Electronic Supplementary Information (ESI)

Bouquet-like calcium sulfate dihydrate: a highly efficient adsorbent for Congo red dye

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

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

C_0 (mg/L) is the initial concentration of dye solution; C_t (mg/L) is the dye concentration at time t.

Eq. S2. Equation for dsorption capacity (q_e, mg/g) of dye onto adsorbent at equilibrium.

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

C_e (mg/L) is the equilibrium concentration of dye solution; m (g) is the mass of adsorbent; and V (L) is the volume of solution.

Eq. S3. Equation for adsorption quantity (q_t, mg/g) of dye onto adsorbent at time t.

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

Eq. S4. Equation for 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) and k_L (L/mg) are Langmuir isotherm constants representing the maximum adsorbed quantity and a function of the free energy of adsorption respectively.

Eq. S5. Equation for separation factor R_L.

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

Eq. S6. Equation for Freundlich model.

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

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

Eq. S7. Equation for D–R model.

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

In this model, q_m (mg/g) 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 Polanyi potential ε.

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

In this model, R (8.314 J/mol/K) is the molar gas constant and T is the absolute temperature expressed in K.

Eq. S9. Equation for mean adsorption free energy.

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

Eq. S10. Equation for 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) denotes the adsorption heat, and k_T (L/mg) is the Temkin isotherm constant.

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

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

In this equation, R (8.314 J/mol/K) is the molar gas constant, T is the absolute temperature expressed in K, and K_q (L/g) is the distribution coefficient of adsorbent

that equals to q_e/C_e.

Eq. S12. Equation for ln*Kq*.

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

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

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

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

Eq. S14. Equation for 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·min)) denotes the rate constant of the pseudo-second-order adsorption.

Eq. S15. Equation for Elovich kinetic model.

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

In this model, α (mg/(g·min)) refers to the initial adsorption rate, and β (g/mg) represents the Elovich desorption constant.

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

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

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

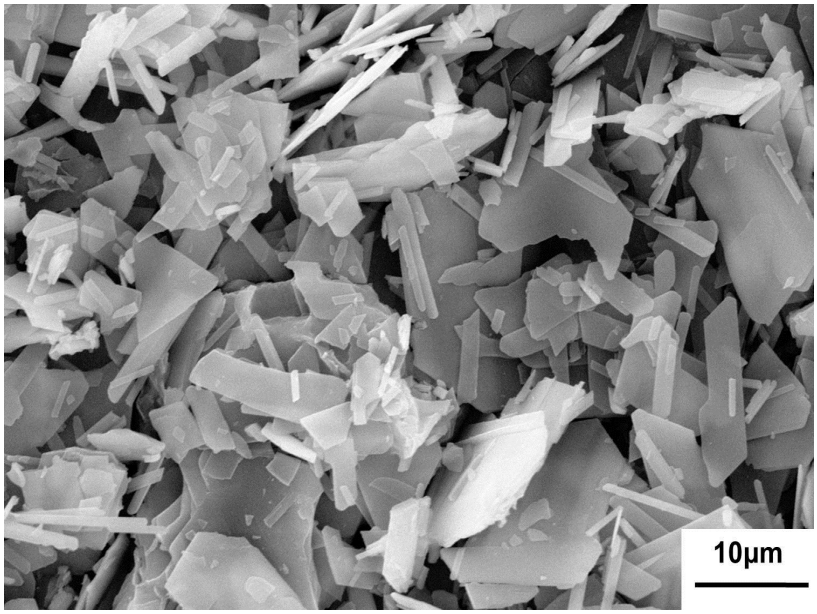


Fig. S1. SEM image of CSD formed from $CaCl_2$ and $KAl(SO_4)_2 \cdot 12H_2O$ in 0.05% CMC solution.

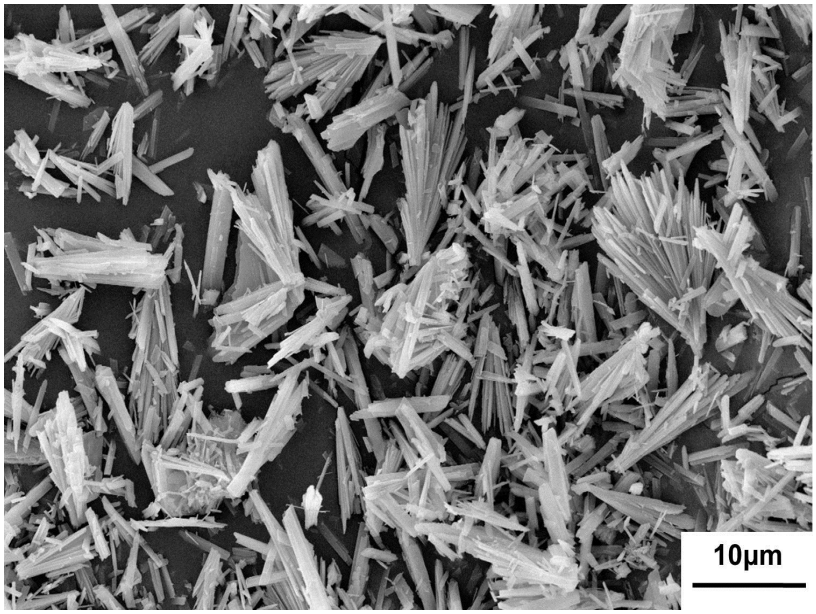


Fig. S2. SEM image of CSD formed from $CaCl_2$ and $KAl(SO_4)_2 \cdot 12H_2O$ in 0.20% CMC solution.

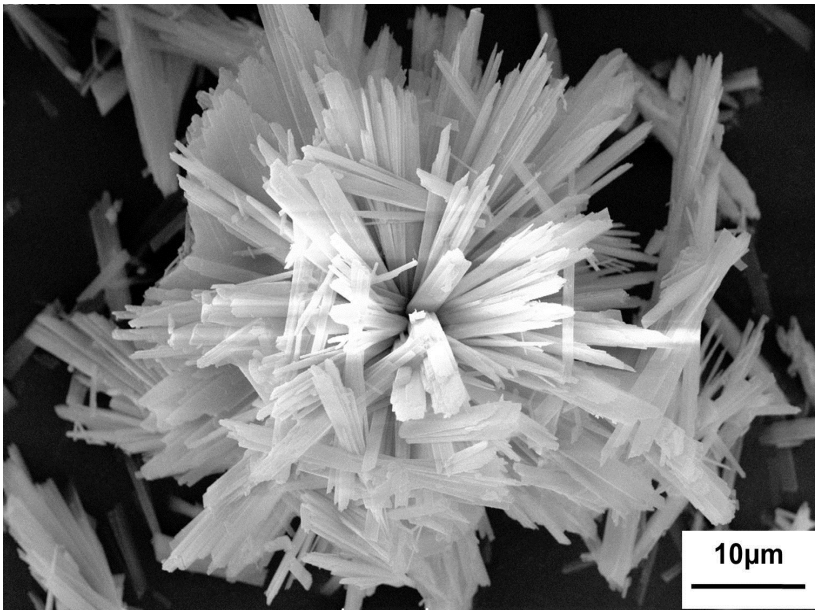


Fig. S3. SEM image of CSD formed from $CaCl_2$ and $KAl(SO_4)_2 \cdot 12H_2O$ in 0.40% CMC solution.

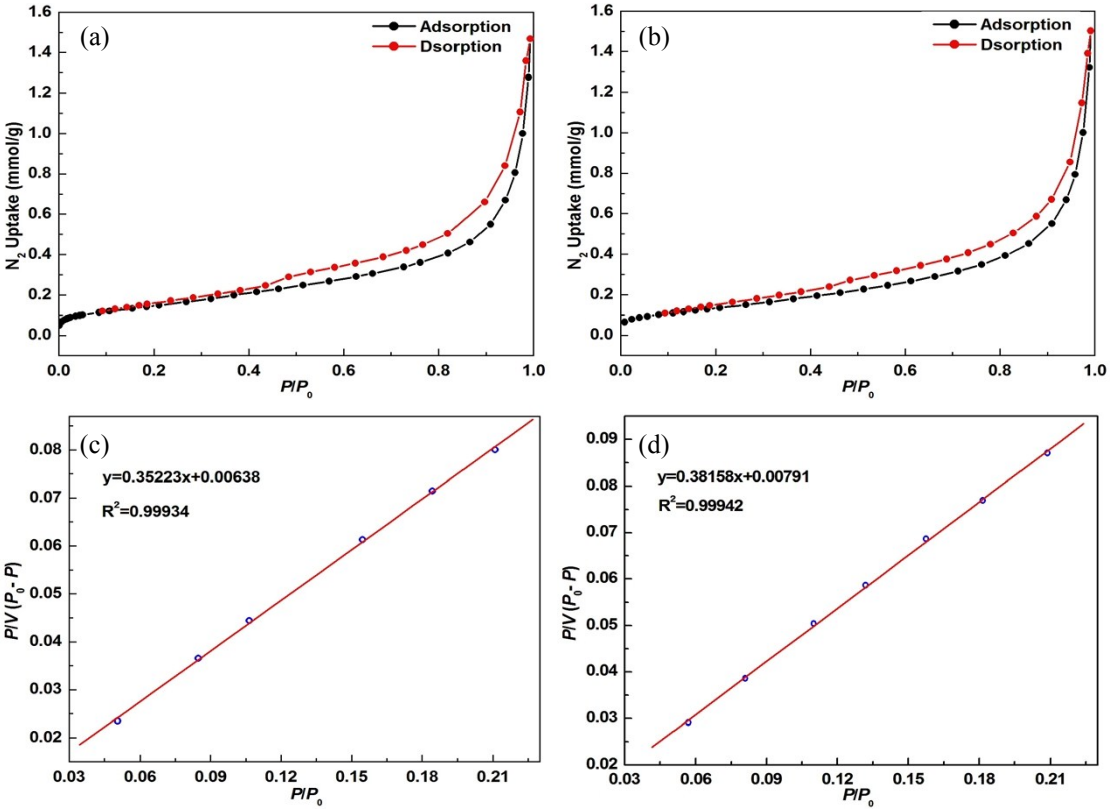


Fig. S4. Nitrogen adsorption-desorption isotherms and BET curves of (a, c) BCSD and (b, d) LCSD obtained at 77 K.

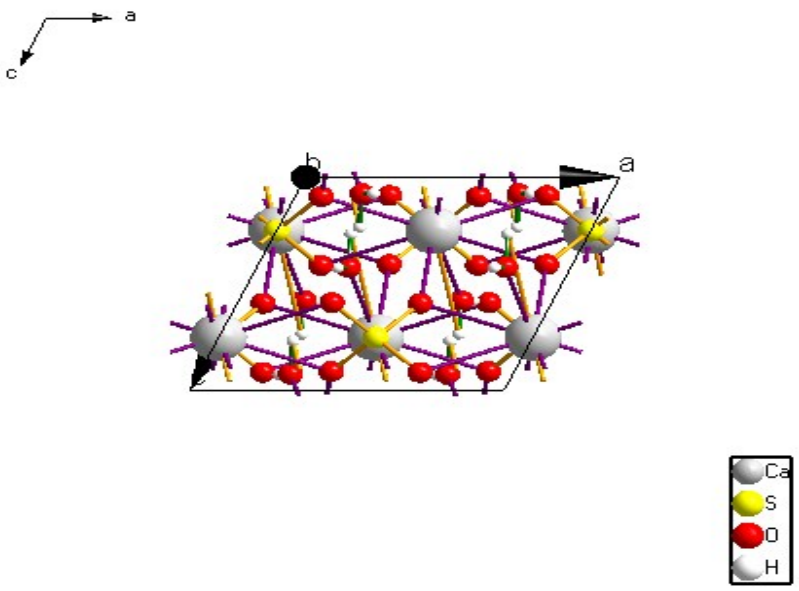


Fig. S5. Structure of CSD in (020) plane.

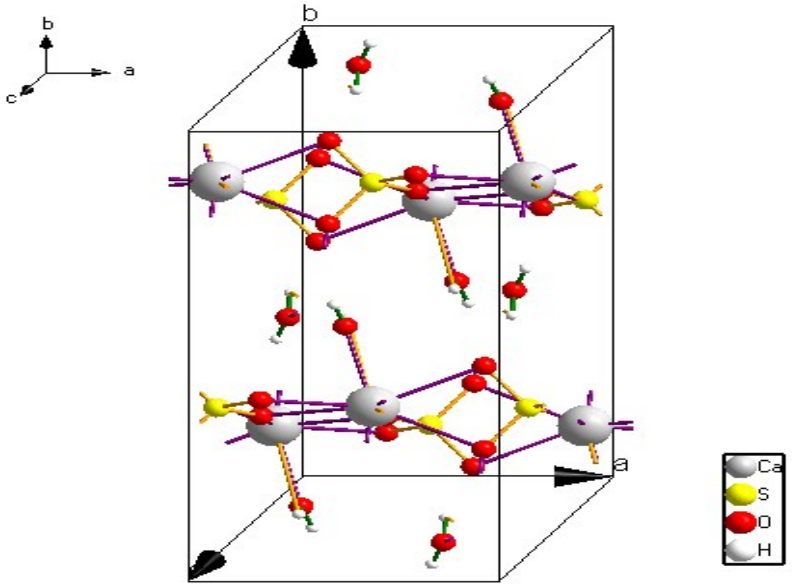


Fig. S6. Structure of CSD in (021) plane.

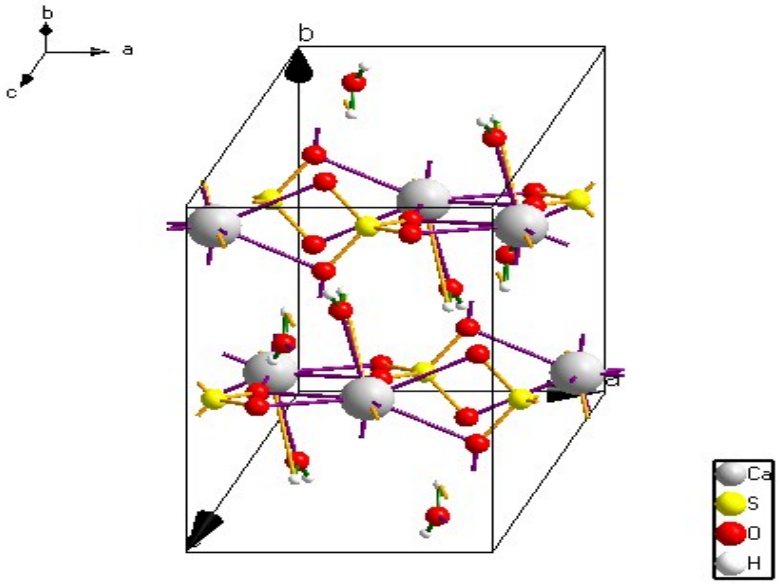


Fig. S7. Structure of CSD in (041) plane.

Table S1. The structures and maximum absorption wavelengths of three organic dyes.

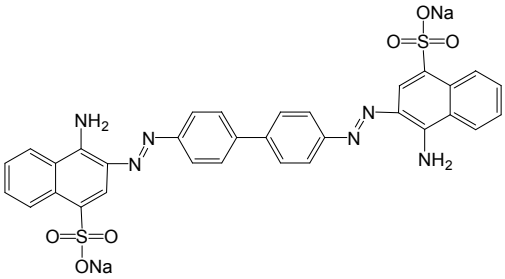
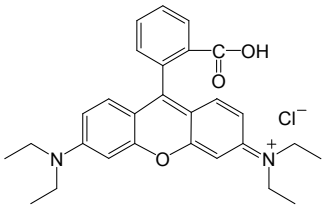
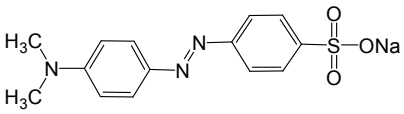
Dye	Structure	λ_{max} (nm)
Congo red		498
Rhodamine B		554
Methyl Orange		464

Table S2. The adsorption isotherm parameters for adsorption of CR onto BCSD and LCSD with four different models.

Isotherm models/parameters	LCSD	BCSD
Langmuir		
q_{max} (mg/g)	100.80	1224.09
k_L (L/mg)	0.1039	0.0220
R^2	0.9944	0.9997
R_L	0.031-0.088	0.011-0.434
Freundilich		
k_F ((mg/g)(L/mg)$^{1/n}$)	22.43	216.43
n	2.9261	3.8658
R^2	0.9096	0.9258
D-L		
q_m (mg/g)	78.33	934.441
k_D (mol^2/kJ^2)	4.57 x 10^{-6}	4.84 x 10^{-5}
E (kJ/mol)	0.3308	0.1016
R^2	0.8236	0.7863
Temkin		
k_T (L/mg)	1.17	0.54
b (kJ/mol)	0.1203	0.0130
R^2	0.9315	0.9811

Table S3. Comparison of adsorption capabilities of BCSD with other adsorbents for CR.

Adsorbents	q_{max} (mg/g)	References
Maghemite nanoparticles	208.33	[9]
Surfactant-modified zeolites	69.94	[10]
$MgAl_2O_4$ spinel	845.5	[21]
Graphene oxide/chitosan/silica	294.12	[32]
Amphiprotic cotton fiber	113.1	[34]
Activated carbon fibers	512	[36]
Polypyrrole-polyaniline nanofibres	270.27	[40]
Magnetic Fe_3O_4@graphene	33.66	[44]
$K_{1.33}Mn_8O_6$ nanowires	103.4126	[45]
BCSD	1224.09	This study

Table S4. The thermodynamic parameters for adsorption of CR onto BCSD and LCSD.

Samples	ΔH^0, kJ/mol	ΔS^0, J/(mol·K)	ΔG^0, kJ/mol					R^2
			20 °C	25 °C	30 °C	35 °C	40 °C	
BCSD	-76.40	-191.56	-20.24	-19.57	-17.66	-17.13	-16.70	0.9610
LCSD	-15.59	-6.89	-17.50	-17.71	-17.72	-17.95	-17.54	0.8536

Table S5. The kinetic parameters for adsorption of CR onto BCSD and LCSD with four different models.

Kinetic models/Parameters	LCSD	BCSD
Pseudo-first-order		
q_e (exp) (mg/g)	88.7931	1177.828
q_e (cal) (mg/g)	48.4909	529.81
k_1 (1/min)·10^{-3}	7.14	10.8
R^2	0.84383	0.79265
Pseudo-second-order		
q_e (cal) (mg/g)	88.6525	1240
k_2 (g/(mg·min))·10^{-4}	4.43	0.34
R^2	0.98841	0.99411
Elovich		
α (mg/(g·min))	89.6778	212.2231
β (g/mg)·10^{-3}	98.85	4.96
R^2	0.89886	0.87557
Intra-particle diffusion		
k_{1d} (mg/(g·min$^{1/2}$)	18.6567	176.2879
C_1	0	0
$(R_1)^2$	1.0000	1.0000
K_{2d} (mg/(g·min$^{1/2}$)	2.7588	70.0874
C_2	38.2769	252.8543
$(R_2)^2$	0.9280	0.9812
K_{3d} (mg/(g·min$^{1/2}$)	1.8483	3.2034
C_3	49.7030	1097.7527
$(R_3)^2$	0.9110	0.9063