Supplementary information

Graphene-decorated porous ceramics for efficient removal of Cr(VI)

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Supplementary data 1

Materials

Granule porous ceramic (AA) (diameter between 2 mm and 8 mm, average pore size is 3.822 nm) was obtained from chemical filler company of Pingxiang, Jiangxi, China. Citric acid monohydrate was purchased from Sinopharm Chemical Reagent Company, China. Potassium dichromate ($K_2Cr_2O_7 \ge 99.8\%$) was brought from Xilong Chemical Co.Ltd., China. All reagents are of analytical grade and used received. Distilled water was used throughout the experiments, unless otherwise mentioned.

The optimal sintering time for preparation of GDPC





Fig. S1: (A) Photographs of different time heat-treated ceramics which have been soaked in CA solution at different time and (B) The adsorption capacity of the different time heat-treated samples to Cr(VI) (the adsorption was kept for 10 h at

room temperature and the concentration of Cr(VI) was 62.5 ppm).

Fig. S1A shows the heat-treated samples at different time ranging from 6 to 40 min at 500 °C. The sample was gradually carbonized over time and 15 min was found to be the optimal heat treatment time (as shown in Fig. S1B). However, if the annealing time exceeded 25 min, the coated carbon on the surface of the sample was disappeared. When the heat-up time was 40 min, the carbon on the inner surface of the sample was also vanished. Fig. S1B shows the adsorption capacity of different heat-treated samples. It could be noticed that the adsorption peak was red-shifted from 350 nm to 372 nm when the heating time is over 25 min. The phenomenon might be explained by the reason that the carbon on the surface was burned away after heating for a long time. Without the decoration of graphene, Cr_2O_7 was transformed to $CrO_4^{2^2}$. As the heating time was extended to 40 min, the adsorption peak at 372 nm was higher than original Cr(VI)-contained solution, probably because some other chemical reaction might also happen with the help of AA. Based on these analysis, 15 min was selected as the optimum heating time at 500 °C.

Preparing of different concentration target pollutant

0.707 g potassium dichromate was dissolved in 500 ml distilled water to obtain 500 ppm (mg L⁻¹) of chromium stock solution. Other desired Cr(VI) ion solution was prepared by changing the weight of potassium dichromate or diluting the stock Cr(VI) ions solution.

Supplementary data 2

Constant weight method to calculate graphene loading in AA

Blank porous ceramics (AA) were washed and dried in vacuum oven and then, the dried AA were weighted on electronic scales. The weighted AA were handed in crucible and put into muffle furnace. The furnace was programmed from room temperature to 500 °C in 50 min, and held for 15 min at 500 °C. The heated sample was taken out from the furnace and put into desiccator quickly. Subsequently, the sample was cooled to room temperature and weighted again. Finally, repeating the progress till the sample weight did not change. The a_1 , a_2 , a_3 prepared before were soaked into equal proportion of CA solution, and then GDPC(a_1), GDPC(a_2), GDPC(a_3) were got as explained it before.

The weight		The weight		The weight	
change of	m _{GDPC(a1)}	change of	m _{GDPC(a2)}	change of	m _{GDPC(a3)}
AA (m _{AA})		AA (m_{AA})		AA (m_{AA})	
3.0542 g		3.0269 g		3.0262 g	
2.9293 g		2.8918 g		2.8871 g	
2.9094 g		2.8749 g		2.8797 g	
2.9008 g		2.8679 g		2.8774 g	2.8754 g
2.8836 g	2.9157 g	2.8643 g	2.8795 g	2.8698 g	
2.8847 g		2.8667 g		2.8692 g	
2.8797 g		2.8633 g		2.8675 g	
2.8802 g		2.8632 g		2.8663 g	

Table S1. The constant weight method to calculate graphene loading in AA

Where Wgraphene= $100\%*(m_{GDPCai}-m_{AA})/m_{GDPCai}$ (i=1,2,3), the value of AA weight was kept two decimal places. According to this method, the weight percentages of graphene in GDPC(a₁), GDPC(a₂) and GDPC(a₃) were 1.37%, 0.69%, and 0.35%, respectively.



Fig. S3: Adsorption capacity of Cr(VI) on $GDPC(a_1)$, $GDPC(a_2)$ at different dose compared with a_0 in (A) and (B) (The lower the absorbance is, the higher the adsorption capacity is).

Fig. S3A and B shows a direct correlation between $GDPC(a_1)$ and $GDPC(a_2)$'s dose and removal efficiency of Cr(VI) compared with a_0 . Both 0.25 g $GDPC(a_1)$ and 0.25 g $GDPC(a_2)$ could almost totally remove 10 ml 62.5 ppm Cr(VI) effectively. However, a_0 could not adsorb Cr(VI) and the maximum absorption wavelength got red-shifted at the same. It seems that such a phenomenon has noting to do with the dose of a_0 . This stranger behavior was not observed when the porous ceramics was decorated by graphene. The reason has been given in supplementary data 1. Thus, the superior absorption ability of GDPC is confirmed.

Supplementary data 4



Fig. S4: EDS picture of $GDPC(a_1)$ without adsorption of potassium dichromate, and no chromium elements was found on the map.

Supplementary data 5



Fig. S(5): (A) and (B) UV/vis data showing time dependent removal of Cr(VI) on GDPC(a₂) and GDPC(a₃), respectively.

Supplementary data 6

Table S2. Comparison of adsorption rate constants, correlation coefficients values of GDPC, calculated and experimental adsorption capacity (q_e) of graphene on GDPC (obtained at the same concentrations of Cr(VI)) between the pseudo-first-order kinetic and pseudo-second-order kinetic.

C ₀ (Cr) (ppm)	q _{e,exp} — (mg g ⁻¹)	Pseudo- first -order kinetic			Pseudo-second-order kinetic		
		k ₁ (L h ⁻¹)	q _e (mg g ⁻¹)	R ²	k ₂ [g/(mg h)]*10 ³	q _e (mg g ⁻¹)	R ²
62.5 (GDPC(a ₁))	173.24	0.9313	223.18	0.9748	0.2728	208.35	0.9912
62.5 (GDPC(a ₂))	354.35	0.9107	459.59	0.9747	0.3529	410.48	0.9977
62.5 (GDPC(a ₃))	709.5	0.6022	587.89	0.9864	0.3663	803.03	0.9980