Electronic Supplementary Material (ESI) for Environmental Science: Nano. This journal is © The Royal Society of Chemistry 2018

> **Supporting Information for** 1 2 Halloysite nanotube@carbon with rich carboxyl group as a 3 multifunctional adsorbent for the efficient removal of cationic Pb(II), 4 anionic Cr(VI) and methylene blue (MB) 5 6 7 Penglei Wang^a, Yuanyuan Tang^{a*}, Yunsong Liu^{a,b}, Tao Wang^a, Pengfei Wu^a, Xiao-Ying Lu^c 8 a. School of Environmental Science and Engineering, Guangdong Provincial Key Laboratory of Soil and Groundwater Pollution 0 Control, Southern University of Science and Technology, 1088 Xueyuan Blvd, Nanshan District, Shenzhen 518055, China. 10 b. College of Urban and Environment Sciences, Peking University, Beijing 100871, China 11 c. Faculty of Science and Technology, Technological and Higher Education Institute of Hong Kong, Hong Kong, P.R. China. 12 *Corresponding author. Dr. Yuanyuan Tang, E-mail: tangyy@sustc.edu.cn; Tel.: (+86)-755-88015460 13 14 15 16 17 18 19 20 21 Including Supporting Information A for sample characterization and analysis, and five adsorption equations; and Supporting Information B for 1 Scheme, 3 Tables, 1 22 Scheme and 6 Figures in 15 pages 23 24

1 Supporting Information A

2

3 **1. Sample characterization**

4

FTIR spectra were collected using a FT-IR 380 spectrometer (FT-IR 380, Thermo 5 Scientific) in the range of 4000-500 cm⁻¹ with resolution of 1.5 cm⁻¹, number of scans 6 of 64 and the KBr tablet with ~ 2 % sample concentration. The surface morphology of 7 samples was analyzed using a scanning electron microscopy (SEM) operating at 8 3.0 kV (Zeiss Merlin). For SEM analysis, the sample was first dispersed in ethanol and 9 then the obtained suspension was dropped onto the silicon wafer. The zeta-potential 10 11 of the sample was measured by the Malvern Zetasizer Nano ZS90, and the sample was previously dispersed in water with concentration of the 0.2 g L⁻¹. Brunauer-12 Emmett-Teller surface area (S_{BET}) of the samples was obtained by N₂ adsorption-13 desorption using Automated Gas Sorption Analyzer (ASAP 2020, Micromeritics) 14 with pressure and temperature as 550 µm Hg and 180 °C in the degassing procedure 15 of samples. The multipoint method was used to calculate the SBET. The XPS 16 measurements were performed in a Sengyang SKL-12 electron spectrometer equipped 17 with a VG CLAM 4 MCD electron energy analyzer. X-ray source is a twin-anode 18 (Mg/Al) source from VG (Model XR3E2). The XPS spectra were recorded using an 19 achromatic Al Ka excitation (1486.6 eV) at 10 kV, with an emission current of 15 mA. 20 The scan is conducted at pass energy of 20.0 eV, with dwell time of 0.2 ms and step 21 size of -0.10 eV, and number of scans as 4. The peak deconvolution was performed by 22 XPSPEAK version 4.1. Thermogravimetric analysis (TG) and differential 23 thermogravimetric analysis (DTG) were carried out using a TGA analyzer (Nietzsche, 24 STA449F3) under air atmosphere from 30 °C to 700 °C at 10 °C min⁻¹. 25

26

27 2. Adsorption and measurement of pollutants

28

29 The adsorption experiment was performed in a sealed 100 mL breaker flask, using a

1 batch model with 20 mg of Halloysite@carbon with rich carboxyl group (HNT@CRC) added in 50 mL solution containing one type of pollutants (Pb(II), Cr(VI) or MB). 2 The pH values of the above solutions were adjusted to desired value using $0.1 \text{ mol } L^{-1}$ 3 NaOH solution and 0.1 mol L⁻¹ HCl solution. The adsorption solution was shaken 4 with a speed of 200 rpm at 25 °C and then filtered through a 0.22 µm membrane. The 5 concentration of MB was quantified by measuring the absorbance of the solution 6 using UV-vis spectrophotometer (Agilent, Cary 60) at wavelength of 667 nm. The 7 concentrations of Pb(II) and Cr(VI) were determined by inductively coupled 8 plasma-optical emission spectroscopy (ICP-OES, PerkinElmer, Optima 8000). The 9 adsorption capacity of Pb(II), Cr(VI) and MB adsorbed onto the HNT@CRC at time t 10 (min) was calculated according to the following equation (Eq.S1): 11

12

13

$$Q_{\rm t} = \frac{(C_o - C_{\rm t})V}{m}$$
 Eq. S1

14

15 where C_o and C_t (mg L⁻¹) are the concentrations of pollutants at the initial state and 16 time *t*, respectively. *V* (L) is the volume of the solution, and *m* (g) is the mass of the 17 adsorbent.

18

19 3. Adsorption kinetics equations

20

The models of pseudo-first-order, pseudo-second-order and intra-particle diffusion are
expressed by Eq.S2, Eq.S3 and Eq.S4, respectively.¹⁻³

23

25

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \qquad \text{Eq.S2}$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e}$$
Eq.S3

 $26 Q_t = K_p t^{1/2} + C Eq.S4$

27 where Q_e and Q_t (mg g⁻¹) are the amount of adsorbed pollutant at equilibrium and at

1 time *t*, respectively. K_1 , K_2 and K_p are the rate constants of the pseudo-first-order 2 model (min⁻¹), the pseudo-second-order model (mg.g⁻¹.min⁻¹) and the intra-particle 3 diffusion model (mg·g⁻¹·min^{-0.5}), respectively. C (mg g⁻¹) is a constant associated 4 with the thickness of the boundary layer.

5

6 4. Adsorption isotherm equations

7

8 The Langmuir and Freundlich models can be described by Eq.S5 and Eq.S6,
9 respectively.³

10

11

	$Q = \frac{Q_m K_L C_e}{Q_m K_L C_e}$	
12	$\mathcal{L}_e = 1 + K_L C_e$	Eq. S5

 $Q_e = K_F C_e^{1/n} \qquad \text{Eq. S6}$

14

where Q_m is the saturated adsorption capacity (mg g⁻¹). K_L (L mg⁻¹) is the Langmuir constant related to the affinity between an adsorbent and pollutants, and K_F (mg g⁻¹)·(mg⁻¹ L)^{1/n} is the Freundlich constant indicating the interaction energy between adsorbents and pollutants. n is a constant reflecting the energetic heterogeneity.

19

20 5. The experimental procedure of adsorption-desorption cycles of HNT@CRC-8 21

For each cycle, the HNT@CRC-8 after Cr(VI) adsorption was collected and put into 30 mL dilute ammonia water (15%), shaken at 200 rpm under 25°C for 4 h. Then the adsorbent was washed to neutral by deionized water and collected for reuse. Similarly, the HNT@CRC-8 after MB or Pb(II) adsorption was separated and immersed into 30 mL 0.1 mol L⁻¹ HCl for 4 h, and then the adsorbent was washed by deionized water to neutral and for the next round use.

28 Supporting Information B

2 Table S1. Textural parameters of HNT@CRC.							
-	Sample	S _{BET}	Average pore diameter	V _T	Vmicro	Vmeso	
		(m ² g ⁻¹)	(nm)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	
-	HNT@CRC-0	22.84	11.439	0.0653	0.0004	0.0649	
	HNT@CRC-2	20.41	14.183	0.0724	0.0004	0.0720	
	HNT@CRC-4	18.80	21.143	0.0928	0.0005	0.0923	
	HNT@CRC-6	17.57	21.201	0.0996	0.0006	0.0990	
	HNT@CRC-8	16.66	26.206	0.1091	0.0007	0.1084	
	HNT@CRC-10	13.90	33.048	0.1152	0.00178	0.1134	

Table S1. Textural parameters of HNT@CRC

3 V_T: total pore volume; V_{micro}: micropore volume ; V_{meso}: mesopore volume 4

5

Table S2. Kinetic parameters for the adsorption of Pb(II), Cr(VI) and MB by HNT@CRC-8

		-	_			
pseudo-first-order				pseudo -second-order		
Pollutants	$Q_{cal.}(mg \ g^{-l})$	$K_{l}(min^{-l})$	R^2	$Q_{cal.}(mg g^{-l})$	$K_2(mg.g^{-1}min^{-1})$	R^2
Pb(II)	45.63	2.10×10^{-3}	0.8823	114.3	1.27×10 ⁻³	0.9984
Cr(VI)	55.91	1.84×10-3	0.9061	92.33	9.00×10-5	0.9802
MB	132.7	2.02× 10 ⁻³	0.9643	226.8	3.26×10-4	0.9989

2 Table S3. Adsorption isotherm parameters for Pb(II), Cr(VI) and MB by HNT@CRC-8 at 25 °C Langmuir model Freundlich model $K_a(L mg^{-1})$ R^2 R^2 $K_F (mg g^{-l}) \cdot$ pollutants $q_{max\,(cal.)}(mg.g^{-l})$ п $(mg^{-1} L)^{1/n}$ 184.95 Pb(II) 0.03704 0.9912 0.2567241.460 0.9894 Cr(VI) 140.87 0.07172 0.9947 0.19417 48.163 0.9855 711.49 MB 0.01728 0.9424 0.29662 108.52 0.9933 3



Scheme S1. Schematic illustration for the formation of HNT@CRC. Firstly, the glucose is dehydrated into a furan-like molecule (furfural aldehyde and/or 5-(hydroxymethyl)-2-furaldehyde) and then undergoes copolymerization with the acrylic acid ⁴. The presence of HNT can effectively prevent the usual homogeneous nucleation of carbon species from the bulk solution and promote the heterogeneous deposition of carbonaceous matter on the surface of halloysite nanotubes to generate a well-defined nanostructured composite⁵. Finally, the HNT@CRC is obtained after the hydrothermal carbonization of the. HNT@polymer latex.











3 **Fig.S4** Absolute and normalized adsorption capacity of single hydrothermal carbon 4 (SHC), single carbon with rich carboxyl group (SHCRC) and HNT@CRC-8 for 5 Pb(II), Cr(VI) and MB. The adsorption experiments were carried out with conditions 6 as below: The adsorbent dosage is 0.4 g L⁻¹ and the initial concentration of each 7 pollutant is 100 mg L⁻¹. The adsorption time for Pb(II), Cr(VI) and MB is 300 min, 50 8 h, and 480 min, respectively. The initial pH for the Pb(II), Cr(VI) and MB solution is 9 set as 6.0, 2.0, and 5.5, respectively.





Fig.S6 The linear fitting plots of pseudo-first-order, pseudo-second-order and intraparticle diffusion model for the adsorption kinetic of Pb(II), Cr(VI) and MB by
HNT@CRC-8

References 2

- 3 1. Y. S. Ho and G. McKay, Pseudo-second order model for sorption processes. Process 4 Biochem., 1999, 34, 451-465.
- 5 2. Y. S. Ho, Review of second-order models for adsorption systems. J. Hazard. Mater., 2006, 6 136, 681-689.
- 7 3. H. N. Tran, S.-J. You, A. Hosseini-Bandegharaei and H.-P. Chao, Mistakes and 8 inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical 9 review. Water Res., 2017, 120, 88-116.
- 10 4. B. Hu, K. Wang, L. Wu, S. H. Yu, M. Antonietti and M. M. Titirici, Engineering carbon 11 materials from the hydrothermal carbonization process of biomass. Advanced Materials, 2010, 12 22, 813-828.
- 13 5. L. F. Chen, H. W. Liang, Y. Lu, C. H. Cui and S. H. Yu, Synthesis of an attapulgite 14 clay@carbon nanocomposite adsorbent by a hydrothermal carbonization process and their 15 application in the removal of toxic metal ions from water. Langmuir ,2011, 27, 8998-9004.
- 16

S15