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Supporting Information

Design of Preorganized Adsorbent for the Removal of Chromate from Wastewater under Neutral Conditions

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Chemicals

Tetramethyldiaminomethane were purchased from Energy Chemical. Other necessary chemicals, obtained from Sinopharm Chemical Reagent Beijing Co., Ltd, China, are of analytical reagent grade. The water used in all experiments was ultra-pure water with specific resistance more than 18.0 M Ω cm (Millipore Milli-Q). The required concentration of Cr(VI) was prepared by diluting the stock solution of K₂Cr₂O₇ (2000 mg·L⁻¹)

Characterization

FTIR were recorded on KBr pellets though Bruker Vertex 700. ¹H-NMR spectra were recorded on a Bruker ARX-400 MHz spectrometer and referenced to solvent signals. BET was surveyed by N_2 isotherms adsorption on KUBO X1000. Transmission electron microscopy (TEM) images were obtained from JEM-1400. Scanning electron microscope (SEM) images were obtained from Fei Quanta Feg250. XRD patterns of the prepared samples were acquired with a D8 Focus using CuK radiation (40 kV, 300 mA) of wavelength 0.154 nm to confirm the structure of the materials. The species and valence of elements on the surface of the adsorbent were tested by X-ray photoelectron spectroscopy (XPS)from Thermo Scientific (VG Multilab 2000). The concentrations of Cr(VI) were examined with flame atomic absorption spectrometer (FAAS) by Perkin-Elmer.

Calculation

All calculations were performed with density functional theory (DFT) method as implemented in Gaussian09 package. A set of possible functional groups (N+-C-N+, Cr(VI) adsorption) has been optimized using the B3LYP/6-31 G (d,p) functional to identify the most probable adsorption mechanism.

Synthesis of graphene oxides (GO)

GO was synthesized using modified Hummers method through graphite powder, $H_2SO_4,\,NaNO_3$ and $KMnO_4.$

Synthesis of preorganized structure (PS)

Similar synthesis routes were discussed in previous paper.^{2,3} Under reflux in 25 mL N, N-dimethylformamide, tetramethyldiaminomethane and 1-bromododecane were constantly stirred for 24 h at 70 $^{\circ}$ C. The mixture was purified in turn by NaCl solution and hexane. Then the mixture was reacted with 3 mol/L NaOH and 3 mol/L HNO₃ in proper sequence. AgNO₃ acidified with HNO₃ detects the absence of bromide ion. Finally preorganized structure was obtained.

Preparation of adsorbent (PS-GO)

The required amount of GO (wt. %) and PS (Table S1) was taken in a beaker flask in acetone medium and stirred overnight at room temperature. The resulting mixture was washed thoroughly with acetone and water, filtered and dried under vacuum and used for further adsorption studies.

Sample Name	PS (g)	GO (g)	Acetone (mL)
GO	0	0.05	25
5% PS-GO	1	0.05	25
10% PS-GO	1	0.1	25
15% PS-GO	1	0.15	25
20% PS-GO	1	0.2	25
25% PS-GO	1	0.25	25

Table S1. Synthesis condition of PS-GO

The structure and characterization of PS



Fig. S1. The structure of PS (a), FTIR spectra of PS (b), 1H-NMR spectrum (400MHz) of PS in CDCl3 (c)

The characterization of PS-GO



Fig. S2. SEM image of GO (a), SEM image of PS-GO (b), XRD for GO and PS-GO (c)

Batch adsorption experiments

The experiments on the removal of Cr(VI) by PS-GO were investigated at different pH, adsorption time, initial Cr(VI) concentration, adsorbent mass, co-existing ions and temperature. The pH of the solution was adjusted by HNO₃ and NaOH. After attaining equilibrium, the solutions was filtered using 0.22 μ m syringe filter, then the concentration of Cr(VI) was tested by FAAS. The Cr(VI) removal efficiency (E, %) and adsorption capacity (q_e, mg/g) were determined by the following equation:

$$E(\%) = \frac{C_{o} - C_{e}}{C_{o}} \times 100$$
(S1)
$$q_{e} = \frac{C_{o} - C_{e}}{m} V$$
(S2)

where C_o and C_e (mg/L) are the initial and equilibrium concentration of Cr(VI), respectively, while V (mL) is the volume of the Cr(VI) solution and m (g) is the mass of the PS-GO.



Fig. S3. Optimization of PS loading in GO (0.025 g PS-GO, Cr(VI) concentration=300 mg/L, pH=7, temperature=25 °C and time for adsorption1 hour),

Adsorption kinetics

The kinetic experiment was studied for 100 mg/L, 200 mg/L Cr(VI) solution at pH=6.5, T=25 °C and m=0.025 g. Pseudo-first order, pseudo-second order and the intra-particle diffusion models were applied to fit the data.

$$log(q_e - q_t) = log q_e - \frac{k_1 t}{2.303}$$
(S3)
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(S4)
$$q_t = k_{id} t^{1/2} + C_i$$
(S5)

where $k_1(1/min)$ is the pseudo-first-order rate constants, $q_t (mg/g)$ is the amount of Cr(VI) uptake at any interval of time t, $k_2 (g/mg/min)$ is the pseudo-first-order rate constant. k_{id} is the intraparticle diffusion rate constant of stage i (mg/g/min^{1/2}) and Ci is the intercept of stage i.



Fig. S4 The effect of time on the removal of Cr(VI) by PS-GO (a), The pseudo-first order of Cr(VI) removal on PS-GO(b), The pseudo-second order of Cr(VI) removal on PS-GO (c)

pseudo-first-order				pseudo-	pseudo-second-order			
Co	k ₁	q _e	R ²	k ₁	q _e	R^2		
(ppm)	(1/min)	(mg/g)		(g/(mg·min))	(mg/g)			
200	2.3×10 ⁻²	13.26	0.9202	7.16×10 ⁻³	39.93	0.9996		
100	2.41×10 ⁻²	5.23	0.9791	1.97×10 ⁻²	19.81	0.9992		

Table S2. The kinetic parameters for Cr(VI) adsorption by PS-GO.

Table S3. Intraparticle diffusion constants for the adsorption of Cr(VI) onto PS-GO at different initial concentrations.

Co(mg/L)	K _{1d}	C ₁	$(R_1)^2$	K _{2d}	C ₂	$(R_2)^2$	K _{3d}	C ₃	(R ₃) ²
100	3.92	16.57	0.998	1.54	26.15	0.965	0.38	34.89	0.962
200	1.81	10.66	0.982	0.60	14.29	0.993	0.28	16.67	0.999

Adsorption isotherms

The adsorption isotherms of Cr(VI) were implemented by varying initial concentration of Cr(VI) from 280 to 480 mg/L at 298K, 308 K and 318 K. The experimental data was applied to Langmuir and Freundlich isotherm model

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$
(S6)
$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$
(S7)
$$R_L = \frac{1}{1 + bC_o}$$
(S8)

where q_m (mg/g) is the maximum adsorption capacity, b (L/mg) is the equilibrium constant, K_F and n are the Freundlich constant.



Fig. S5 Langmuir model for Cr(VI) removal on PS-GO (c)

Table S4. Langmuir and Freundlich adsorption isotherm parameters for Cr(VI) removal on PS-GO composite.

Temperature	Langmuir				Freundlich			
(K)	q _m (mg/g)	b (L/mg)	R ²	R_L	1/n	k _f (L/g)	R ²	
298K	78.86	0.078	0.9945	0.026	0.180	30.37	0.973	
308K	79.05	0.093	0.9954	0.022	0.160	34.17	0.974	
318K	78.43	0.124	0.9941	0.016	0.137	38.63	0.971	

The effect of coexisting anions



Fig. S6 The effect of coexisting anions on the adsorption of Cr(VI)

As we know, the adsorption of Cr(VI) may be affected by other anions in wastewater. Therefore, experiments were performed to study the effect of commonly present anions such as Cl⁻, NO₃⁻, SO₄²⁻, CO₃²⁻ and PO₄³⁻ (The concentration of coexisting anions is 0.5, 1.0, 1.5, 2.0, 2.5 times than Cr(VI)). As shown in Fig. S5, other anions have the influence of different levels, which is reflected by the following sequence of the Cr(VI) adsorption capacity: Cl⁻ > NO₃⁻ > SO₄²⁻ > CO₃²⁻ > PO₄³⁻.

Type of adsorbent	рН	t (min)	q _m (mg/g)	Ref.
PS-GO	2-9	20 min	79	This work
HDTMA	7	60 min	3.5	4
CS-CTA-MCM	7		34	5
AMRs	7	1200	37.0	6
GMA/MBA	7		46	7
ILFC	7	240	55	8

Table S5. Adsorption of Cr(VI) by traditional adsorbent

Desorption experiment

Recycling properties of the adsorbent is an important factor considering practical efficiency application. Fig. S7 showed the removal varied in ten adsorption-regeneration cycles. It was found that, after ten recycling, the removal efficiency of Cr(VI) ions were about 89 ± 1.20 %. It is obvious that the adsorption capacity of the absorbent was almost constant during ten cycles. The adsorbed Cr(VI) was released from PS-GO by 0.5M NaOH, meanwhile, the active sites were occupied by OH⁻. Then, the adsorption sites were regenerated by doping the NO₃⁻ through HNO₃. The regenerability and reusability imply that the materials can maintain stabilization successfully for ten cycles at least without loss of its original adsorption efficiency.



Fig. S7 Adsorption-desorption cycles.

Column adsorption experiments:

Column studies were accomplished in a glass column with 1 cm internal diameter and 25 cm height. The breakthrough curve was used to evaluate the capability of the column which told the concept of the breakthrough point where the effluent concentration exceeds the maximum allowable discharge concentration of a specific water contaminant. The breakthrough time (t_b) shows the time at which the outlet metal concentration reached the maximum allowable value (5% of inlet concentration). This curve can be obtained by plotting the dimensionless concentration C_t/C_o (where C_t is the effluent adsorbate concentration) versus time or volume of the effluent. The total adsorbed Cr(VI) ions, q_{total} (mg), in the column for a specific flow rate and initial concentration can be calculated from following equation:

$$q_{total} = \frac{Q}{1000} \int_{0}^{t_{total}} C_{ad} = \frac{Q}{1000} \int_{0}^{t_{total}} (C_{o} - C_{t}) dt$$
(S9)

where the Q, C_{ad} , t_{total} are the volumetric flow rate (mL/min), adsorbed metal concentration (mg/L) and total time of flow (min), respectively,

Among these, the Thomas model is widely used. The linearized form of Thomas model can be expressed as follows:

$$\ln(\frac{C_o}{C_t}) = \frac{k_{Th}q_om}{Q} - k_{Th}C_ot$$
(S10)

where k_{Th} is the Thomas model constant (mL/(mg·min)), q_o is the adsorption capacity (mg/g),

Effect of influent concentration: The column adsorption experiments were carried out with the initial concentration of Cr(VI) from 50 to 200 mg/L, while the mass and were kept constant at 1.0 g and 3 mL/ min, respectively.

Effect of bed mass: when the flow rate of Cr(VI) is 3 mL/ min and the initial concentration of Cr(VI) is 100 mg/L, the column adsorption experiments were carried out with the mass of adsorbent from 0.6 g to 1.3 g.

Effect of flow rate: when the flow rate of Cr(VI) is 3 mL/ min and the initial concentration of Cr(VI) is 100 mg/L, the column adsorption experiments were carried out with the flow rate from 1 to 6 mL/min.

Co	Flow rate	m(g)	t _b (min)	Q _e	$k_{Th} \times 10^{-3}$	R ²
(mg/L) 100	(mc/mm) 1	1.0	186.8	(mg/g) 82.34	(min) 1.16	0.912
100	3	1.0	52.5	71.93	2.26	0.931
100	6	1.0	22.4	65.38	9.43	0.925
50	3	1.0	137.6	54.97	1.6	0.938
200	3	1.0	32.9	85.91	5.17	0.954
100	3	0.6	37.7	46.53	4.39	0.945
100	3	1.3	221.3	85.98	1.53	0.963

Table S6 Experimental data for column parameters calculated at various conditions.

- 1. W.S.H. Jr, R. E. Offeman, Preparation of graphitic oxide. J. Am. Chem. Soc. 1958, 80, 1339.
- 2. Renu Sharma, Ajar Kamal, Maryam Abdinejad. Advances in the synthesis, molecular architectures and potential applications of gemini surfactants. Adv. Colloid. Interfac. 2017, 248, 35-68.
- 3. K. Parikh, B. Mistry, S. Jana, S. Gupta, R. V. Devkar, Physico-biochemical studies on cationic gemini surfactants: role of spacer. J. Mol. Liq. 2015, 206, 19-28.
- 4. Jinhua W., Xiang Z., Bing Z., Rapid adsorption of Cr (VI) on modified halloysite nanotubes. Desalination. 2010, 259, 22-28.
- Kun L., Pei L., Jun C., Shoujun X., Efficient adsorption of both methyl orange and chromium from their aqueous mixtures using a quaternary ammonium salt modified chitosan magnetic composite adsorbent. Chemosphere, 2016, 154, 310-318.
- Jyh Herng Chen, Kai-Chung Hsu, Yu-Min Chang. Surface Modification of Hydrophobic Resin with Tricaprylmethylammonium; Chloride for the Removal of Trace Hexavalent Chromium. Industrial & Engineering Chemistry Research, 2013, 52, 11685-11694.
- 7. Atia A. A. Synthesis of a quaternary amine anion exchange resin and study its adsorption behaviour for chromate oxyanions. Journal of Hazardous Materials, 2006, 137, 1049-1055.
- Zhi-yun Kong, Jun-fu Wei, Yong-hua Li, Rapid removal of Cr(VI) ions using quaternary ammonium fibers functioned by 2-(dimethylamino)ethyl methacrylate and modified with 1-bromoalkanes. Chemical Engineering Journal, 2014, 254, 365-373.
- 9. Dong Z., Zhao L., Covalently bonded ionic liquid onto cellulose for fast adsorption and efficient separation of Cr(VI): batch, column and mechanism investigation. Carbohydrate Polymers, 2018, 189, 90-197.