

## Supporting Information

# Ordered Mesoporous Carbons and Their Corresponding Column for High Efficient Removal of Microcystin-LR

Wei Teng<sup>a</sup>, Zhangxiong Wu<sup>b</sup>, Jianwei Fan<sup>c</sup>, Hong Chen<sup>a</sup>, Dan Feng<sup>a</sup>, Yingying Lv<sup>a</sup>, Jinxiu Wang<sup>a</sup>, Abdullah M. Asiri<sup>d</sup> and Dongyuan Zhao<sup>\*a,b</sup>

<sup>a</sup> Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, and Advanced Materials Laboratory, Fudan University, Shanghai 200433, P. R. China.

<sup>b</sup> Department of Chemical Engineering, Monash University, Clayton, VIC 3800, Australia

<sup>c</sup> College of Environmental Science and Engineering, State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092, P. R. China

<sup>d</sup> Chemistry Department and The Center of Excellence for Advanced Materials Research, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia.

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## EXPERIMENTAL SECTIONS

Three distinct mesoporous carbons, including 2D hexagonal mesostructure FDU-15<sup>1</sup>, 3D cubic mesostructure FDU-16<sup>2</sup> and bimodal mesopore MCS/C<sup>3</sup> were synthesized by a solvent evaporation-induced self-assembly (EISA) method with triblock copolymer Pluronic F127 as a structure-directing agent and phenolic resin as a carbon precursor according to previous reports.

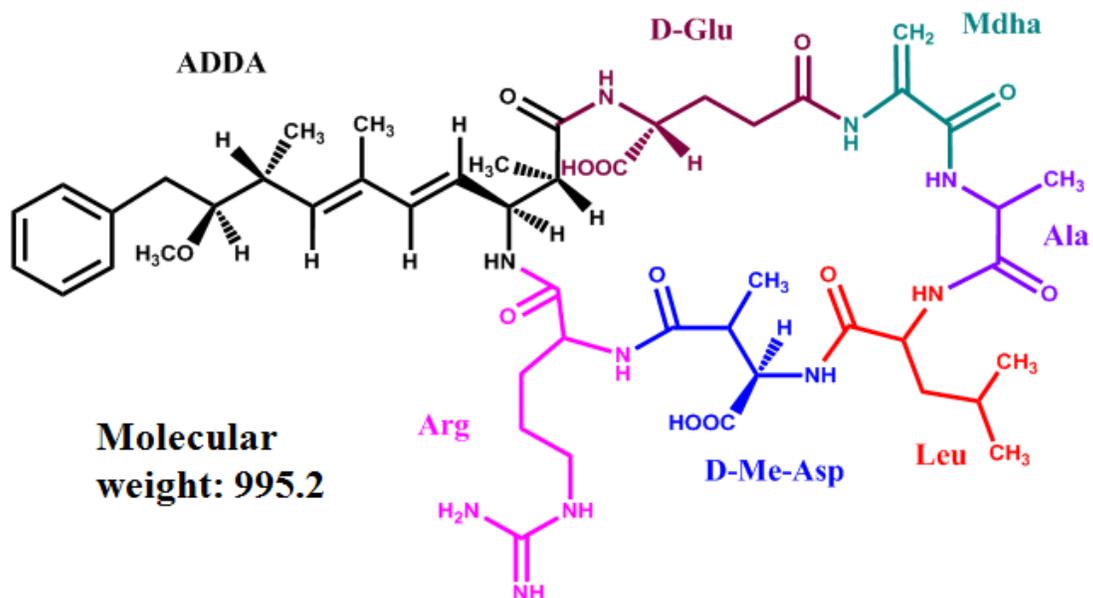
**Synthesis of carbon precursors.** The resol precursors with low-molecular-weight, were prepared from phenol and formaldehyde through the base catalysis. In a typical procedure, 8.0 g of phenol was melted at 42 – 45 °C in a flask and mixed with 0.34 g of 20 wt % NaOH aqueous solution under stirring. After 10 min, 5.24 g of formaldehyde (37 wt %) was added. Then the mixture was heated to 70 °C for further stirring. After 1 h, the mixture was cooled to room temperature. The pH value was adjusted with 2 M HCl solution until it reached a value of ~ 7.0. Subsequently, water was removed by vacuum evaporation at below 45 °C. The ethanol-soluble phenolic resins (resol) were dissolved in ethanol (20 wt %) for the further use.

**Synthesis of the bimodal pore mesoporous carbon MCS/C.** Its parents, the mesoporous silica-carbon composites (MCS), were firstly prepared by the tri-constituent co-assembly approach. 1.6 g of Pluronic F127 was dissolved in 8.0 g of ethanol with 1.0 g of 0.2 M HCl and stirred for 1 h at 40 °C to obtain a clear solution. 2.08 g of TEOS and 5.0 g of 20 wt % resols were added in sequence. After being stirred for 2 h, the mixture was transferred into dishes to evaporate ethanol at ambient temperature overnight and thermopolymerize at 100 °C for 24 h. The as-made mesostructured silica-resin composites were scraped from the dishes and ground into fine powders. Carbonization was carried out in a tubular furnace at 350 °C for 3 h and at 900 °C for 2 h under nitrogen protection to obtain the mesoporous silica-carbon composites (MCS). The heating rate was 1 °C/min below 600 °C and 5 °C/min above 600 °C. The bimodal pore mesoporous carbon (MCS/C) was recovered after dissolution of the silica component in the composite

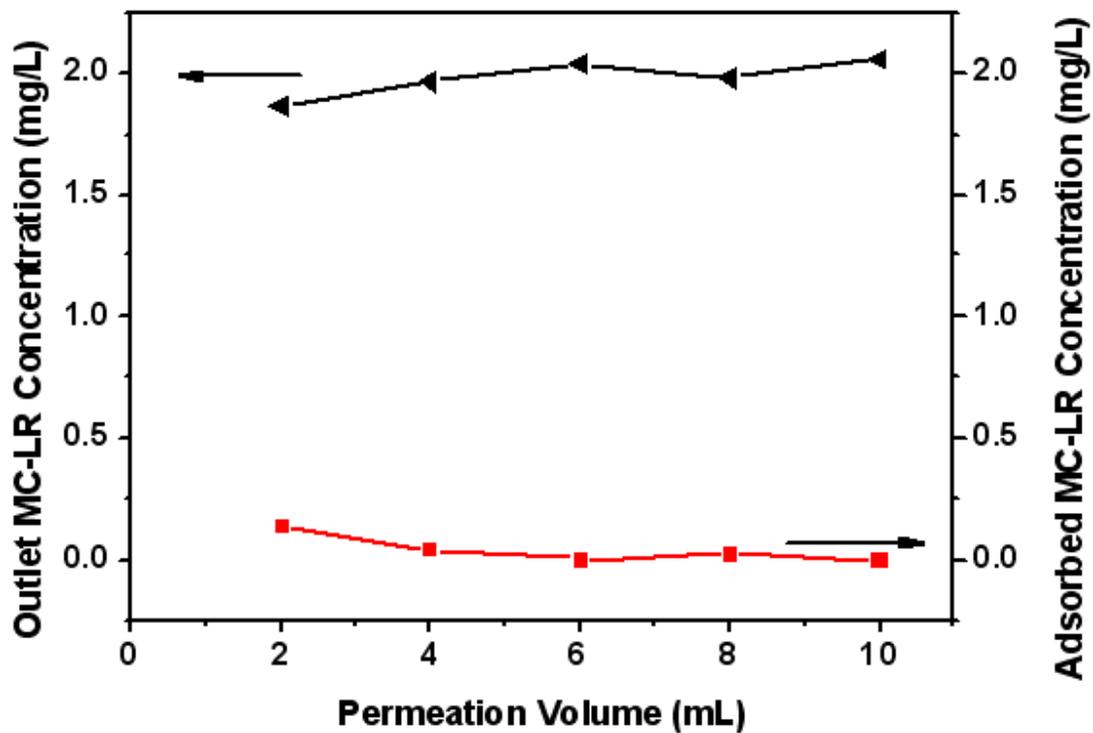
sample MCS by 10 wt % HF solution at room temperature, filtration, washing with water and drying at 100 °C.

**Synthesis of 2D hexagonal mesoporous carbon FDU-15.** Typical synthesis procedure was as following. Firstly, 3.0 g of Pluronic F127 was dissolved in 30.0 g of ethanol to obtain a clear solution and then 15.0 g of 20 wt % phenolic resins ethanolic solution was added. After being stirred for 10 min, the mixture was poured into dishes to evaporate ethanol at ambient temperature overnight and thermopolymerize at 100 °C for 24 h in sequence. The as-made composites were scraped from the dishes into a tubular furnace. Carbonization was carried out at 350 °C for 3 h and at 900 °C for 2 h under nitrogen protection. The heating rate was 1 °C/min below 600 °C and 5 °C/min above 600 °C. Finally, the collected carbonized products were FDU-15.

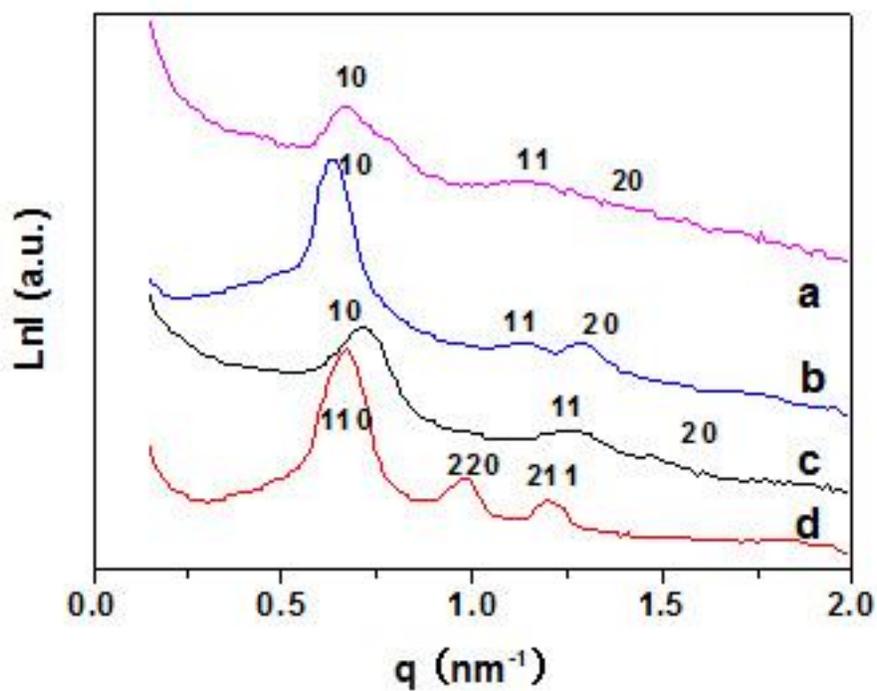
**Synthesis of 3D cubic mesoporous carbon FDU-16.** Mesoporous carbon FDU-16 with 3D cubic mesostructure (*Im3m*) were synthesized by a procedure similar to that of the mesoporous carbon FDU-15, using triblock copolymer F127 (1.00 g), ethanol (15.0 g), resol precursor solution (10.0 g).



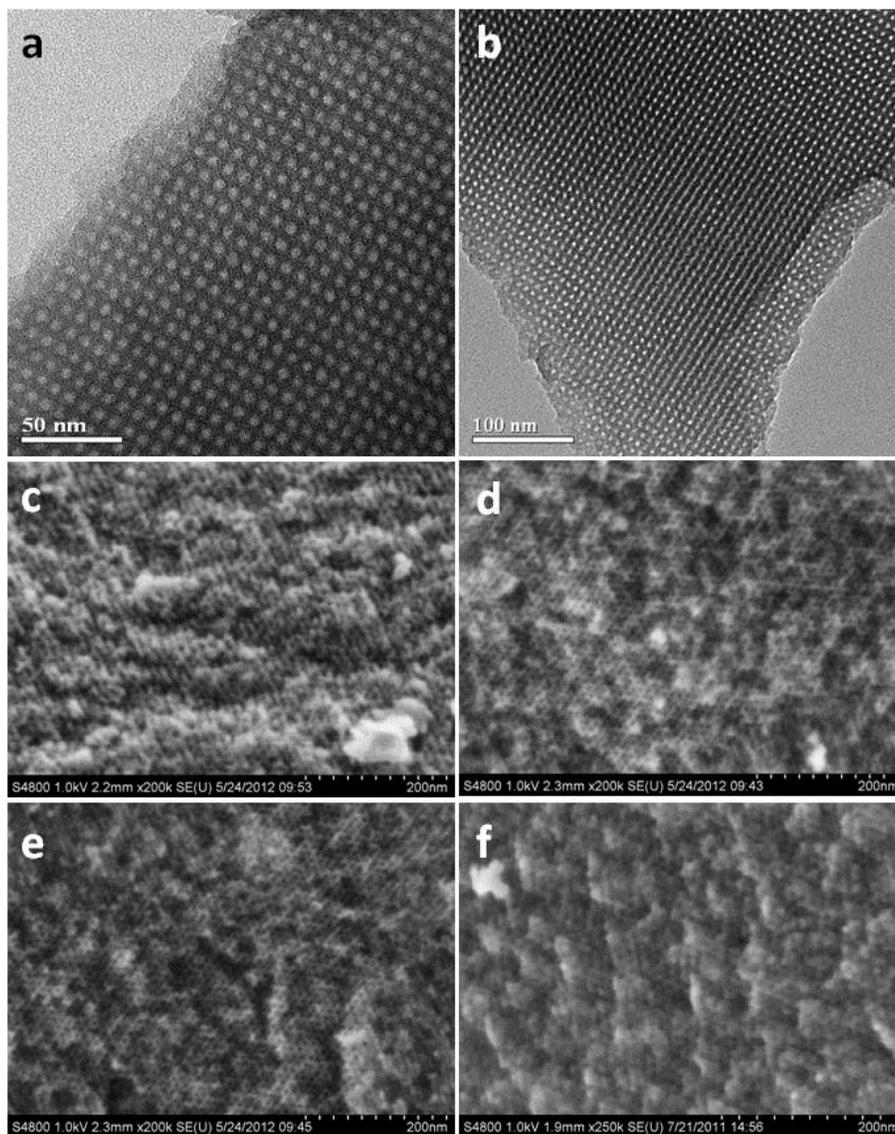
**Figure S1.** Structure and molecular weight of MC-LR.



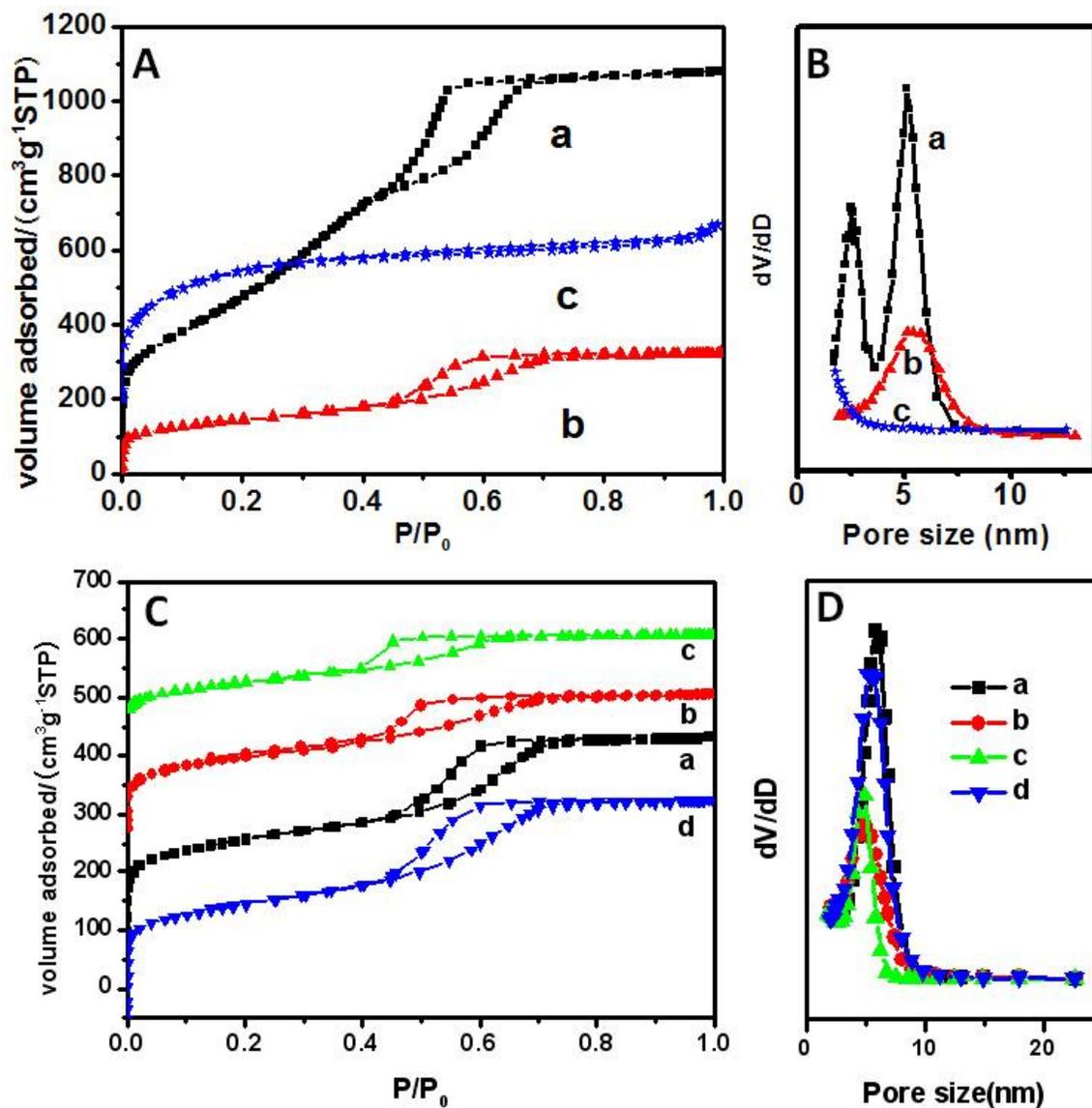
**Figure S2.** Outlets and adsorbed MC-LR concentration *versus* the permeation volume of MC-LR feed solution by flowing through the set of blank device without adsorbents filler, with a feed concentration of  $2 \text{ mg L}^{-1}$ .



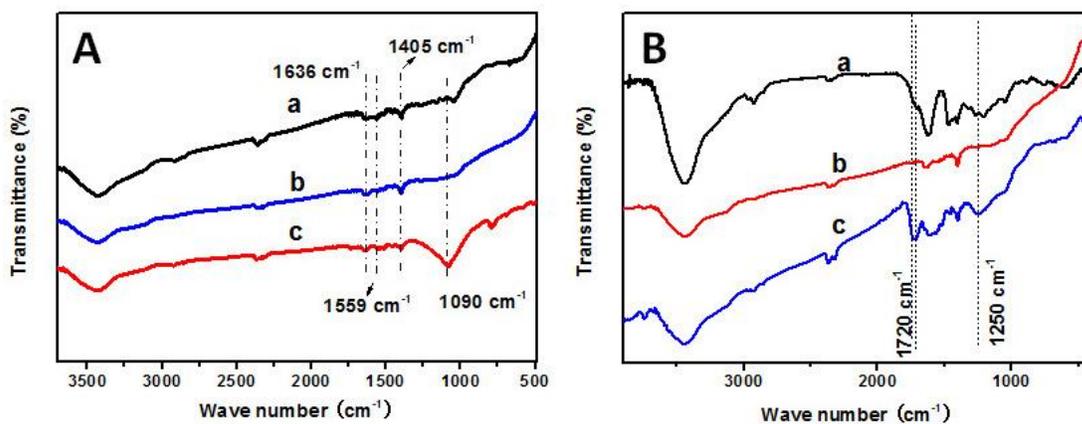
**Figure S3.** SAXS patterns of the mesoporous carbon MCS/C-APS prepared from mesoporous carbon composite after etching silica component by HF solution and treating with APS (a), 2D hexagonal mesoporous carbon FDU-15- $x$  after being carbonized at different temperature: (b) 350 °C (FDU-15-350) and (c) 900 °C (FDU-15-900) and 3D cubic mesoporous carbon FDU-16-600 (d).



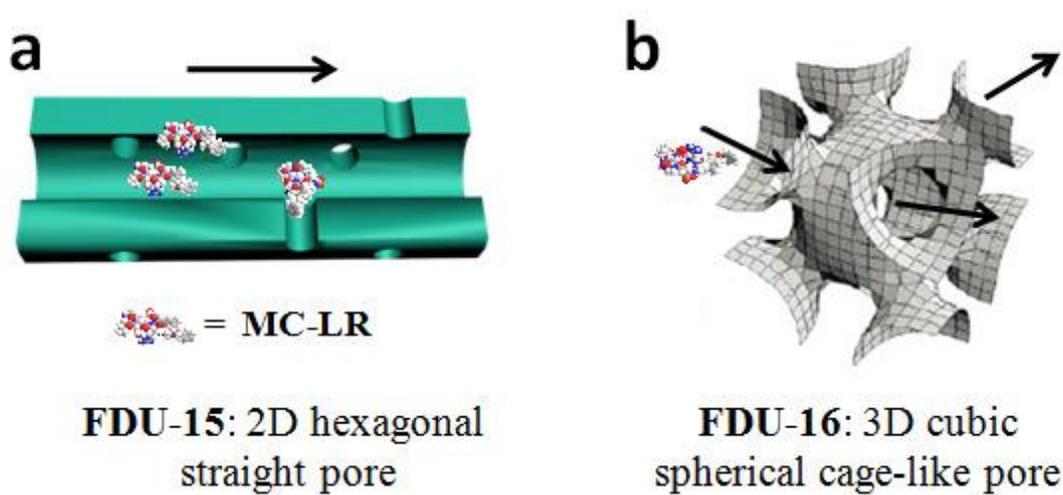
**Figure S4.** TEM images (a, b) of the 3D cubic mesoporous carbon FDU-16-600 viewed along the [100] (a) and [110] (b) directions; and HRSEM images (c-f) of the mesoporous carbon MCS/C obtained from the silica-carbon composite after etching silica component (c, d), 2D hexagonal mesoporous carbon FDU-15-900 (e) and 3D cubic mesoporous carbon FDU-16-600 (f).



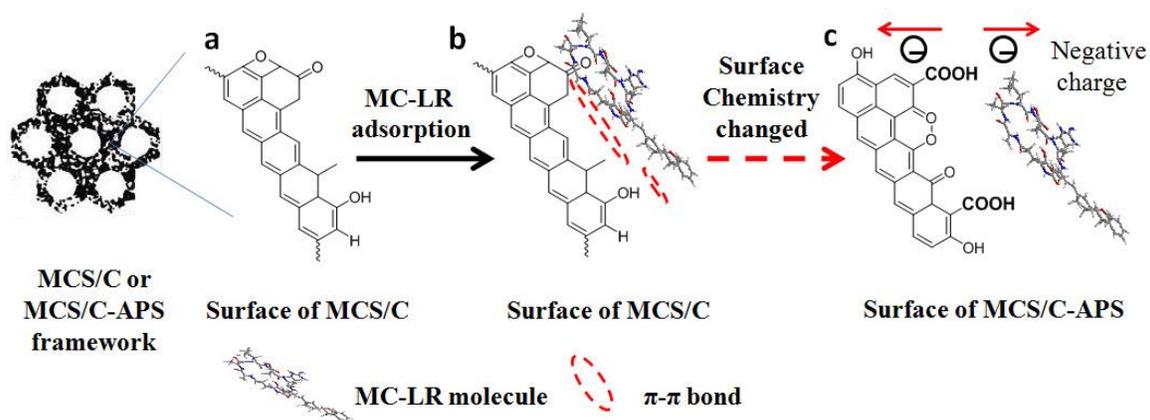
**Figure S5.** Nitrogen sorption isotherms (A) and the corresponding pore size distribution curves (B) of the mesoporous carbon MCS/C obtained from the silica-carbon composite after etching silica component (a), 2D hexagonal mesoporous carbon FDU-15-900 (b), and the commercial PAC (c). Nitrogen sorption isotherms (C) and corresponding pore size distributions (D) of the 2D hexagonal mesoporous carbon FDU-15-x after carbonization at different temperature: (a) 350 °C (FDU-15-350), (b) 600 °C (FDU-15-600) and (c) 900 °C (FDU-15-900), and 3D cubic mesoporous carbon FDU-16-600 (d).



**Figure S6.** FTIR spectra of (A) the mesoporous carbon MCS/C obtained from the silica-carbon composite after etching silica component (a), 2D hexagonal mesoporous carbon FDU-15-900 (b) and the commercial powdery active carbon (PAC) (c); and (B) the 2D hexagonal mesoporous carbon FDU-15-*x* after carbonization at different temperature: (a) 350 °C (FDU-15-350), (b) 900 °C (FDU-15-900), and the mesoporous carbon MCS/C-APS prepared from mesoporous carbon composite after etching silica component by HF solution and treating with APS (c).



**Figure S7.** Illustration of the effect on MC-LR adsorption from mesostructure: MC-LR molecules can easily entrance into 2D hexagonal FDU-15 with straight mesopore channels (a) and difficultly into 3D body-centered cubic FDU-16 with spherical cage-like mesopores (b).



**Figure S8.** Illustration of the force between MC-LR molecules and mesoporous carbon with different surface chemistry: (a) the surface of the mesoporous carbon MCS/C obtained from the silica-carbon composite after etching silica component, (b) MC-LR molecules adsorbed on the surface of the mesoporous carbon MCS/C and (c) MC-LR molecules adsorbed on the surface of mesoporous carbon MCS/C-APS prepared from the mesoporous carbon composite after etching silica component by HF solution and treating with APS.

**Table S1.** Structural, textural parameters and adsorption capacity of MC-LR for the mesoporous carbon adsorbents.

Sample name	$S_{\text{BET}}(\text{m}^2/\text{g})$	$S_{\text{Me}}(\text{m}^2/\text{g})$	$D(\text{nm})$	$V_t(\text{cm}^3/\text{g})$	$X_{\text{MC-LR}}^a(\text{mg}/\text{g})$
FDU-16-600	690	290	4.8	0.44	14.8 <sup>b</sup>
FDU-15-350	537	325	5.2	0.40	22.1
FDU-15-600	729	388	5.1	0.57	48.2
FDU-15-900	915	382	4.7	0.68	57.3
MCS/C-APS	1290	1290	2.3, 4.9	0.96	142

<sup>a</sup> The MC-LR adsorption data on mesoporous carbon adsorbents were carried out at the same test conditions with 2 mg L<sup>-1</sup> of initial concentration, 0.2 mg of adsorbents, 200 rmp of shaking speed, 4 h of contact time, 25 °C in deionized water.

**Table S2.** Comparison of MC-LR adsorption capacity of different adsorbents.

Adsorbents	Adsorbents Dosage (mg)	MCs initial Concentration (mg/L)/(solution volume)	Contact time	q <sub>e</sub> (μg/g)	Refs
MCS/C	0.025	5/(5 mL)	4 h	526000	Our work
PAC	0.1	5/(5 mL)	4 h	64500	Our work
Activated carbon	0.0005	0.07-3.03/(5 mL)	72 h	200000	[4]
Granular activated carbon	Coconut shell	0.25/(100 mL)	72 h	14500	[5]
Carbon nanotube	10	21.5/(10 mL)	24 h	14800	[6]
Magnetic Nanoparticles	1	1.5/(1 mL)	5 min	60	[7]

## References:

- 1 Y. Meng, D. Gu, F. Q. Zhang, Y. F. Shi, H. F. Yang, Z. Li, C. Z. Yu, B. Tu and D. Y. Zhao, *Angew. Chem. Int. Ed.*, 2005, **44**, 7053.
- 2 Y. Meng, D. Gu, F. Zhang, Y. Shi, L. Cheng, D. Feng, Z. Wu, Z. Chen, Y. Wan, A. Stein and D. Y. Zhao, *Chem. Mater.*, 2006, **18**, 4447.
- 3 R. Liu, Y. Shi, Y. Wan, Y. Meng, F. Zhang, D. Gu, Z. Chen, B. Tu and D. Y. Zhao, *J. Am. Chem. Soc.*, 2006, **128**, 11652.
- 4 P. Pendleton, R. Schumann and S. H. Wong, *J. Colloid Interf. Sci.*, 2001, **240**, 1.
- 5 W. J. Huang, B. L. Cheng and Y. L. Cheng, *J. Hazard. Mater.*, 2007, **141**, 115.
- 6 H. Yan, A. Gong, H. He, J. Zhou, Y. Wei and L. Lv, *Chemosphere*, 2006, **62**, 142.
- 7 M. Gao, C. Deng, Z. Fan, N. Yao, X. Xu, P. Yang and X. Zhang, *Small*, 2007, **3**, 1714.