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.

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

$C_e$ (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.

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

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.
\[
\ln q_e = \ln k_F + \frac{1}{n} \ln C_v
\]

In this model, \( k_F \) ((mg\textcdot g\(^{-1}\))(L\textcdot 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\textcdot g\(^{-1}\)) and \( k_D \) (mol\(^2\cdot kJ\)) 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 \( \varepsilon \).

\[
\varepsilon = RT \ln \left( 1 + \frac{1}{C_v} \right)
\]

In this model, \( R \) (8.314 J\textcdot mol\(^{-1}\)\textcdot 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.

\[
q_e = \frac{RT}{b} \ln k_T + \frac{RT}{b} \ln C_v
\]

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

**Eq. S11.** Equation for the Gibb’s free energy \( \Delta G^0 \).

\[
\Delta G^0 = -RT \ln K_q
\]

In this equation, \( R \) (8.314 J\textcdot mol\(^{-1}\)\textcdot K\(^{-1}\)) is the molar gas constant, \( T \) is the absolute temperature expressed in K, and \( K_q \) (L\textcdot g\(^{-1}\)) is the distribution coefficient of an
adsorbent that equals to $q_e C_e^{-1}$.

**Eq. S12.** Equation for the ln$Kq$.

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

**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·mg$^{-1}$·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, $\alpha$ (mg·g$^{-1}$·min$^{-1}$) refers to the initial adsorption rate, and $\beta$ (g·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·g$^{-1}$·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 FGD gypsum confirmed by XRF analysis.

| Material     | 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 FGD gypsum confirmed by EDX analysis.

| Material     | 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 FGD gypsum confirmed by EDX analysis.

| Material               | 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·g$^{-1}$)    | 853.54 | 86.38  |
| $k_L$ (L·mg$^{-1}$)        | 0.0151 | 0.1913 |
| $R^2$                      | 0.9979 | 0.9912 |
| $R_L$                      | 0.027-0.143 | 0.022-0.054 |
| Freundlich                 |        |        |
| $k_F$ ((mg·g$^{-1}$)(L·mg$^{-1}$)$^{1/n}$) | 100.33 | 49.55  |
| $n$                        | 3.0252 | 9.1466 |
| $R^2$                      | 0.8587 | 0.8498 |
| D-L                        |        |        |
| $q_m$ (mg·g$^{-1}$)        | 703.42 | 70.25  |
| $k_D$ (mol$^2$·kJ$^{-2}$)  | $1.22 \times 10^{-4}$ | $2.13 \times 10^{-7}$ |
| $E$ (kJ·mol$^{-1}$)        | 0.0433 | 1.2654 |
| $R^2$                      | 0.8944 | 0.7564 |
| Temkin                     |        |        |
| $k_T$ (L·mg$^{-1}$)        | 0.21   | 646.77 |
| $b$ (kJ·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                        | $q_{\text{max}}$ (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]   |
| $\alpha$-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 | $\Delta H^0$, kJ∙mol$^{-1}$ | $\Delta S^0$, J∙mol$^{-1}$∙K$^{-1}$ | $\Delta G^0$, kJ∙mol$^{-1}$ | $R^2$ |
|---------|-----------------------------|-----------------------------------|----------------------------|-------|
| 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·g$^{-1}$) | 750.63      | 66.64       |
| $q_e$ (cal) (mg·g$^{-1}$) | 522.60      | 23.22       |
| $k_1$ (min$^{-1}$)·10$^{-3}$ | 5.20        | 6.03        |
| $R^2$                    | 0.8875      | 0.9064      |
| Pseudo-second-order      |             |             |
| $q_e$ (cal) (mg·g$^{-1}$) | 746.27      | 66.85       |
| $k_2$ (g·mg$^{-1}$·min$^{-1}$)·10$^{-4}$ | 0.25 | 9.40 |
| $R^2$                    | 0.9508      | 0.9992      |
| Elovich                  |             |             |
| $\alpha$ (mg·g$^{-1}$·min$^{-1}$) | 239.83    | 46.75       |
| $\beta$ (g·mg$^{-1}$)·10$^{-3}$ | 11.08     | 116.95      |
| $R^2$                    | 0.8007      | 0.9225      |
| Intra-particle diffusion  |             |             |
| $k_{1d}$ (mg·g$^{-1}$·min$^{-1/2}$) | 126.93  | 12.31       |
| $C_1$                    | 0           | 0           |
| $(R_1)^2$                | 1.0000      | 1.0000      |
| $K_{2d}$ (mg·g$^{-1}$·min$^{-1/2}$) | 18.64 | 3.77 |
| $C_2$                    | 266.77      | 20.20       |
| $(R_2)^2$                | 0.8897      | 0.9124      |
| $K_{3d}$ (mg·g$^{-1}$·min$^{-1/2}$) | 6.61 | 0.53 |
| $C_3$                    | 568.79      | 53.79       |
| $(R_3)^2$                | 0.9492      | 0.9784      |