Carbon Dots Modified Mesoporous Organosilica as an Adsorbent for the Removal of 2, 4-Dichlorophenol and Heavy Metal Ions

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Adsorption formulas

The adsorbed amount was calculated using equation (1), where q_e represents the adsorption capacity (mg/g) of the adsorbent at equilibrium. C_0 and C_e are the initial and equilibrium concentrations of metal ions (mg/L), respectively. V is the volume of the aqueous solution (L), while W is the mass (g) of adsorbent.

$$q_e = \frac{(c_o - c_e)}{W} V \quad \text{----------Equation (1)}$$

To verify the adsorption type, the batch adsorption experiment data were fitted by Langmuir[1] and Freundlich[2] models respectively. The Langmuir model was used to characterize the maximum adsorption capacity of the adsorbents, which is expressed as equation (2):

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad \text{----------Equation (2)}$$

Where q_m stands for the maximum adsorption capacity (mg/g) of the adsorbents, and b represents the strength of adsorption capacity (L/mg). A larger value of b reflects a better adsorption performance.

The Freundlich model is a kind of semi-empirical equation suitable for the description of heterogeneous adsorption, which it is expressed as equation (3):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{----------Equation (3)}$$

Where K_f stands for the Freundlich constant about the adsorption capacity of the adsorbents (mg/g), and 1/n is the intensity of the adsorption performance (L/mg). A smaller value of 1/n means a better adsorption performance.

We used two simplified kinetic models of Lagergren pseudo-first-order and pseudo-

second-order models[3] to process the data, which are expressed as equation (4) and (5) respectively:

Pseudo-first-order model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{----------Equation (4)}$$

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{----------Equation (5)}$$

Where q_t represents the adsorption at time t (min), q_e is the adsorption capacity at adsorption equilibrium obtained through experiments, k_1 and k_2 are the kinetic rate constants for the pseudo first and second order models, respectively.

Table S1 Adsorption parameters fitted from Freundlich equation

Sample	Freundlich model		
	K_f (mg/g)	1/n (L/mg)	R^2
MS-ex (10℃)	6.22	0.36	0.907
CD-MS (10℃)	23.86	0.22	0.870

Table S2 Kinetic parameters for 2, 4-DCP adsorption on CD-MS

Kinetic Models	Kinetic constants		
	q_e (mg/g)	k (g/(mg • min))	R^2
Pseudo-1st-order-model	62.70	2.01×10^{-2}	0.971
Pseudo-2nd-order-model	99.90	7.93×10^{-4}	0.999

Table S3 Adsorption parameters fitted from Langmuir equation and kinetic parameters of metal ions on CD-MS fitted from pseudo-first-order equations

Adsorbate	Langmuir curve			Pseudo-first-order model			
	q_m (mg/g)	$b\times10^{-2}$ (L/mg)	R^2	q_e (mg/g)	q_{e1} (mg/g)	k_1 (g/(mg • min))	R^2
Cu (II)	109.05	1.60	0.915	66.14	42.34	0.07	0.902
Pb (II)	140.25	1.00	0.880	100.18	83.62	0.11	0.995
Hg (II)	173.01	2.30	0.701	128.87	146.79	0.12	0.958

Table S4 Thermodynamic parameters for the metal ion adsorption at different temperatures

Temperature	Freundlich model		Cu(II)/Pb(II)/Hg(II)
(°C)	Kf ($mg^{1-(1/n)}L^{1/n}g^{-1}$)	n	R^2
25	3.23/2.60/7.41	1.53/1.38/1.55	0.997/0.993/0.974
35	2.80/4.85/6.69	1.37/1.27/1.34	0.995/0.999/0.993

Table S5 The maximum adsorption capacity values (mg/g) of Cu (II)，Hg (II), Pb (II) and 2,4-DCP by CD-MS in the present study and by some recently reported adsorbents .

Adsorbent	Cu(II)	Hg(II)	Pb(II)	2,4-DCP	Reference
Vinyl silica hollow spheres	54.7	--	75.6	--	[4]
Diamine modified mesoporous silica	66.58		~70	--	[5]
Diamine-functionalized SBA-15	27.22	--	96.43	--	[6]
Mercapto-Modified Silica Particles	--	115.87	10.42	--	[7]
Sulfur-Functionalized Silica Microspheres	--	63.2	--	--	[8]
Silica gel func tionalized with a ditopic zwitterionic Schiff base ligand	41.6	--	--	--	[9]
Multifunctional fibrous silica composite	--	115.47	--	--	[10]
Thiourea-containing silica gel hybrid materials	--	148	--	--	[11]
Organoclays	--	--	33.78	96.15	[12]
Agricultural Solid Waste	--	--	--	19.12	[13]
Organobentonite	--	--	--	281.8	[14]
Polyaniline/silica gel composites based surface imprinted polymers (MIP–PAS)	--	--	--	49.5	[15]
Carbon dots modified mesoporous silica	66.06	128.824	100.02	99.70	This work[a]

[a] The initial concentration of Hg (II) and Pb (II) is 10^{-3} M; Cu (II): $2*10^{-3}$ M; temperature: 25 ^{o}C, pH=7.0.

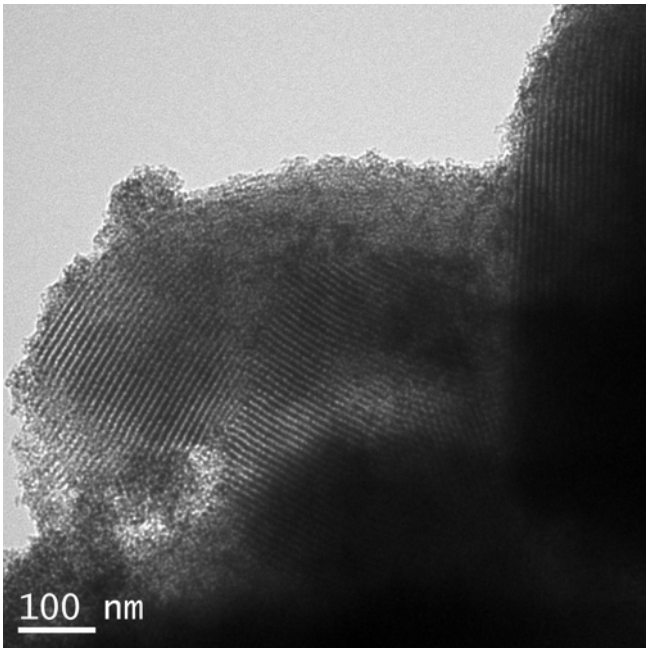

Figure S1 TEM image of CD-MS.

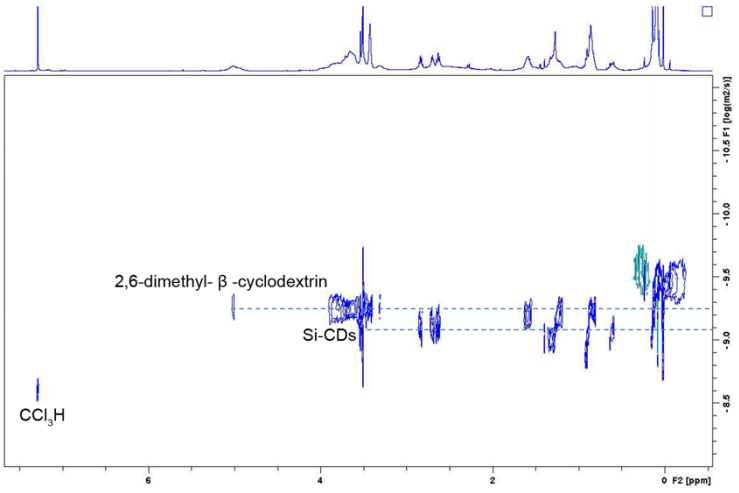

Figure S2 1 H 2D DOSY-NMR spectrum of the CD in CCl_3D. The diffusion coefficient of the cyclodextrin standard was measured as $10^{-9.25}$ m^2 s^{-1}. An average diffusion coefficient of CD was measured as $10^{-9.08}$ m^2 s^{-1}. The size of CD was determined to be 1.4 $\times(10^{-9.25}/10^{-9.08})\approx$1.0 nm, where 1.4 is the size of reference of cyclodextrin.

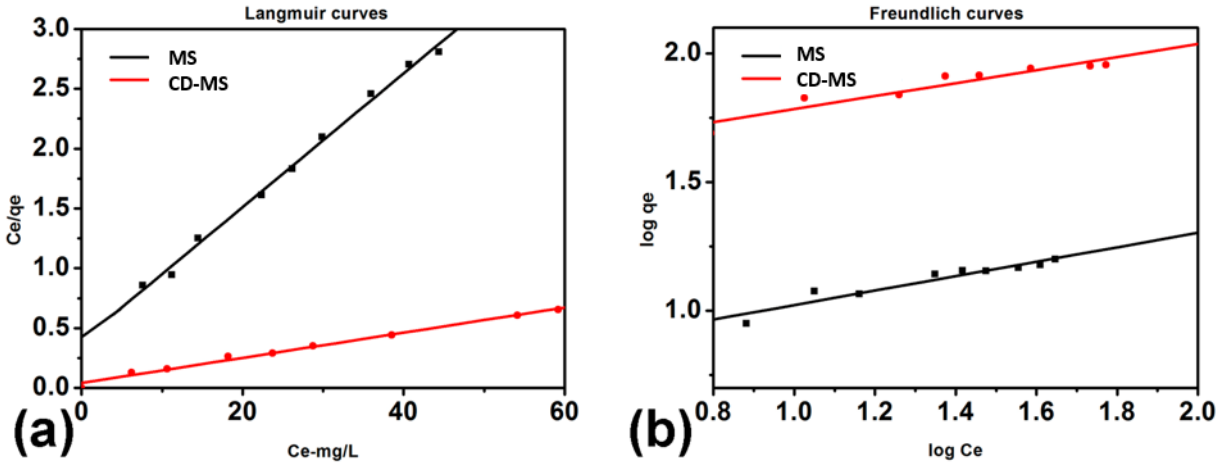

Figure S3 Fitting curves of Langmuir (a) and Freundlich (b) models for the 2, 4-DCP adsorption.

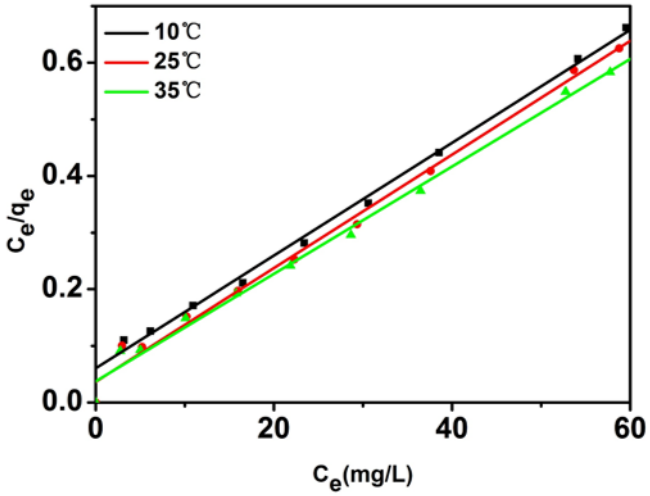

Figure S4 Fitting curves of Langmuir model for the 2, 4-DCP adsorption on CD-MS at different temperatures.

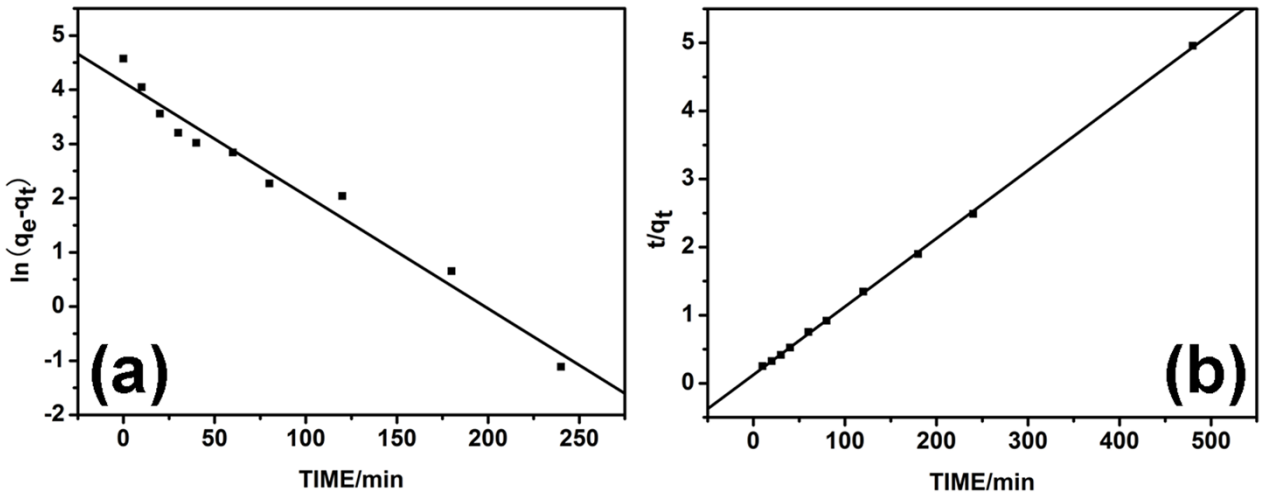

Figure S5 Fitting curves of Level 1(a) and Level 2(b) dynamic models of the 2, 4-DCP adsorption on CD-MS. The initial concentration of 2, 4-DCP is 60 mg/L.

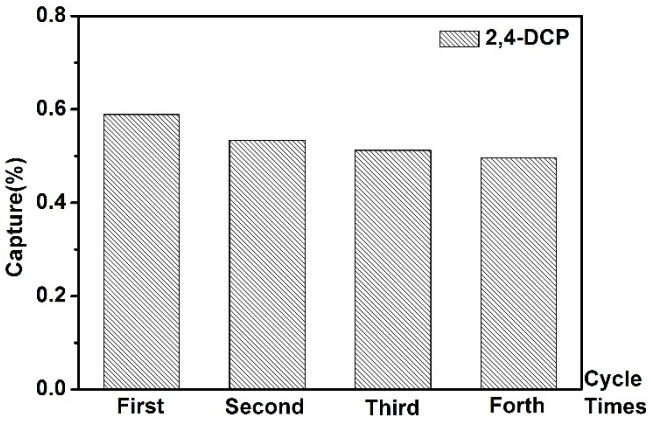

Figure S6 The reusability performance of CD-MS to the adsorption of 2, 4-DCP. Initial concentration of 2, 4-DCP is 20 mg/L; contact time: 4h; temperature:25±1 °C; adsorbent dose: 0.2 g/L.

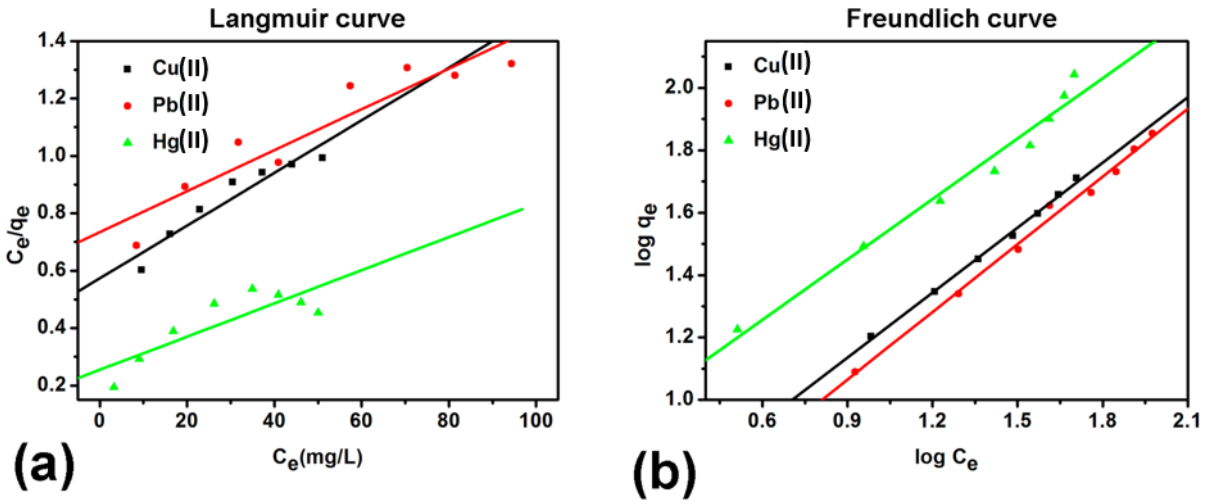

Figure S7 Fitting curves of Langmuir (a) and Freundlich (b) models for metal ion adsorption on CD-MS.

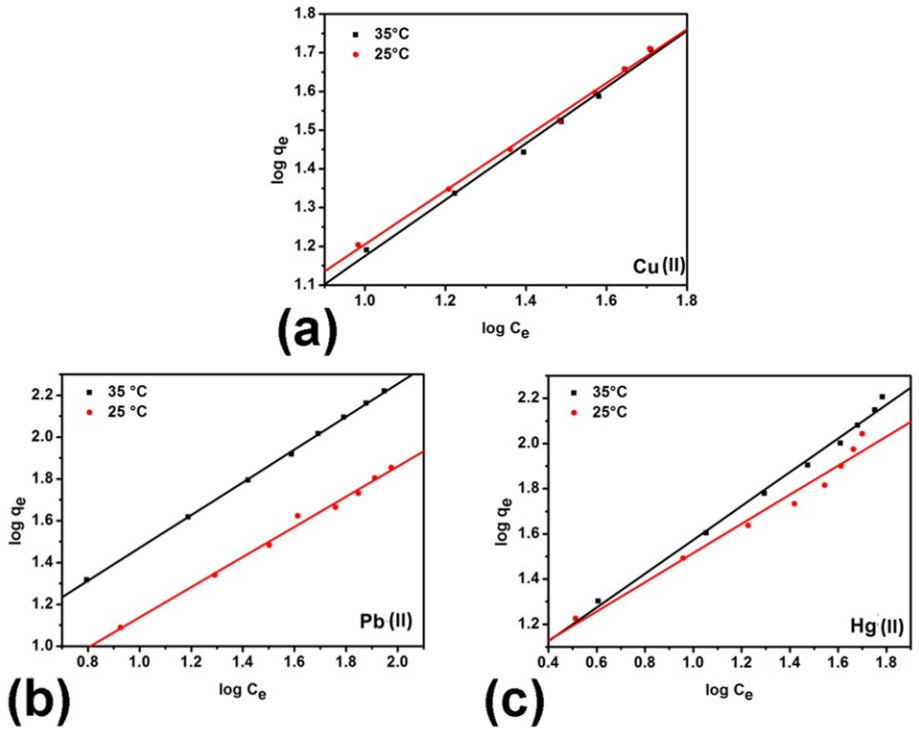

Figure S8 Fitting curves of Freundlich model for the adsorption of Cu (II) (a), Pb (II) (b) and Hg (II) (c) at different temperatures.

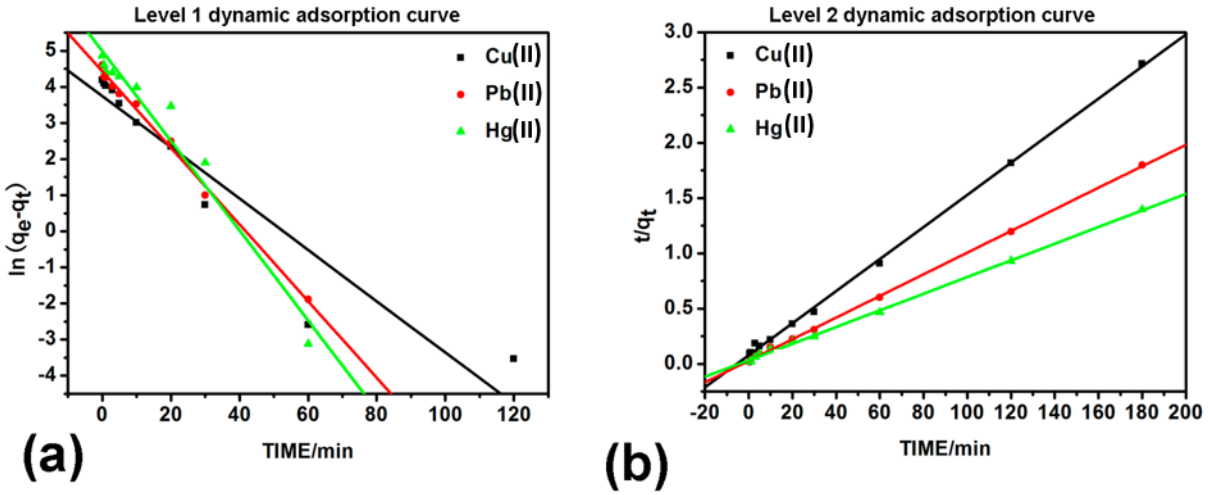

Figure S9 Fitting curves of Level 1 (a) and Level 2(b) dynamic models for metal ions adsorption on CD-MS.

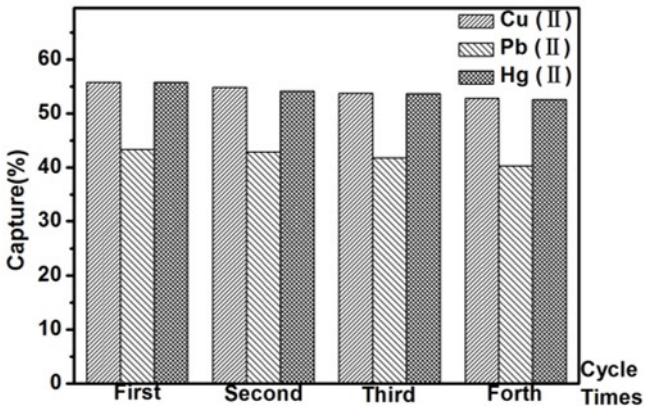

Figure S10 The reusability performance of CD-MS to the adsorption of metal ions. Initial concentration of Cu (II), Pb II) and Hg II) is 10^{-3} M; contact time:3 h; temperature:25±1 °C; Adsorbent dose: 1 g/L.

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