Supporting Information

Self-Assembled Nanocomposite of HKUST-1 and Laponite: Towards Hydrogel with High Mechanical Strength for Selective Dye Adsorption and Column Chromatographic Separation

Jyoti,[a] Chhaya,[a] Vinod Kumar[a] and Anindita Chakraborty*[b]

[a]*Department of Chemistry, School of Basic Sciences, Central University of Haryana, Mahendergarh 123031, Haryana, India*

[b]*Special Centre for Nano Sciences, Jawaharlal Nehru University, New Mehrauli Road, New Delhi, Delhi 110067, India*

E-mail: anindita.chemistry1@gmail.com

Table of Contents

PXRD patterns of as-synthesized HKUST-1 and simulated HKUST-1

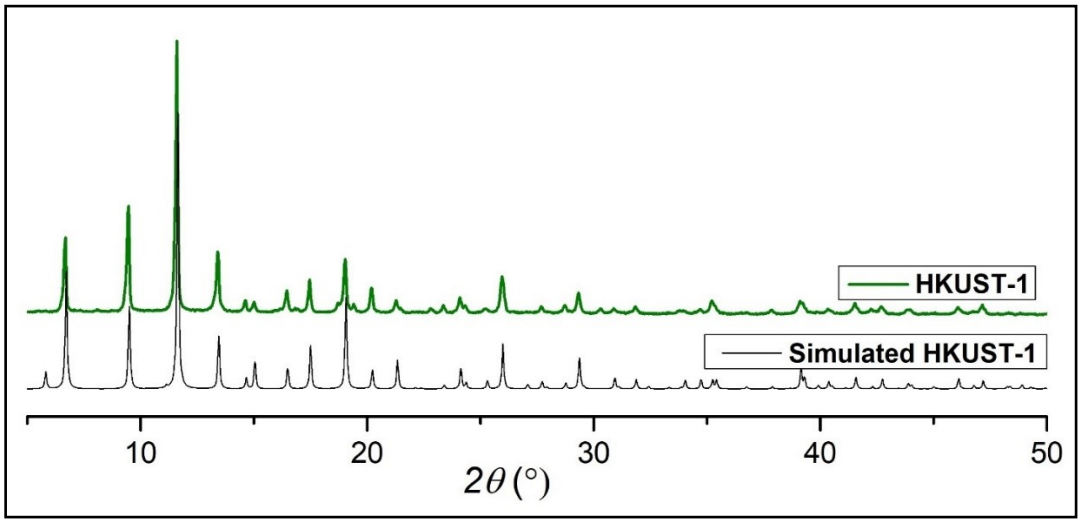


Fig. S1 PXRD patterns of as-synthesized HKUST-1 and Simulated HKUST-1.

Optimization of hydrogel nanocomposite

To synthesize the hydrogel nanocomposite, we initially focused on optimizing the reaction conditions for the composite formation. We prepared several batches under varied reaction conditions to identify the optimal parameters. The hydrogel nanocomposite formulation involved an *ex-situ* synthetic process, starting with preparing a stock solution of HKUST-1 i.e., 20 mg of HKUST-1 was dispersed in 4 ml of methanol by sonication for about 45 minutes at 35 °C. Simultaneously, different amount of LP (10, 15 & 16 mg) was dispersed in 1 ml water. Following this, the HKUST-1 suspension (ranges from 400-900 µl) was added to the LP solution under sonication at 35 °C. Entry no. 2 (**Table S1**) was selected for further studies, which yielded instant gel termed as **HKUST-1@LP (Fig. S2).**

Optimization table of reaction conditions for gel formation

Table S1. Optimisation of reaction conditions for gel formation

Entry	Amount of HKUST-1 suspension in methanol (µl)	Amount of laponite in 1 ml H_2O		
		10 mg	15 mg	**16 mg**
1	400	Viscous fluid	Viscous fluid	Viscous fluid
2	**500**	Viscous fluid	Viscous fluid	**Instant Gel formation**
3	600	Viscous fluid	Viscous fluid	Viscous fluid
4	700	Viscous fluid	Viscous fluid	Viscous fluid
5	800	Viscous fluid	Viscous fluid	Viscous fluid
6	900	Viscous fluid	Viscous fluid	Viscous fluid

Inverted image displays the formation of stable HKUST-1@LP hydrogel

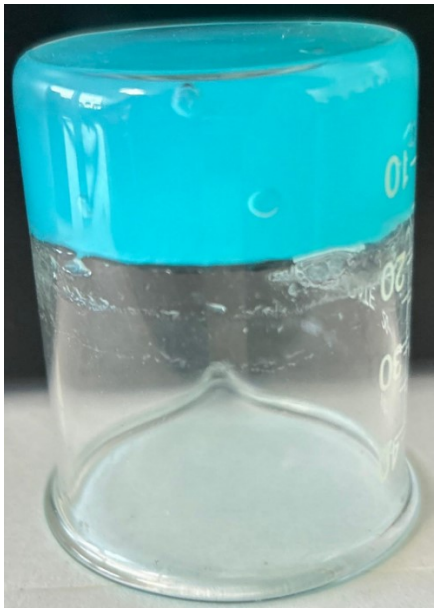


Fig. S2 Inverted image displays the formation of stable **HKUST-1@LP** hydrogel.

PXRD patterns

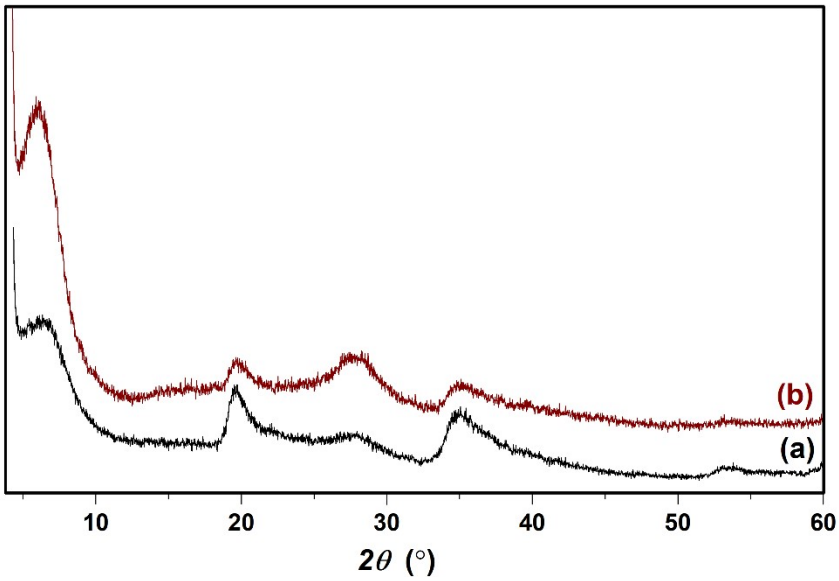


Fig. S3a PXRD patterns of (a) LP and (b) **HKUST-1@LP** xerogel.

Chemical stability of HKUST-1 phase in the composite

To understand the chemical stability of HKUST-1 phase in the composite, we have carried out additional experiments. Specifically, 20 mg of HKUST-1 was dispersed in 4 ml of methanol by sonication for about 45 minutes at 35 °C. This stock solution of HKUST-1 (20 mg in 4 ml MeOH) was immerged in 8 ml of water and sonicated. The resulting mixture was allowed to stand for 2 minutes, and an identical batch was prepared and left to stand for 1 hour. Afterward, the samples were centrifuged, and the MOF solids were collected and dried. The dried materials were analyzed by PXRD. The obtained pattern (**Fig. S3b**) clearly shows that the characteristic diffraction peaks of HKUST-1 are retained, confirming that the HKUST-1 framework does not undergo decomposition under the applied conditions. These results verify the chemical integrity and structural stability of HKUST-1 within the composite.

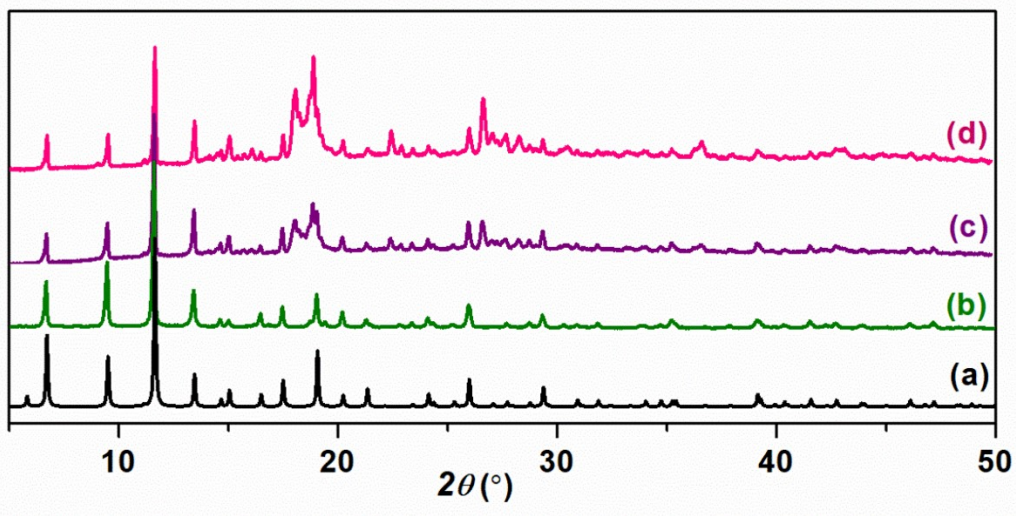


Fig. S3b PXRD patterns of (a) Simulated HKUST-1, (b) as-synthesized HKUST-1, (c) and (d) HKUST-1 sample immersed in water under conditions identical to the synthesis for 2 min and 1 hour, respectively.

TGA plots of as-synthesized HKUST-1, LP and HKUST-1@LP xerogel

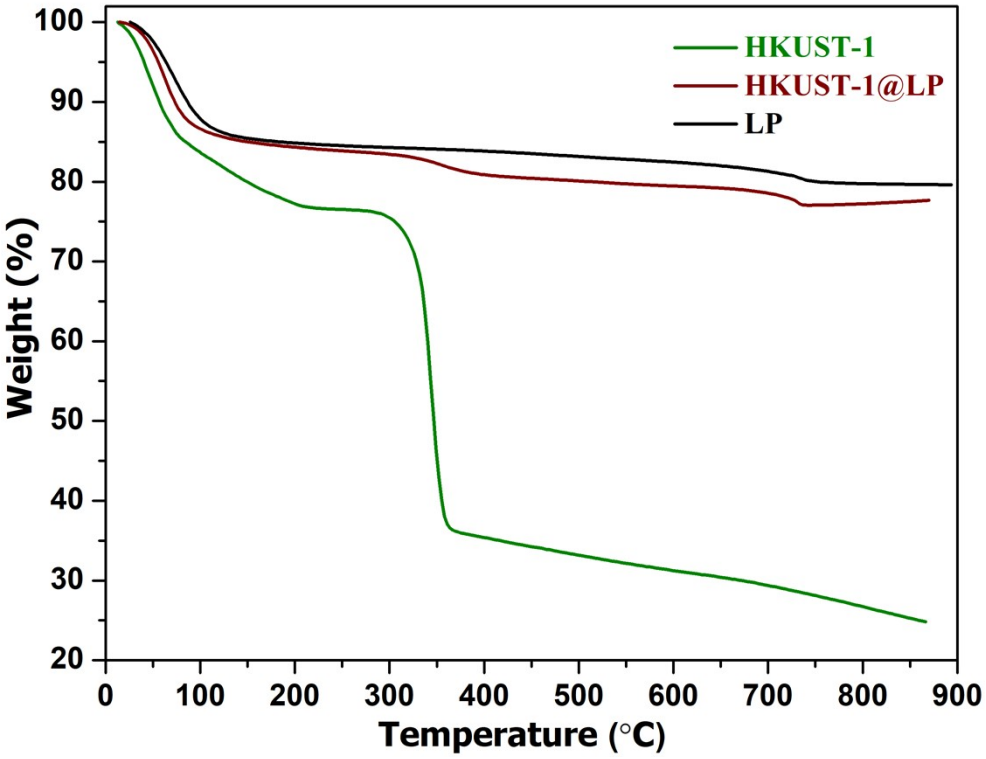


Fig. S4 TGA plots of as-synthesized HKUST-1, LP and **HKUST-1@LP** xerogel.

FESEM images, particle size distribution histogram and elemental mapping

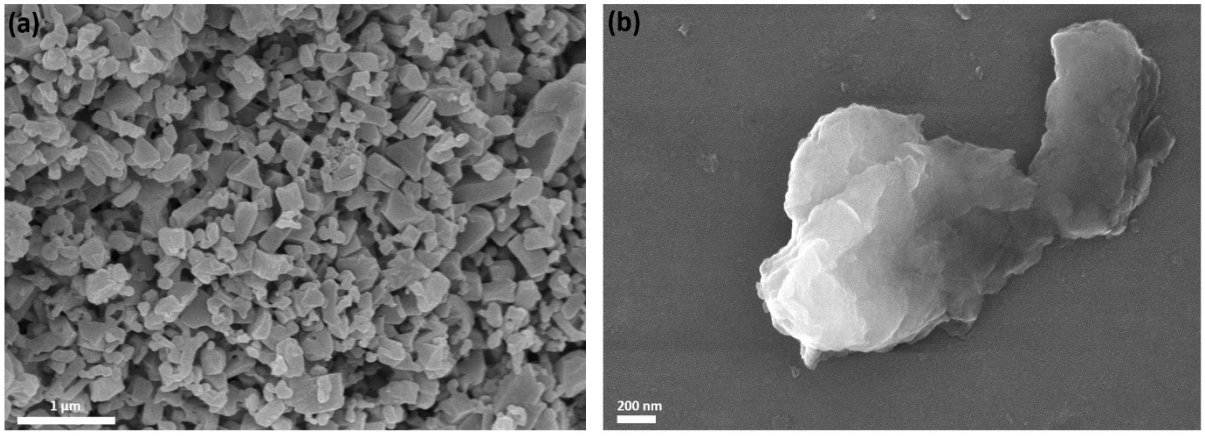


Fig. S5 FESEM images of (a) as-synthesized HKUST-1 and (b) **HKUST-1@LP** xerogel.

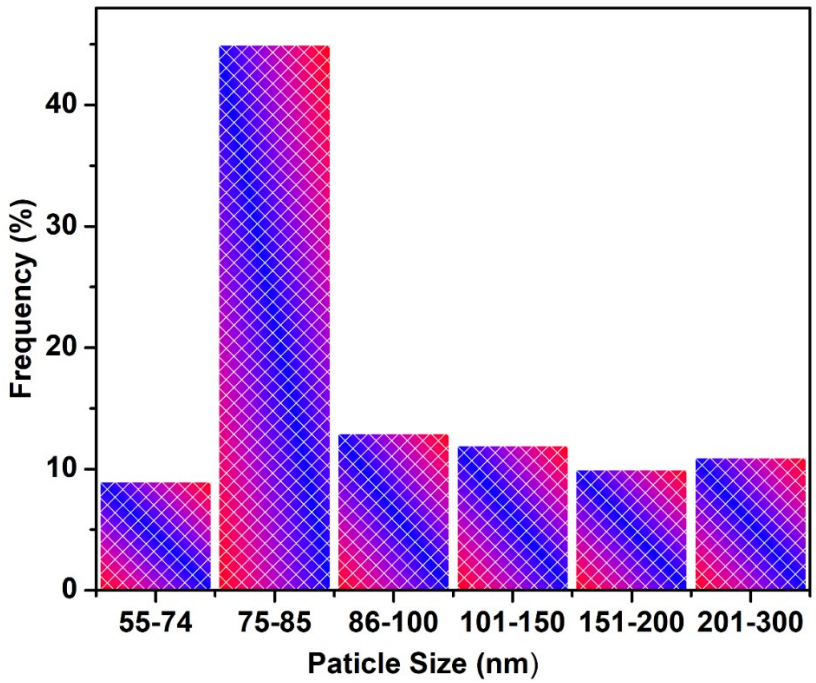


Fig. S6 The particle size distribution histogram plot of as-synthesized HKUST-1.

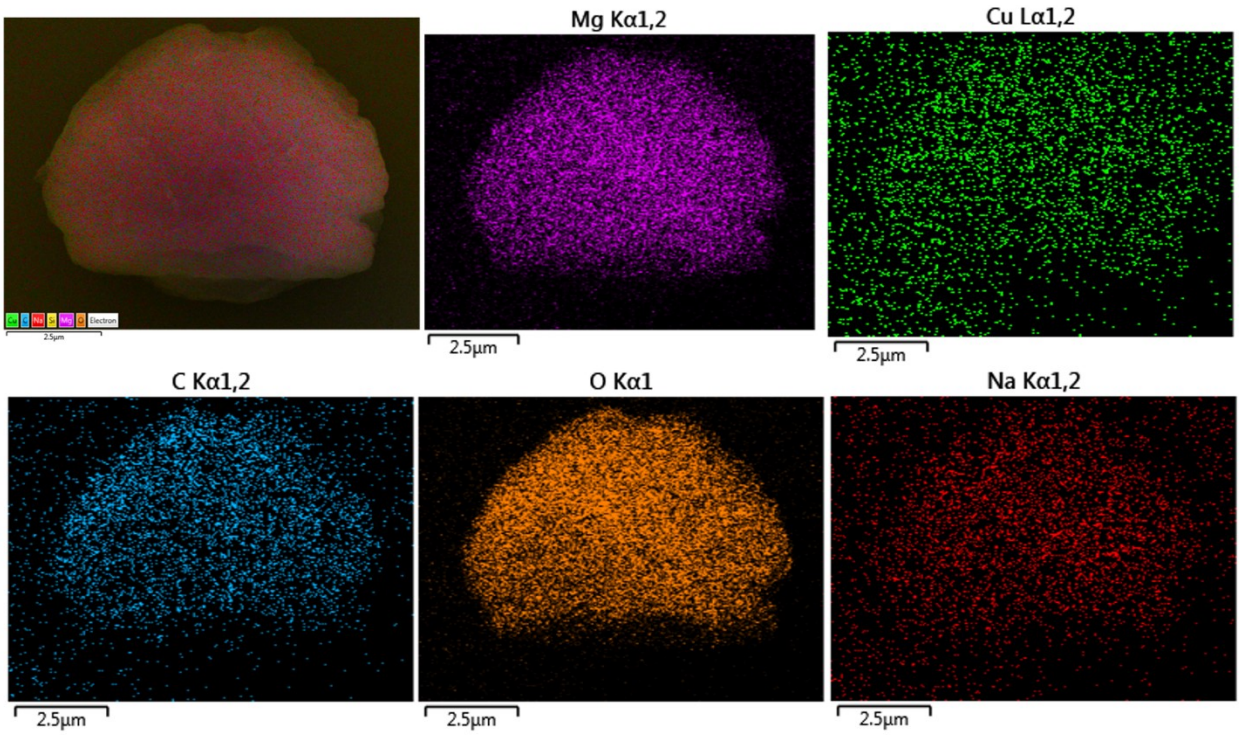
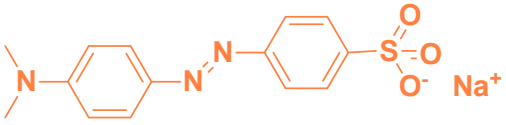
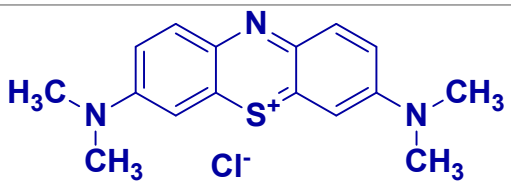
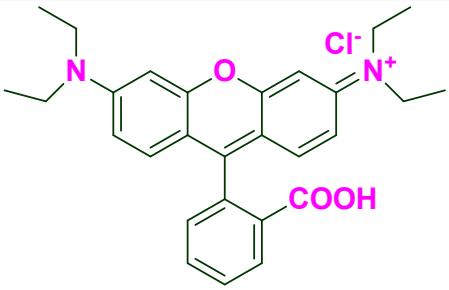


Fig. S7 Elemental mapping of **HKUST-1@LP** xerogel showing uniform distribution of the elements (Cu from as-synthesized HKUST-1 and Mg, Na from LP) throughout the sample.

Structure and size of dyes

Table S2: Chemical structure, maximum wavelengths and size of dye used.

Dyes	Molecular Structure	Size
Methyl Orange (Anionic)		2.6X6.5X15.8 Å
Methylene Blue (Cationic)		4.59X8.01X16.7 Å
Rhodamine B (Cationic)		6.79X11.80X15.78 Å

UV-vis plots of dye adsorption

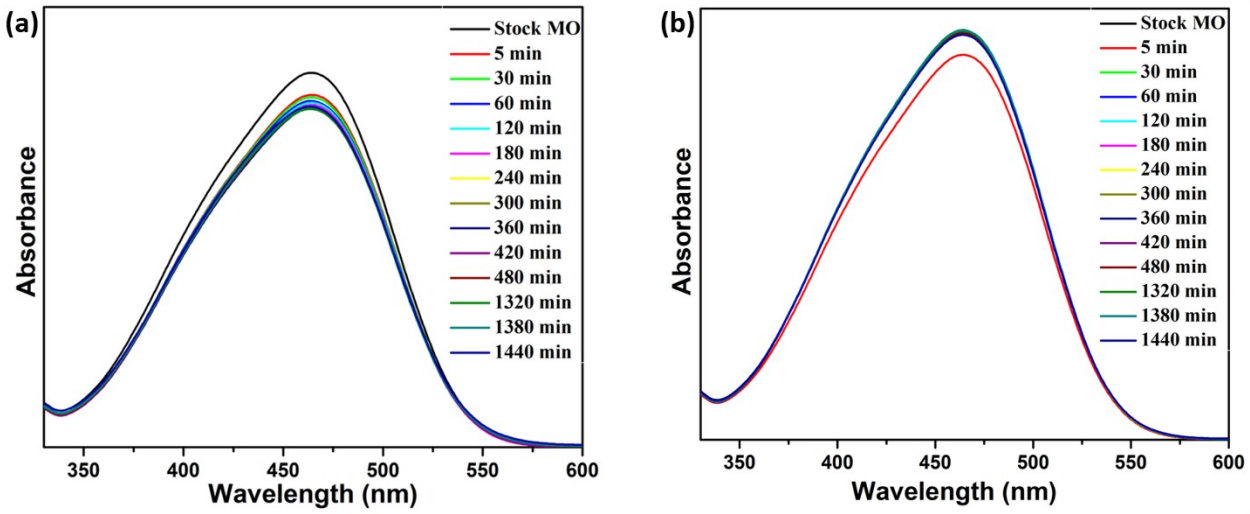


Fig. S8 UV-vis plots of adsorption of MO dye (a) using **HKUST-1@LP** xerogel and (b) using LP.

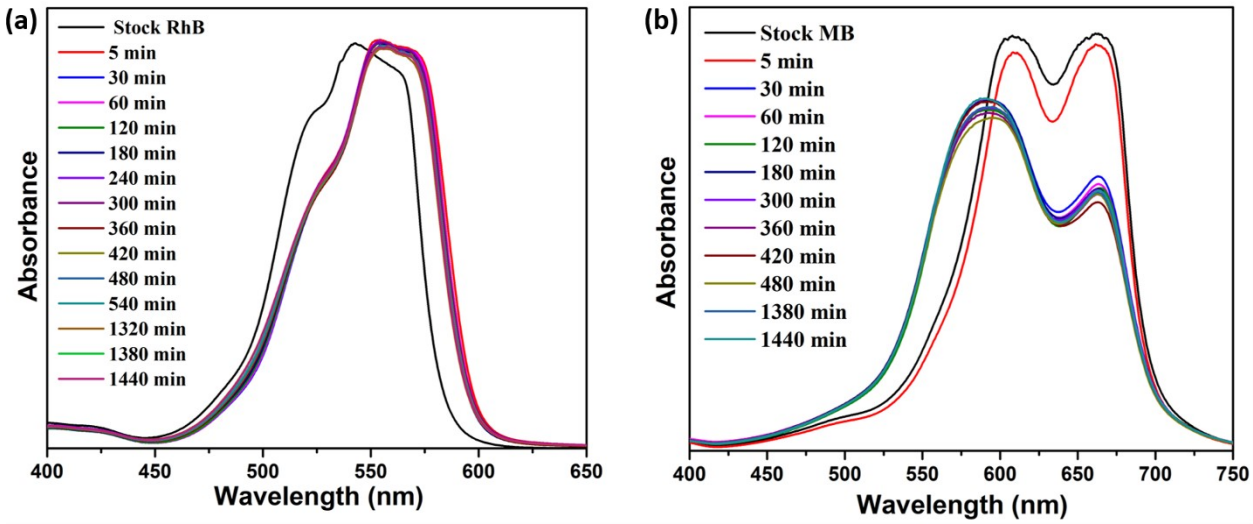


Fig. S9 UV-vis plots of dye adsorption using LP with (a) RhB and (b) MB dyes.

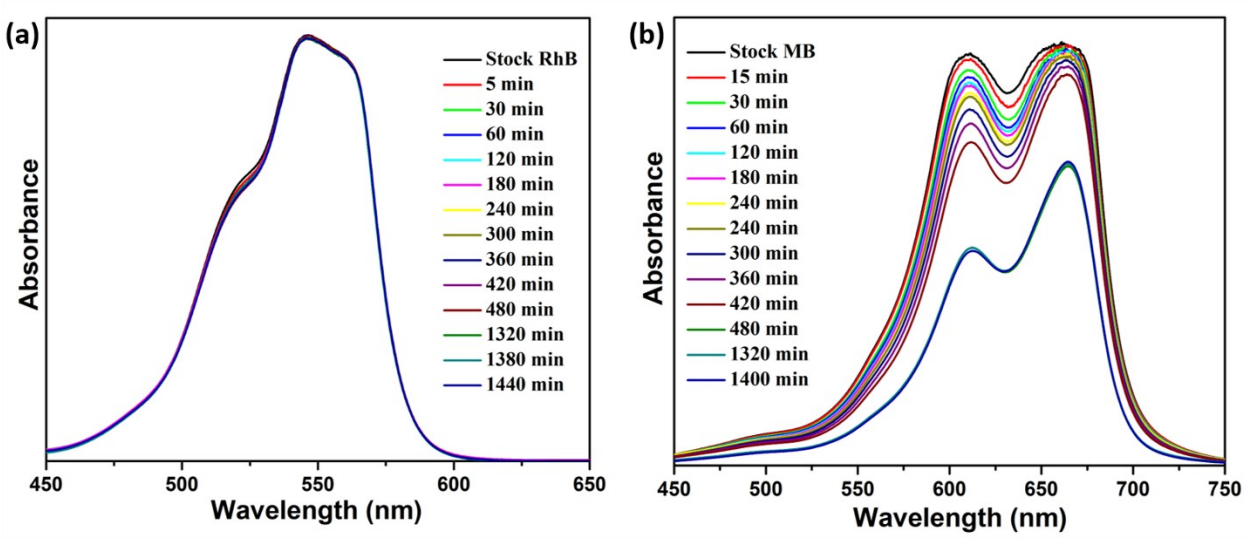


Fig. S10 UV-vis plots of dye adsorption using as-synthesized HKUST-1 with (a) RhB and (b) MB dyes.

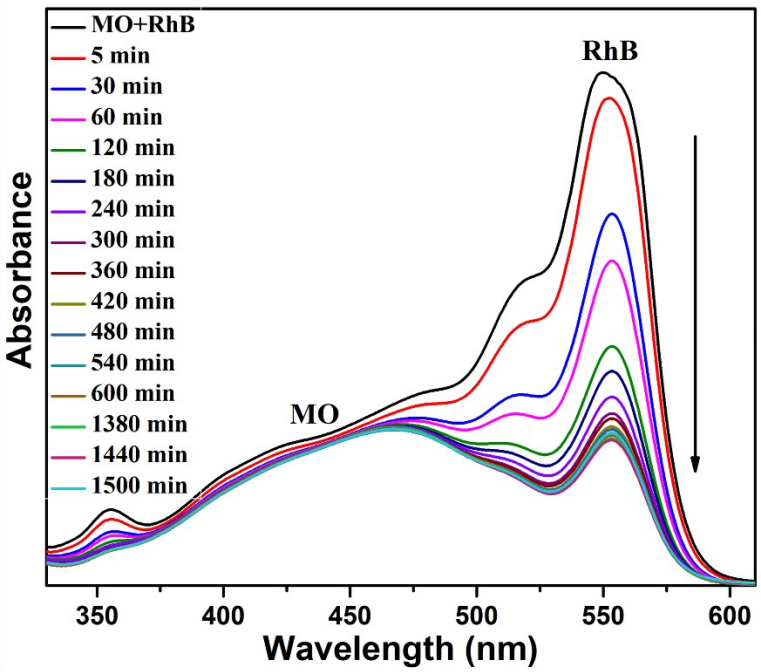


Fig. S11 UV-vis plots of selective dye adsorption from a mixture of MO/RhB by **HKUST-1@LP** xerogel.

Comparative dye adsorption data of HKUST-1-based MOFs/MOF composites

Table S3: Comparative dye adsorption data of HKUST-1-based MOFs/MOF composites

MOFs/MOF composites	Adsorbates	Amount of dye Adsorbed (q_e, mg/g)	References
Cu-BTC[a]	MB	200	*Microporous Mesoporous Mater.,* 2014, **193**, 27.
Cu-btc-1[b]	MB	98.83	*Inorganica Chim. Acta,* 2020, **511**, 119787.
NDA88-Cu	MO	398.8	*J. Clean. Prod.*, 2018, **184**, 949e958.
Cu-BTC[c]	MB	45	*ACS Omega*, 2021, **6**, 33961.
HKUST-AMP-SO_3H	MB	833.33	*RSC Adv.,* 2020, **10**, 9369.
HKUST-1[d]	MB	238.09	*RSC Adv.,* 2020, **10**, 9369.
$Fe_3O_4/Cu_3(BTC)_2$	MB	244	*Sci. Rep.*, 2015, **5**, 1.
Fe_3O_4/HKUST-1	MB	140	*J. Mater. Chem. A*, 2014, **2**, 1795.
Fe_3O_4/HKUST-1/GO	MB	155	*J. Mater. Chem. A*, 2014, **2**, 1795.
Cu-doped BTC	MB	197.90	*J. Environ. Chem. Eng*., 2020, **8**, 104247.

Synthetic conditions: [a]**Cu-BTC**: Hydrothermal method at 100 °C for 10 hours; [b]**Cu-btc-1**: Hydrothermal method at 120 °C for 48 hours; [c]**Cu-BTC**: Synthesized at room temperature; [d]**HKUST-1**: Hydrothermal method at 120 °C for 12 hours.

Gel-column chromatographic dye separation

Fig. S12 Change in the colour of gel-column with time indicating separation of MB and RhB from their mixture using **HKUST-1@LP** hydrogel.

AFM Images of HKUST-1@LP hydrogel thin film

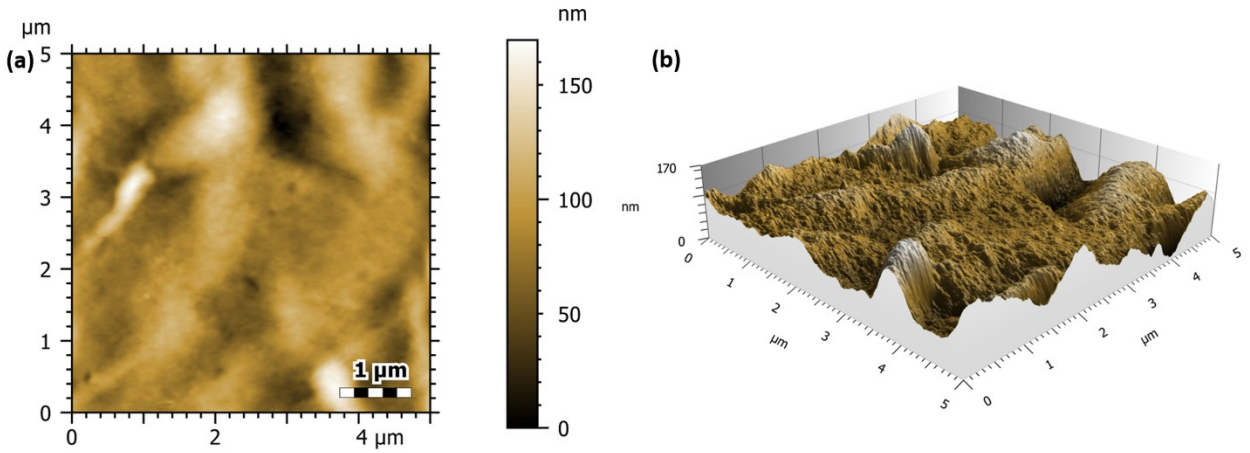


Fig. S13 AFM Images of **HKUST-1@LP** hydrogel thin film (a) 2D height topography and (b) 3D surface roughness profile.

Adsorption Kinetics

The pseudo-second-order rate equation[1]:

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

(1)

where, q_e and q_t (mg/g) are the adsorption capacities of MB at equilibrium and at time t, respectively and k_2 (g $mg^{-1}min^{-1}$) is the rate constant of pseudo-second-order (**Fig. S14**).

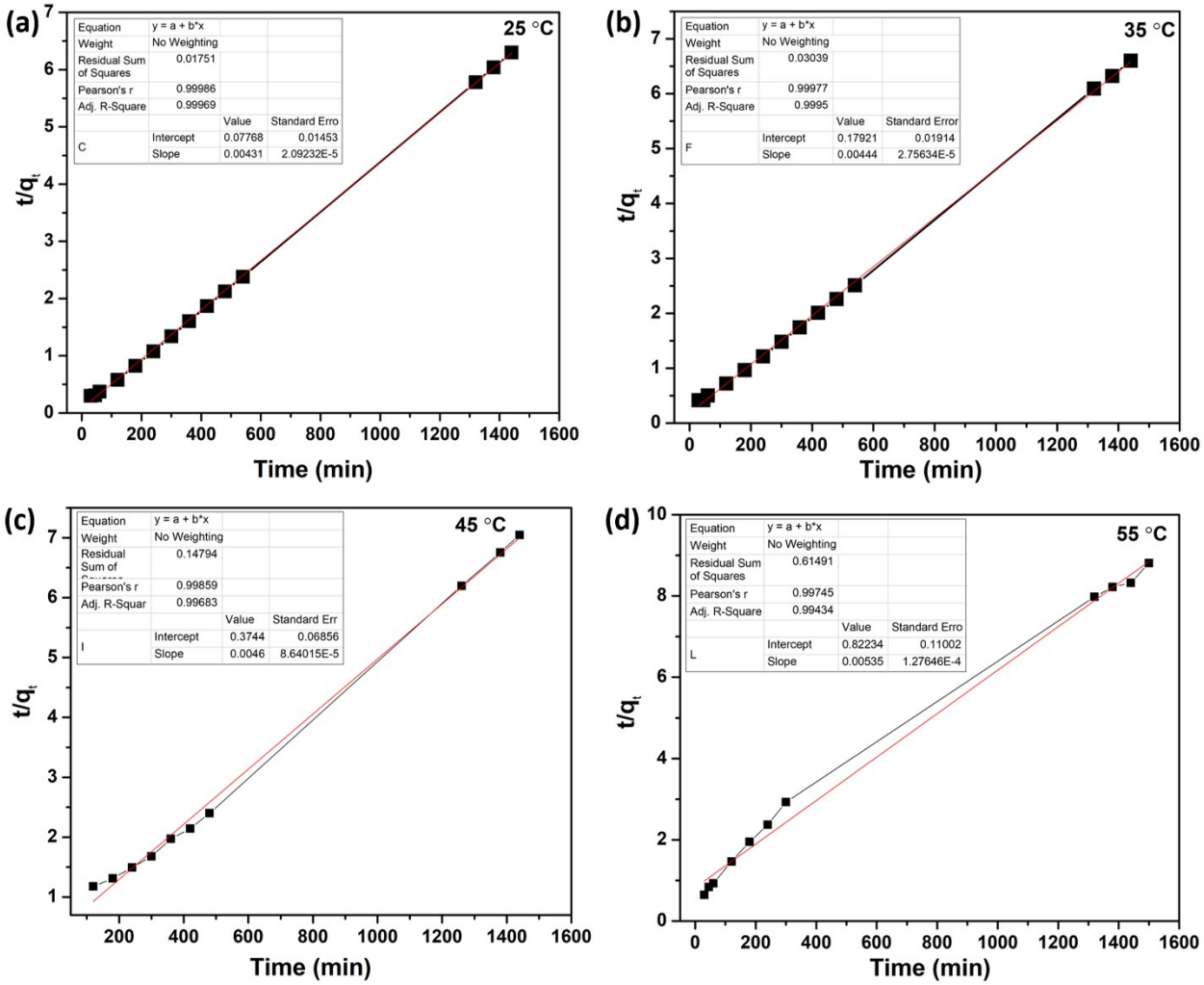


Fig. S14 The adsorption kinetics of MB by **HKUST-1@LP** xerogel at different temperatures, representing pseudo-second order kinetics.

The activation energy was also calculated by thermodynamic parameters with the help of k_2 calculated at different temperatures using the Arrhenius equation (2)[2].

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (2)$$

Here, A represents the Arrhenius factor, R is the gas constant, and T denotes the temperature. A linear plot of $\ln k_2$ versus 1/T for MB adsorption using **HKUST-1@LP** xerogel was constructed to determine the activation energy (E_a) from the slope (**Fig. S15**). The calculated E_a value is 59.49 kJ mol^{-1}, with a high linear regression coefficient of 0.99745, indicating an excellent fit.

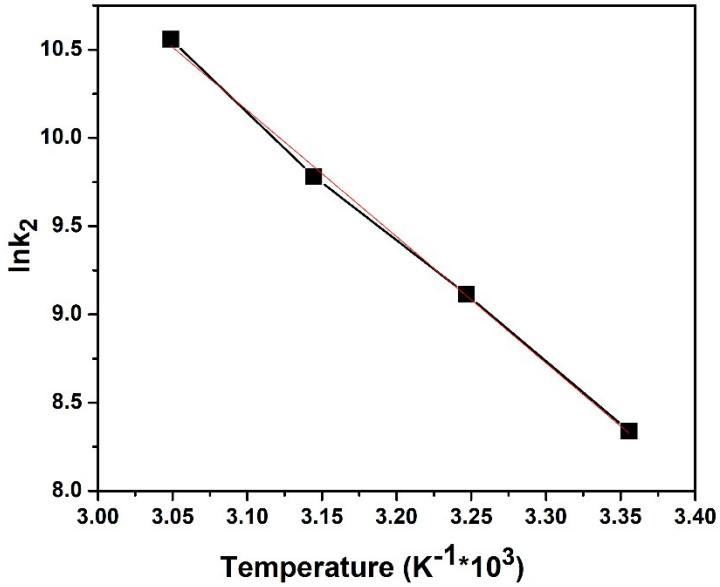


Fig. S15 Arrhenius plot for adsorption of MB dye.

References

1. W.-P. Wu, J. Wu, J.-Q. Liu, M. Trivedi and A. Kumar, *RSC Adv.*, 2017, **7**, 54522. https://doi.org/10.1039/c7ra11221a
2. M. Alkan, Ö. Demirbaş and M. Doğan, *Microporous Mesoporous Mater.*, 2007, **101**, 388. https://doi.org/10.1016/j.micromeso.2006.12.007