

Supplementary Information
for
Hydrophobic bifunctionalized hexagonal mesoporous silicas as efficient
adsorbents for the removal of Orange IV

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Chemicals and reagents

Tetraethoxysilane (TEOS, $\text{Si}(\text{OEt})_4$, 98.5%), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.5%), ammonium nitrate (NH_4NO_3 , 99.0%), Orange IV ($\text{C}_{18}\text{H}_{14}\text{N}_3\text{O}_3\text{SNa}$, 99%) and mesitylene (C_9H_{12} , 98%) were obtained from Shanghai Chemical Reagent Corporation (Shanghai, China). Hexadecylamine (HDA, $\text{C}_{16}\text{H}_{35}\text{N}$, 90%) was obtained from Alfa Aesar. 3-aminopropyltriethoxysilane (APTES, $\text{C}_9\text{H}_{23}\text{NO}_3\text{Si}$, 99.0%) and phenyl-trimethoxysilane (PTMS, $\text{C}_9\text{H}_{14}\text{O}_3\text{Si}$, 99.0%) were obtained from Aldrich. All chemicals are of analytical reagent grade or better quality.

The details of the synthetic experimental procedures

In a typical synthesis the calculated amounts of ethanol (20.73 g), deionized water (54.00 g), and hexadecylamine (3.26 g) were stirred for 20 min at room temperature. To this gel, mixed solution of TEOS (7.29 g), APTES (2.21 g), and PTMS (0.99 g) was added very slowly under vigorous stirring. The total amounts of TEOS, APTES, and PTMS were 0.05 mol. After 5 min mesitylene (1.63 g) was added as swelling agent. After stirring for 24 h, the mixture was filtered, washed abundantly with deionized water and dried at 378 K in a vacuum oven for 12 h. Subsequently, the template was removed from the as-synthesized material by NH_4NO_3 /ethanol extraction. 1.0 g amount of sample was stirred in a mixture of ethanol (100 mL) and NH_4NO_3 aqueous solution (6 wt %, 5.3 g) for 15 min at 351 K. The residual solid was recovered by filtration and repeatedly washed with an excess of ethanol until the template was removed completely. Thereafter, the material was further dried at 353 K for 12 h. The sample synthesized by this method is designated as Ph-Am-HMS. Similarly, a pure siliceous HMS was synthesized without APTES, PTMS, and mesitylene.

The details of Orange IV adsorption

Stock solution (100 mg/L) of Orange IV was prepared in bi-distilled water and subsequently diluted to required concentrations. Adsorption tests were carried out in a rotary shaker at 200 rpm in 250 mL shaking flasks containing 10 mg adsorbent and 100 mL of dye solutions of definite concentrations. After shaking the flasks for predetermined time intervals, the dye solutions were separated from the sorbents by centrifugation. Dye concentrations in the supernatants were determined using a UV-vis spectrophotometer at 445 nm. The effect of pH

was studied after the adjustment of the dye solutions pH between 2 and 12 using dilute HCl and NaOH solutions. The initial dye concentration was studied in the range of 10 to 100 mg/L, and the dosage of different adsorbents in the comparison tests was studied in the range of 3 to 30 mg.

Adsorbents regeneration procedure:

The desorption of Orange IV from the adsorbent Ph-Am-HMS was conducted using ethanol at 351 K. 1.0 g amount of the above adsorbent was stirred in ethanol (100 mL) for 30 min. The residual solid was recovered by filtration and repeatedly washed for 3 times with an excess of ethanol. Thereafter, the material was further dried at 353 K for 12 h, and then it was used to adsorb Orange IV (100 mg/L) for another time.

The reusability efficiency of the adsorbent Ph-Am-HMS after two cycles could remain above 99%, which indicated that this material owned good reusability. It may be expected to reduce the cost of sorption process in the application.

Kinetic study procedures

The dose of adsorbent, was 10 mg in each flask, and the initial concentrations of the dye solution were 10, 20, and 30 mg/L. Suspensions were stirred for different time intervals (5 min to 4 h) at pH 3 and room temperature. The amount of dyes adsorbed on the adsorbent at time t , q_t (mg/g), was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

where C_0 and C_t (mg/L) are the concentrations of dyes initially and at time t , respectively, m is the weight of adsorbent (g), and V is the volume of the solution (L).

Kinetic modeling not only allows estimation of adsorption rates but also leads to suitable rate expressions characteristic of possible reaction mechanisms. The details of two kinetic models including the pseudo-first-order equation and pseudo-second-order equation are as follows:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

Where q_e and q_t are the adsorption capacity (mg/g) of the adsorbate at equilibrium and at time t (min), respectively. k_1 and k_2 are the rate constants for pseudo-first-order and pseudo-second-order adsorptions, respectively.

Adsorption isotherms

The adsorption isotherms were established by placing 10 mg Ph-Am-HMS in a series of flasks containing 100 mL of dye solution at pH 3 and at the desired initial concentrations from 10 to 100 mg/L. The flasks were conditioned for 4 h at 200 rpm while keeping the temperature constant at 293, 303, or 313 K.

In this work, the adsorption isotherms were studied using three isotherm models. The Henry, Langmuir and Freundlich equations expressed in Equation (4)-(6) were used for modeling these adsorption isotherm data.

$$q_t = k_H c \quad (4)$$

$$q_e = \frac{K_L q_{\max} c_e}{1 + K_L c_e} \quad \frac{1}{q_e} = \frac{1}{q_{\max} K_L c_e} + \frac{1}{q_{\max}} \quad (5)$$

$$q_e = K_F c_e^{1/n} \quad \ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (6)$$

Thermodynamic parameters

The effect of temperature was investigated in 30 mg/L of dye solution with 10 mg Ph-Am-HMS at three constant temperatures (293, 303, 313 K) during equilibrium time. In this study, the free energy change of the sorption reaction is given by Eq. (7).

$$\Delta G^\circ = -RT \ln K_d \quad (7)$$

Where K_d is Langmuir constant (L mg⁻¹), R is the universal gas constant (8.314 J/(mol K)), and T shows the absolute temperature (K). ΔH° and ΔS° were calculated from the Van't Hoff equation (8):

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

When $\ln K_d$ is plotted against $1/T$, a straight line with the slope ($-\Delta H^\circ/R$) and intercept ($\Delta S^\circ/R$) are obtained. The calculated thermodynamic parameters are listed in Table S4.

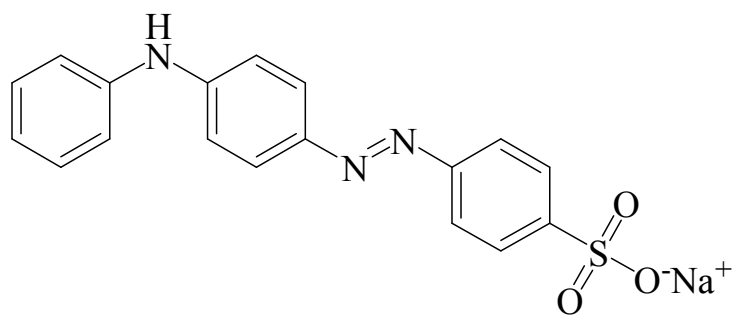


Fig. S1 Chemical structure of dye Orange IV used for adsorption.

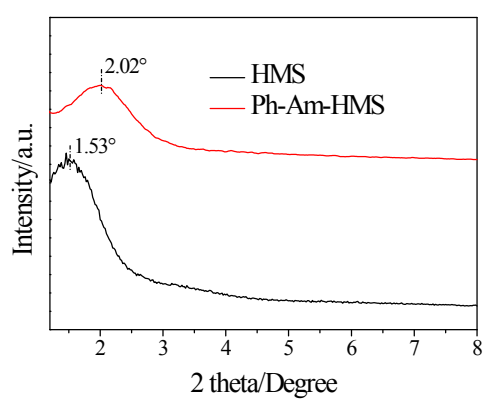


Fig. S2 XRD patterns of HMS and Ph-Am-HMS.

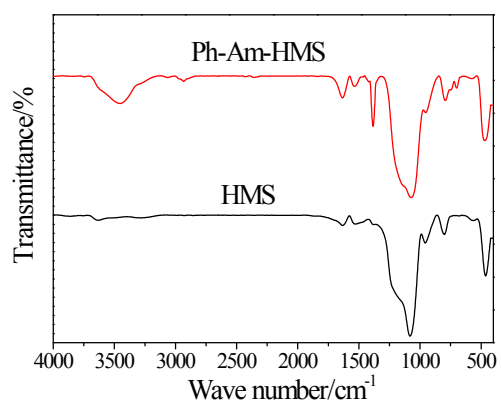


Fig. S3 FT-IR spectra of HMS and Ph-Am-HMS.

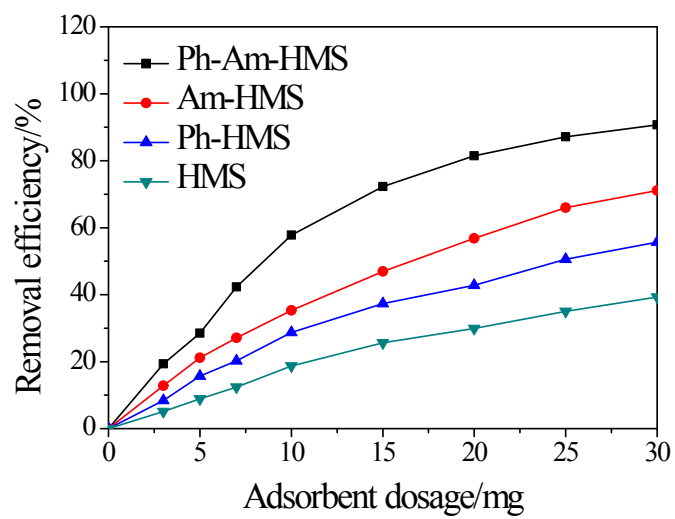


Fig. S4 Removal efficiencies of Orange IV using different adsorbents.

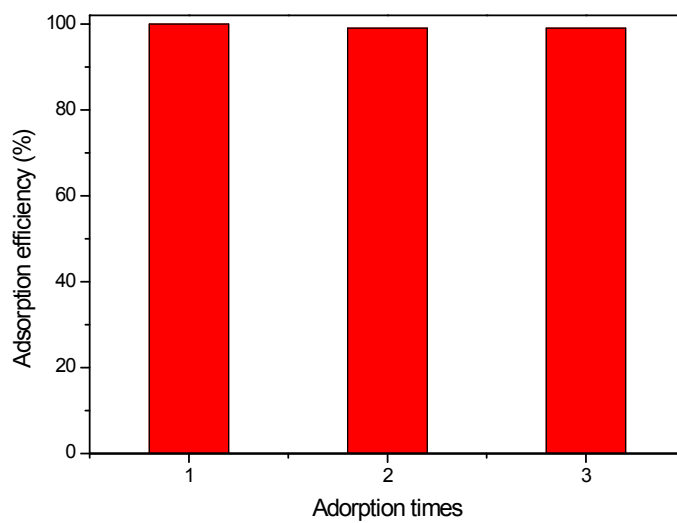


Fig. S5 Reusability test. (Experimental conditions: dye concentration = 100 mg/L, temperature = 303K, adsorbent dosage = 10 mg, aqueous volume = 100 mL, Contacting time is 4 h.)

Table S1 Textural Parameters of Ph-Am-HMS.

sample	Pore size (nm) ^a	Surface	Pore	Water Contact
		Area (m ² /g) ^b	Volume (mL/g) ^a	Angle (°)
HMS	5.2	670	0.900	15.5
Ph-Am-HMS	3.6	371	0.293	105.0

^a Calculated from the desorption branch of the N₂ adsorption-desorption isotherms using the BJH model. ^b The BET method was used to calculate the surface area.

Table S2 Constants and correlation coefficients for the kinetic models.

Model	Parameter	10 mg/L	20 mg/L	30 mg/L
Pseudo-first order model	q_e (mg/g)	38.37	43.89	32.61
	k_1 (min ⁻¹)	0.02087	0.02427	0.01897
	R^2	0.9922	0.9493	0.7857
Pseudo-second order model	q_e (mg/g)	92.00	135.7	173.6
	k_2 (mg/(g·min))	1.302×10^{-3}	1.443×10^{-3}	2.347×10^{-3}
	R^2	0.9985	0.9998	0.9998

Table S3 Constants and correlation coefficients of adsorption isotherms for the adsorption of Orange IV adsorption on Ph-Am-HMS.

Model	Parameter	293K	303K	313K
Henry	K_H	3.177	3.004	2.339
	R^2	0.9539	0.9523	0.9199
Langmuir equation	K_L	0.3540	0.3489	0.3834
	q_{max} (mg/g)	246.3	234.2	216.5
	R^2	0.9208	0.8926	0.9074
Freundlich equation	K_F	76.70	72.54	69.75
	n	3.149	3.142	3.245
	R^2	0.9986	0.9981	0.9983

Table S4 Thermodynamic data for the adsorption of Orange IV.

T (K)	$\ln K_d$	ΔG° (kJ/mol)	ΔS° (J/mol K)	ΔH° (kJ/mol)
293	4.33	-10.55		
303	4.27	-10.76	11.83	-7.06
313	4.24	-11.03		