Electronic Supplementary Information (ESI)

Facile synthesis of $MoO_2/CaSO_4$ composites as highly efficient adsorbents for Congo red and Rhodamine B

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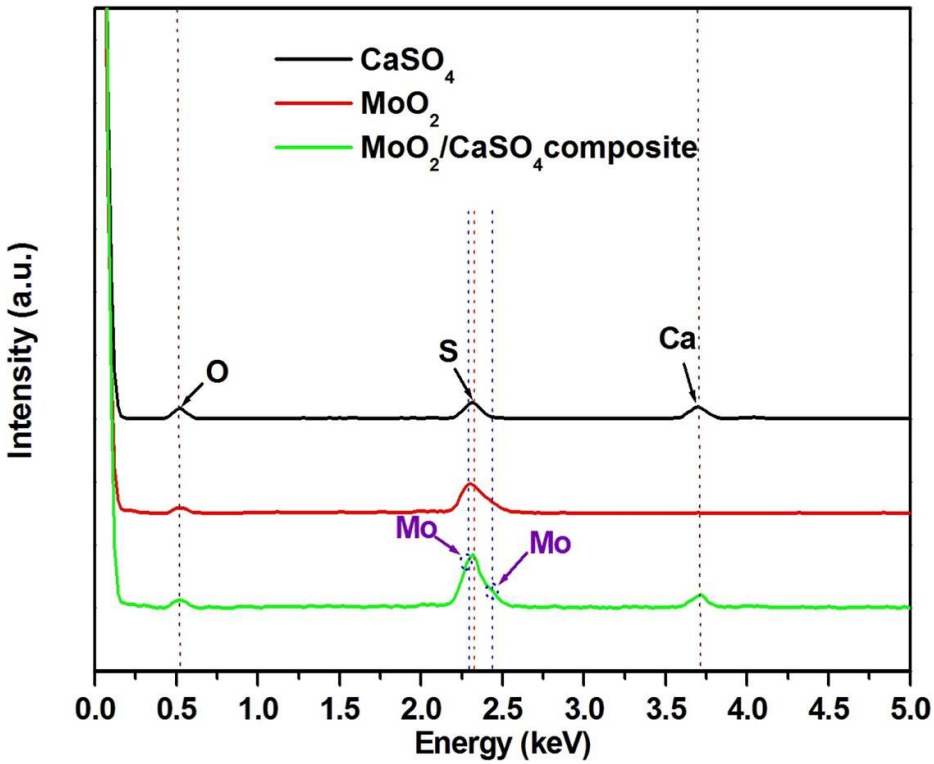

Fig. S1. EDX patterns of $CaSO_4$, MoO_2 and $MoO_2/CaSO_4$ composites.

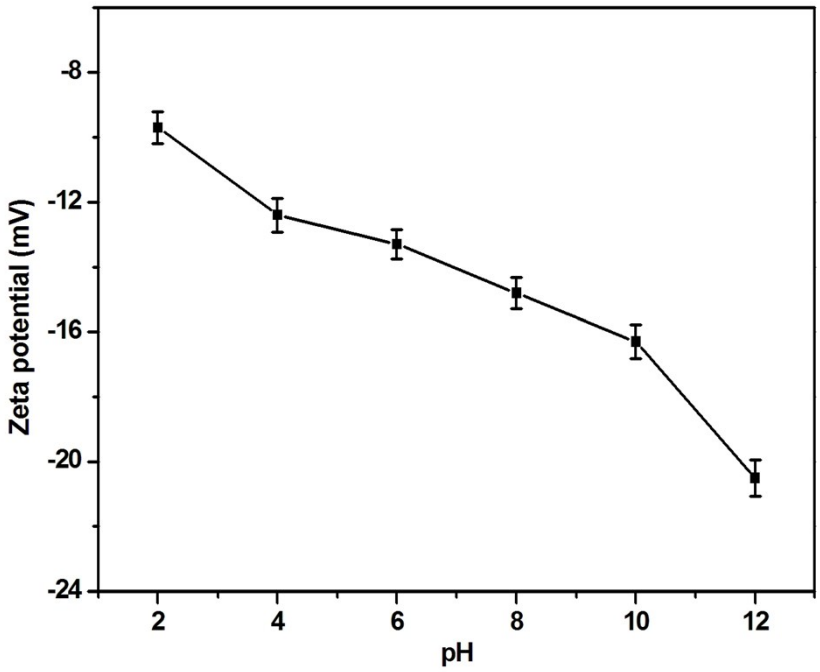

Fig. S2 Zeta potential values of the $MoO_2/CaSO_4$ composite over a pH range between 2.0 and 12.0.

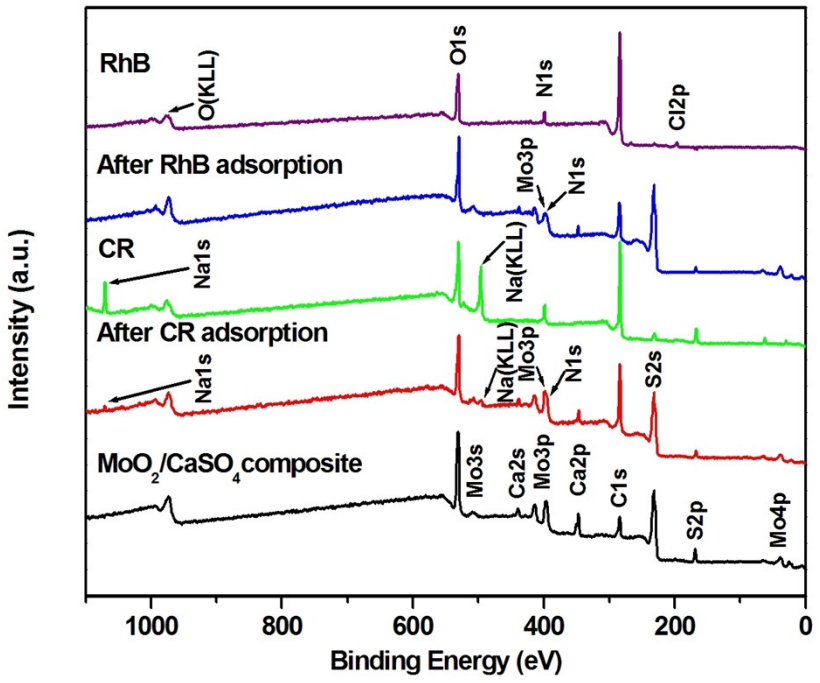

Fig. S3. XPS survey scan spectra of $MoO_2/CaSO_4$ composites, $MoO_2/CaSO_4$ composites after CR adsorption, CR, $MoO_2/CaSO_4$ composites after RhB adsorption and RhB.

Eq. S1. Equation for the removal efficiency (R_e) of a dye onto an adsorbent.

$$R_e = \frac{C_0 - C_t}{C_0} \times 100\%$$

C_0 (mg·L^{-1}) is the initial concentration of a dye solution; C_t (mg·L^{-1}) is the dye concentration at time t.

Eq. S2. Equation for the adsorption capacity (q_e, mg·g^{-1}) of a dye onto an adsorbent at equilibrium.

$$q_e = \frac{C_0 - C_e}{m} V$$

C_e (mg·L^{-1}) is the equilibrium concentration of a dye solution; m (g) is the mass of an adsorbent; and V (L) is the volume of a dye solution.

Eq. S3. Equation for the adsorption quantity (q_t, mg·g^{-1}) of a dye onto an adsorbent at time t.

$$q_t = \frac{C_0 - C_t}{m} V$$

Eq. S4. Equation for the Langmuir model.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max} k_L}$$

In this model, q_{max} (mg·g^{-1}) and k_L (L·mg^{-1}) are Langmuir isotherm constants separately representing the maximum adsorbed quantity and a function associated with the adsorption free energy.

Eq. S5. Equation for the separation factor R_L.

$$R_L = \frac{1}{1 + k_L C_0}$$

Eq. S6. Equation for the Freundlich model.

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e$$

In this model, k_F ((mg·g^{-1})(L·mg^{-1})$^{1/n}$) and n are Freundlich isotherm coefficients, which are separately related to the adsorption capability and the adsorption intensity.

Eq. S7. Equation for the D–R model.

$$\ln q_e = \ln q_m - k_D \varepsilon^2$$

In this model, q_m (mg·g^{-1}) and k_D (mol^2·kJ^{-2}) are the D–R isotherm constants related to the maximum adsorption quantity and the mean adsorption free energy, respectively.

Eq. S8. Equation for the Polanyi potential ε.

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$$

In this model, R (8.314 J·mol^{-1}·K^{-1}) is the molar gas constant, and T is the absolute temperature expressed in K.

Eq. S9. Equation for the mean adsorption free energy.

$$E = \frac{1}{\sqrt{2k_D}}$$

Eq. S10. Equation for the Temkin model.

$$q_e = \frac{RT}{b} \ln k_T + \frac{RT}{b} \ln C_e$$

In this model, b (equal to -ΔH, kJ·mol^{-1}) denotes the adsorption heat, and k_T (L·mg^{-1}) is the Temkin isotherm constant.

Eq. S11. Equation for the Gibb's free energy ΔG^0.

$$\Delta G^0 = -RT \ln Kq$$

In this equation, R (8.314 J·mol^{-1}·K$^{-1)}$ is the molar gas constant, T is the absolute temperature expressed in K, and K_q (L·g^{-1}) is the distribution coefficient of an

adsorbent that equals to $q_e \cdot C_e^{-1}$.

Eq. S12. Equation for the lnKq.

$$\ln Kq = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

Eq. S13. Equation for the pseudo-first-order kinetic model.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

In this model, k_1 (min^{-1}) represents the kinetic rate constant of the pseudo-first-order adsorption.

Eq. S14. Equation for the pseudo-second-order kinetic model.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

In this model, k_2 ($g \cdot mg^{-1} \cdot min^{-1}$) denotes the rate constant of the pseudo-second-order adsorption.

Eq. S15. Equation for the Elovich kinetic model.

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$$

In this model, α ($mg \cdot g^{-1} \cdot min^{-1}$) refers to the initial adsorption rate, and β ($g \cdot mg^{-1}$) represents the Elovich desorption constant.

Eq. S16. Equation for the intra-particle diffusion model.

$$q_t = k_{id} t^{0.5} + C_i$$

In this model, k_{id} ($mg \cdot g^{-1} \cdot min^{-1/2}$) denotes the kinetic rate constant of the intra-particle diffusion at stage i, and C_i is a constant whose value directly affects the boundary layer thickness of molecular diffusion.

Table S1. Chemical composition of FDG gypsum confirmed by XRF analysis.

Material	Content/ wt.%										
	Ca	S	Si	Mg	Al	F	Fe	K	Na	Cl	P
FGD gypsum	59.78	26.17	4.18	4.03	1.81	1.34	1.29	0.57	0.35	0.34	0.14

Table S2. Chemical composition of FDG gypsum confirmed by EDX analysis.

Material	Content/ wt.%						
	O	Ca	S	Mg	Si	Al	Fe
FGD gypsum	55.77	24.43	13.24	3.12	1.68	0.91	0.85

Table S3. Chemical composition of the purified FDG gypsum confirmed by EDX analysis.

Material	Content/ wt.%		
	O	Ca	S
The purified FGD gypsum	58.15	22.27	19.58

Table S4. Isotherm parameters of four different models for the adsorption of CR and RhB onto $MoO_2/CaSO_4$ composites.

Isotherm models/parameters	CR	RhB
Langmuir		
q_{max} ($mg \cdot g^{-1}$)	853.54	86.38
k_L ($L \cdot mg^{-1}$)	0.0151	0.1913
R^2	0.9979	0.9912
R_L	0.027-0.143	0.022-0.054
Freundilich		
k_F ($(mg \cdot g^{-1})(L \cdot mg^{-1})^{1/n}$)	100.33	49.55
n	3.0252	9.1466
R^2	0.8587	0.8498
D-L		
q_m ($mg \cdot g^{-1}$)	703.42	70.25
k_D ($mol^2 \cdot kJ^{-2}$)	1.22×10^{-4}	2.13×10^{-7}
E ($kJ \cdot mol^{-1}$)	0.0433	1.2654
R^2	0.8944	0.7564
Temkin		
k_T ($L \cdot mg^{-1}$)	0.21	646.77
b ($kJ \cdot mol^{-1}$)	0.0144	0.3423
R^2	0.9653	0.8501

Table S5. An adsorptive capacity comparison of the $MoO_2/CaSO_4$ composite with other adsorbents.

Adsorbents	q_{max} (mg·g^{-1})	References
Activated carbon	6.7 (CR) 39.22 (RhB)	[40, 41]
Jute stick powder	35.7 (CR) 87.7 (RhB)	[42]
Kaolinite	22.99 (CR) 46.08 (RhB)	[43, 44]
α-MoO_3/polyaniline composite	76.22 (CR) 36.36 (RhB)	[23]
$MoO_2/CaSO_4$ composite	853.54 (CR) 86.38 (RhB)	This study

Table S6. Thermodynamic parameters for the adsorption of CR and RhB onto $MoO_2/CaSO_4$ composites.

Samples	ΔH^0, kJ·mol^{-1}	ΔS^0, J·mol^{-1}·K^{-1}	ΔG^0, kJ·mol^{-1}					R^2
			20 °C	25 °C	30 °C	35 °C	40 °C	
CR	-22.31	-13.02	-18.11	-18.44	-18.33	-18.02	-17.22	0.9221
RhB	40.11	193.25	-16.19	-17.63	-18.64	-19.01	-20.22	0.9755

Table S7. Kinetic parameters of four different models for the adsorption of CR and RhB onto $MoO_2/CaSO_4$ composites.

Kinetic models/Parameters	CR	RhB
Pseudo-first-order		
q_e (exp) ($mg \cdot g^{-1}$)	750.63	66.64
q_e (cal) ($mg \cdot g^{-1}$)	522.60	23.22
k_1 (min^{-1})$\cdot 10^{-3}$	5.20	6.03
R^2	0.8875	0.9064
Pseudo-second-order		
q_e (cal) ($mg \cdot g^{-1}$)	746.27	66.85
k_2 ($g \cdot mg^{-1} \cdot min^{-1}$)$\cdot 10^{-4}$	0.25	9.40
R^2	0.9508	0.9992
Elovich		
α ($mg \cdot g^{-1} \cdot min^{-1}$)	239.83	46.75
β ($g \cdot mg^{-1}$)$\cdot 10^{-3}$	11.08	116.95
R^2	0.8007	0.9225
Intra-particle diffusion		
k_{1d} ($mg \cdot g^{-1} \cdot min^{-1/2}$)	126.93	12.31
C_1	0	0
$(R_1)^2$	1.0000	1.0000
K_{2d} ($mg \cdot g^{-1} \cdot min^{-1/2}$)	18.64	3.77
C_2	266.77	20.20
$(R_2)^2$	0.8897	0.9124
K_{3d} ($mg \cdot g^{-1} \cdot min^{-1/2}$)	6.61	0.53
C_3	568.79	53.79
$(R_3)^2$	0.9492	0.9784