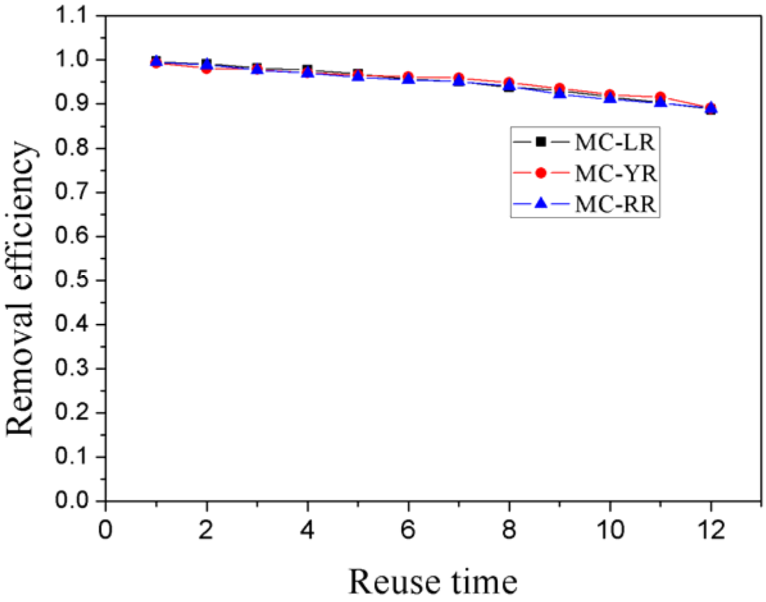

Fig. S7 Changes of the removal efficiency for MC-RR, MC-YR and MC-LR upon the reuse time by using RTMMCSs.

1 J. Liu, Z. S, Y. Deng, Y. Zou, C. Li, X. Guo, L. Xiong, Y. Gao, F. Li and D. Zhao, *Angew. Chem. Int. Ed.* 2009, **48**, 5875.

2 Y. H. Deng, D. W. Qi, C. h. Deng, X. M. Zhang and D. Y. Zhao, *J. Am. Chem. Soc.* 2008, **130**, 28.