Supporting Information for:

Efficient Dye Removal Using Well-Crystallized Layered Double Hydroxides and Oxides: Insights into Kinetics, Thermodynamics, Isotherm and Memory Effect

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Materials and Methods

The powder X-ray diffraction (XRD) was studied with X'pert powder XRD system with Co Kα radiation in the 2θ range of 0-150^{o} having high speed solid-state X'celerator detector. The Fourier Transform – Infrared (FT-IR) analysis for the adsorbent was performed using Jasco FT/IR-4700 by ATR method in 400 – 4000 cm^{-1} wavenumber regions. The thermal gravimetric analysis (TGA) was carried out using STA300 of thermogravimetric analyzer under inert atmosphere having temperature range of 25^{o}-1500^{o}C with a heating rate of 10^{o}C/min. The morphology of the material before dye adsorption was studied using Field Emission Scanning Electron Microscopy (FESEM) using JEOL, JSM-7800F with magnification ranging from 100 X to 300,000 X. The elemental composition of the materials was studied using Thermo scientific XPS system with Al-Kα (1486.8 eV) micro-focused monochromator with variable spot size (50-400 μM) at Ar^{+} energy range 100-400 eV. The specific surface area of the materials before dye adsorption was measured using AutosobiQ Quantachrome instruments by Brunauer-Emmett-Teller (BET) analysis using N_2 adsorption-desorption isotherm techniques at adsorption temperature 77K. The absorbance of dyes before and after adsorption was measured using Shimadzu UV-1900i UV-vis spectrophotometer. Remi RSB 12 water bath shaker was used to attain equilibrium during the adsorption process. Standard deviations for all experiments were calculated from two independent measurements. Zeta potential measurements were carried out using a Horiba SZ-100Z DLS instrument. SEM images and EDX mapping of the nanocomposites after MO dye adsorption were obtained using a TESCAN VEGA 3 instrument. BET analysis of the nanocomposites after MO dye adsorption was performed using N_2 adsorption–desorption isotherm measurements at 77 K with an Anton Paar-Autosorb iQ-XR-AG instrument.

The percentage adsorption and adsorption capacity formula:

$$Percentage\ adsorption = \frac{(C_0 - C_e) * 100}{C_0}$$

$$Adsorption\ Capacity\left(\frac{mg}{g}\right) = (C_0 - C_e)\frac{V}{w * 1000}$$

where,

C_o = Initial dye concentration (mg/l)
C_e = Equilibrium dye concentration (mg/l)
V = Volume of adsorbate (L)
W = Weight of the adsorbent (g)

Adsorption Kinetic Equations

The linearized format of the pseudo-second order rate equation,

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{t}{q_e} \quad \textbf{--------- SEQ1}$$

where,

q_e and q_t = Amount of MO adsorbed at equilibrium time and at specified time

k_2 = Pseudo-second-order rate constant

Adsorption thermodynamics

Different parameters such as enthalpy ΔH, entropy ΔS, and Gibbs free energy ΔG which can be calculated by using the following equations,

$$\Delta G = -RT\ln K \quad \textbf{--------- SEQ2}$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \textbf{--------- SEQ3}$$

where,

K = Adsorption distribution coefficient (q_e/C_e)

R = Universal gas constant (8.314 J/mol/K)

T = Temperature in kelvin

Linear and non-linear forms of Freundlich and Langmuir Adsorption isotherms

Freundlich Adsorption isotherm:

Linear form of Freundlich isotherm model,

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad \text{--------- SEQ4}$$

And the non-linear form is,

$$q_e = k_f C_e^{1/n} \quad \text{--------- SEQ5}$$

where,

q_e is the adsorption capacity at equilibrium

1/n is the heterogeneity factor

k_f is the Freundlich constant

Langmuir Adsorption isotherm:

The linear form of Langmuir isotherm model is given by,

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_l \ q_m} \quad \text{--------- SEQ6}$$

The non-linear form is,

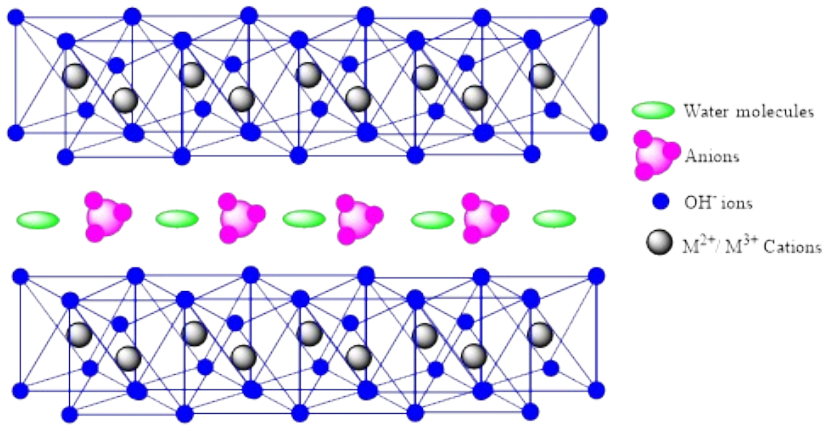
$$q_e = \frac{q_m k_l C_e}{1 + k_l C_e} \quad \text{--------- SEQ7}$$

Where,

q_m is the maximum adsorption capacity

k_l is the Langmuir constant

C_e is the equilibrium concentration of the dye



Scheme S1. Schematic representation of two-dimensional structure of LDH

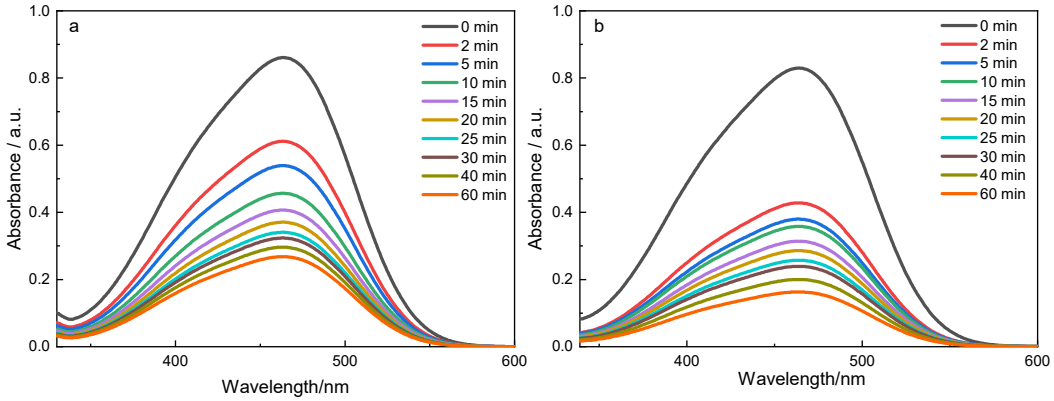


Figure S1. Absorption spectra of MO dye before and after adsorption at various time intervals using (a) MAH and (b) MAO. Experimental conditions: initial dye concentration = 200 mg/L, adsorbent dose = 30 mg, temperature = 30 °C. Different dilution factors were applied to prevent absorbance saturation; these were accounted for in the calculations of both percentage adsorption and adsorption capacity.

hkl plane	**LDH d Spacing (A^o)**		**LDO d Spacing (A^o)**	**LDO few days after calcination d Spacing (A^o)**
	Before Adsorption	After Adsorption	After Adsorption	
(003)	7.4508	7.47106	7.708938	7.531495
(006)	3.744363	3.75233	3.828701	3.780932
(012)	2.548594	2.554552	2.571374	2.549535
(015)	2.264857	2.268375	2.28567	2.321936
(018)	1.919258	1.922213	1.941592	2.085441
(110)	1.514552	1.516571	1.520318	1.51973
(113)	1.485366	1.486912	1.491574	1.478123

Table S1. d-spacing values after adsorption of MO dye on MAH and MAO and LDO few days after calcination.

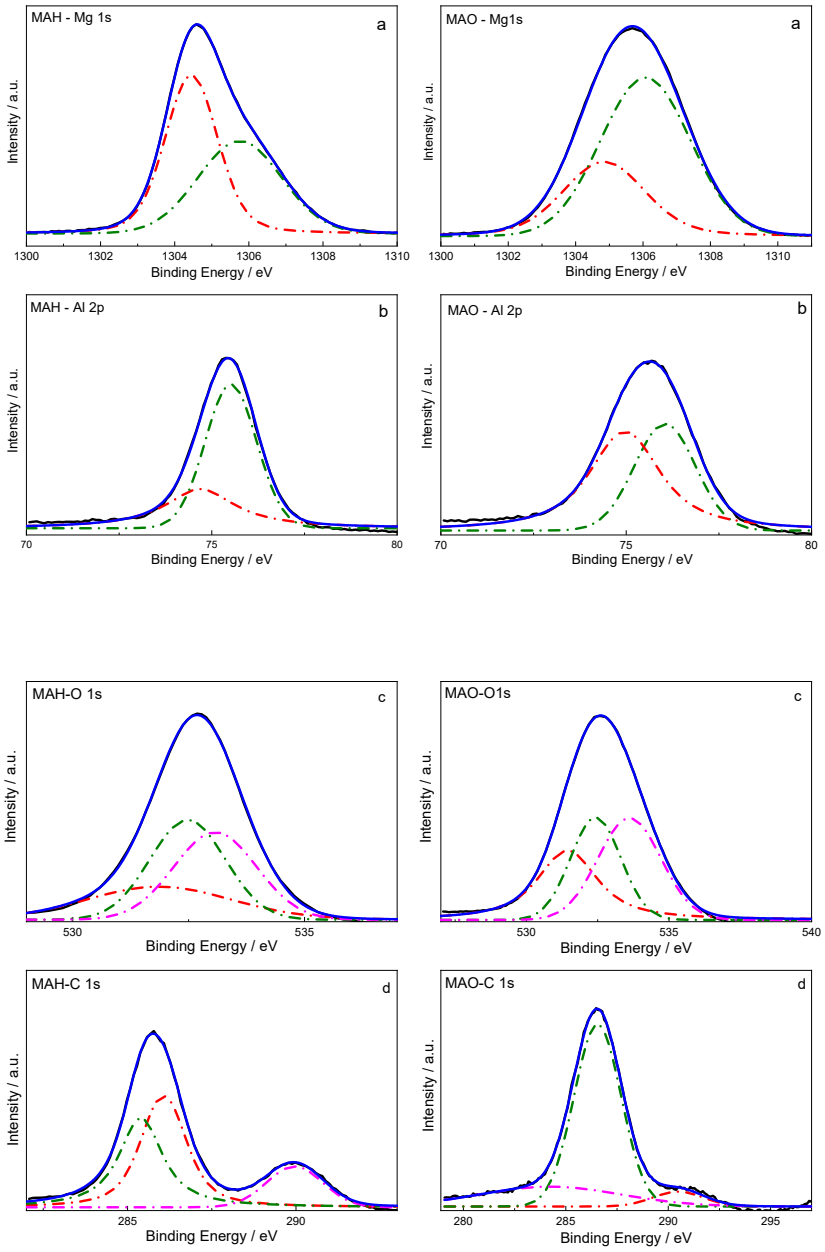


Figure S2. XPS deconvoluted spectra of (a) Oxygen 1s, (b) Carbon 1s, (c) Magnesium 1s and (d) Aluminum 2p Spectra

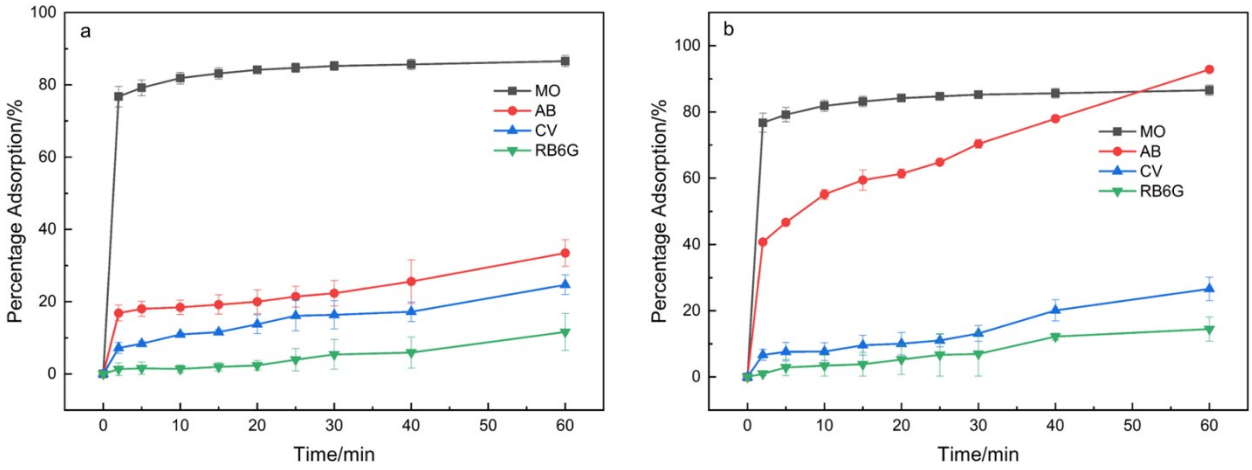


Figure S3. Percentage adsorption of various cationic and anionic dyes over different time intervals using (a) MAH and (b) MAO. Experimental conditions: dye concentration = 200 mg/L, adsorbent dose = 30 mg, temperature = 30 °C.

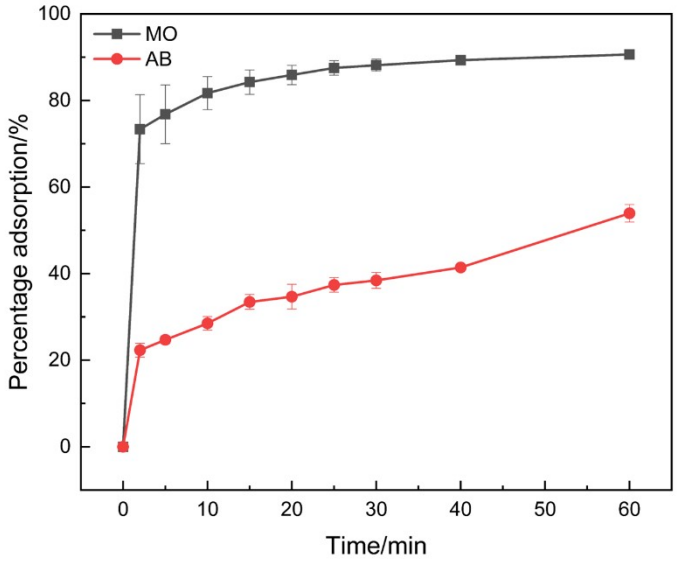


Figure S4. Percentage adsorption of anionic dyes at different time intervals using MAO. Experimental conditions: dye concentration = 500 mg/L, adsorbent dose = 30 mg, temperature = 30 °C.

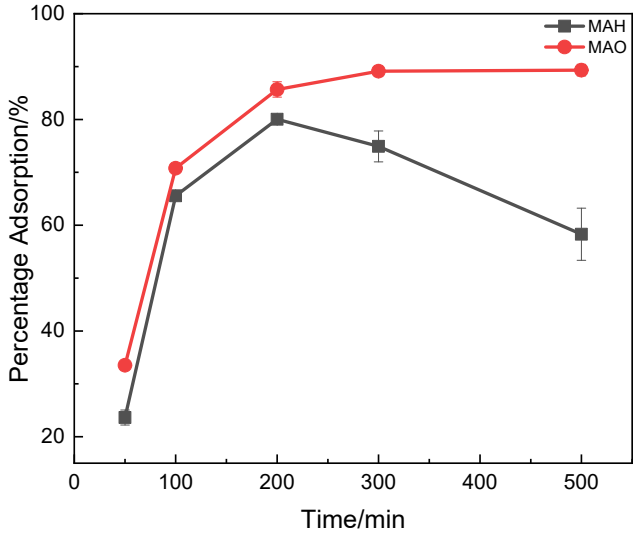


Figure S5. Percentage adsorption of MO dye by MAH and MAO at varying dye concentrations (50, 100, 200, 300, and 400 mg/L). Experimental conditions: adsorbent dose = 30 mg, contact time = 1 hour, temperature = 30 °C.

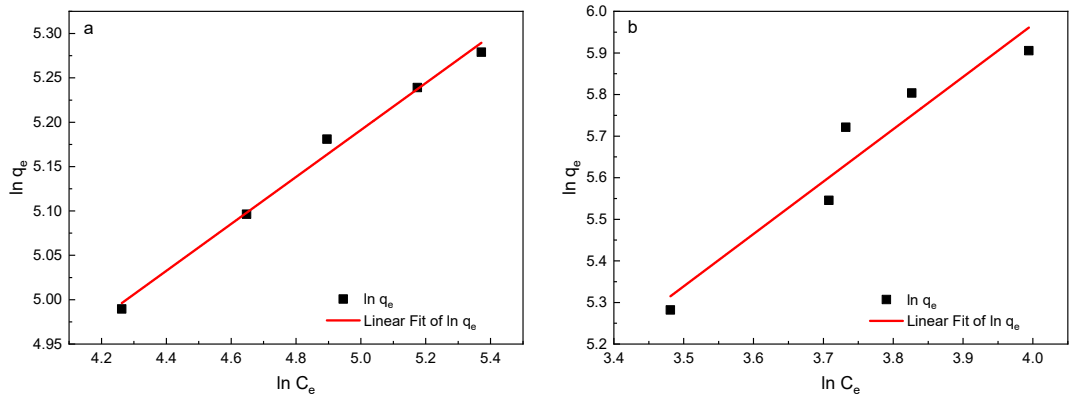


Figure S6. Freundlich adsorption isotherm linear plots of (a) MAH and (b) MAO

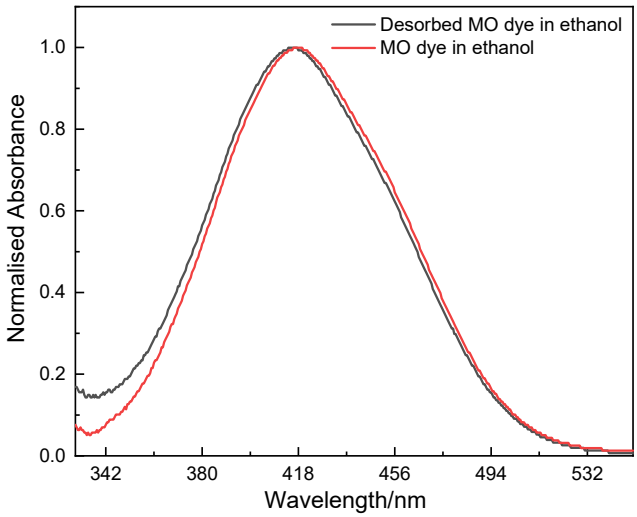


Figure S7. The normalized absorption spectrum of pure MO dye in ethanol and MO dye desorbed from MAO nanocomposite using ethanol

Adsorbent	qe / mg/g	Conditions	Contact time	Reusability	Reference
Ni Mg Al LDO	322.58	MO – 25 mg/L Dose – 0.01 g Temp. - 25°C **Higher adsorption capacity at pH - 10**	80 min	3 cycles	(1)
Fe_3O_4 @ SiO_2	182.50	MO – 100 mg/L Dose – 0.02 g **Temp. - 45°C** **Higher adsorption capacity at pH - 2**	30 min	5 cycles	(2)
Nitrate intercalated Mg Al LDH	583	MO – 0.03 mg/ml Dose – 0.2 mg/ml **Higher adsorption only at 40 - 50°C** **Higher adsorption capacity at pH - 5**	15 min (**40-50°C)**	5 cycles	(3)
Zn (II) Metal organic gel	100	MO – 25 mg/L Dose – 5 mg **Higher adsorption only at 15°C** **Higher adsorption capacity at pH 4-10**	10 min	3 cycles	(4)
Triptycene-based hyper-crosslinked porous polymer	220.82	MO – 500 mg/L Dose – 50 mg Temp. – 25°C **Higher adsorption capacity at pH 7**	60 min	5 cycles	(5)
MAH	265	MO – 500 mg/L Dose – 30 mg Temp. – 30°C **Higher adsorption capacity in the range of pH 3-10** **Independent of pH** After 5th cycle, acid wash restored the adsorption capacity nearly 100%	60 min	6 cycles (MAO)	**This work**
MAO	324		10 min		

Table S2. Comparison of different adsorbents with MO dye

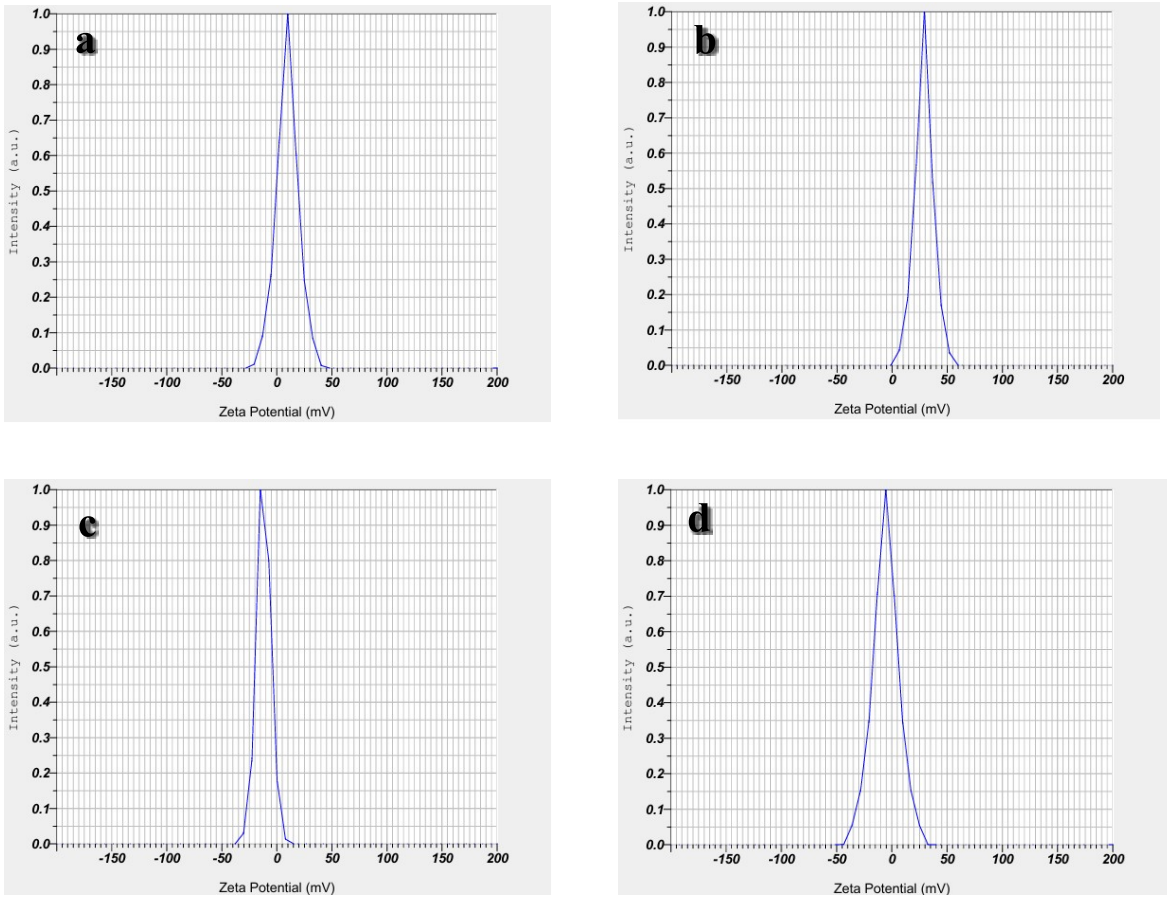


Figure S8. Zeta potential analysis of nanocomposites before and after adsorption of MO dye. (a) MAH, (b) MAO, (c) MO-MAH and (d) MO-MAO.

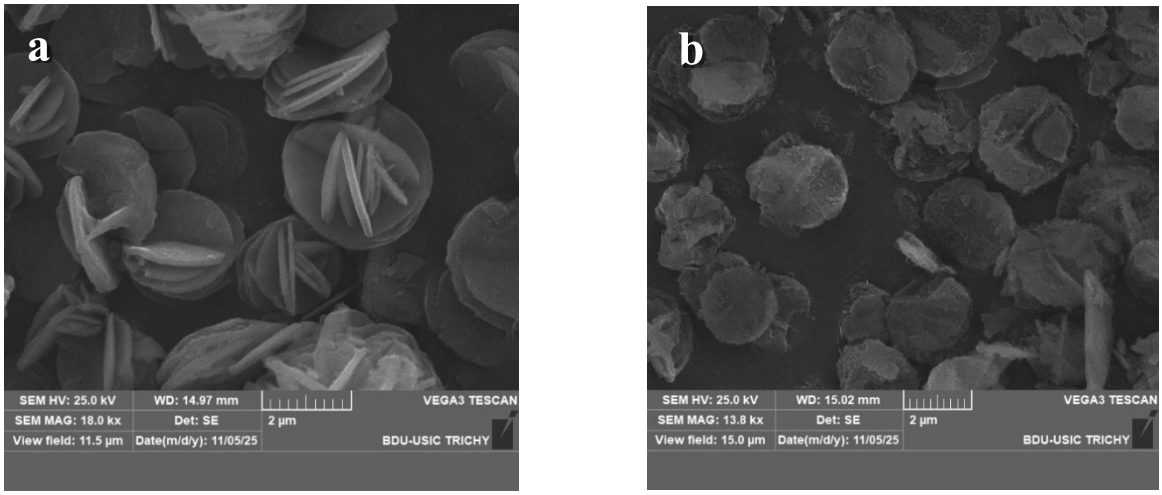


Figure S9. SEM images of nanocomposites after adsorption of MO dye. (a) MAH and (b) MAO.

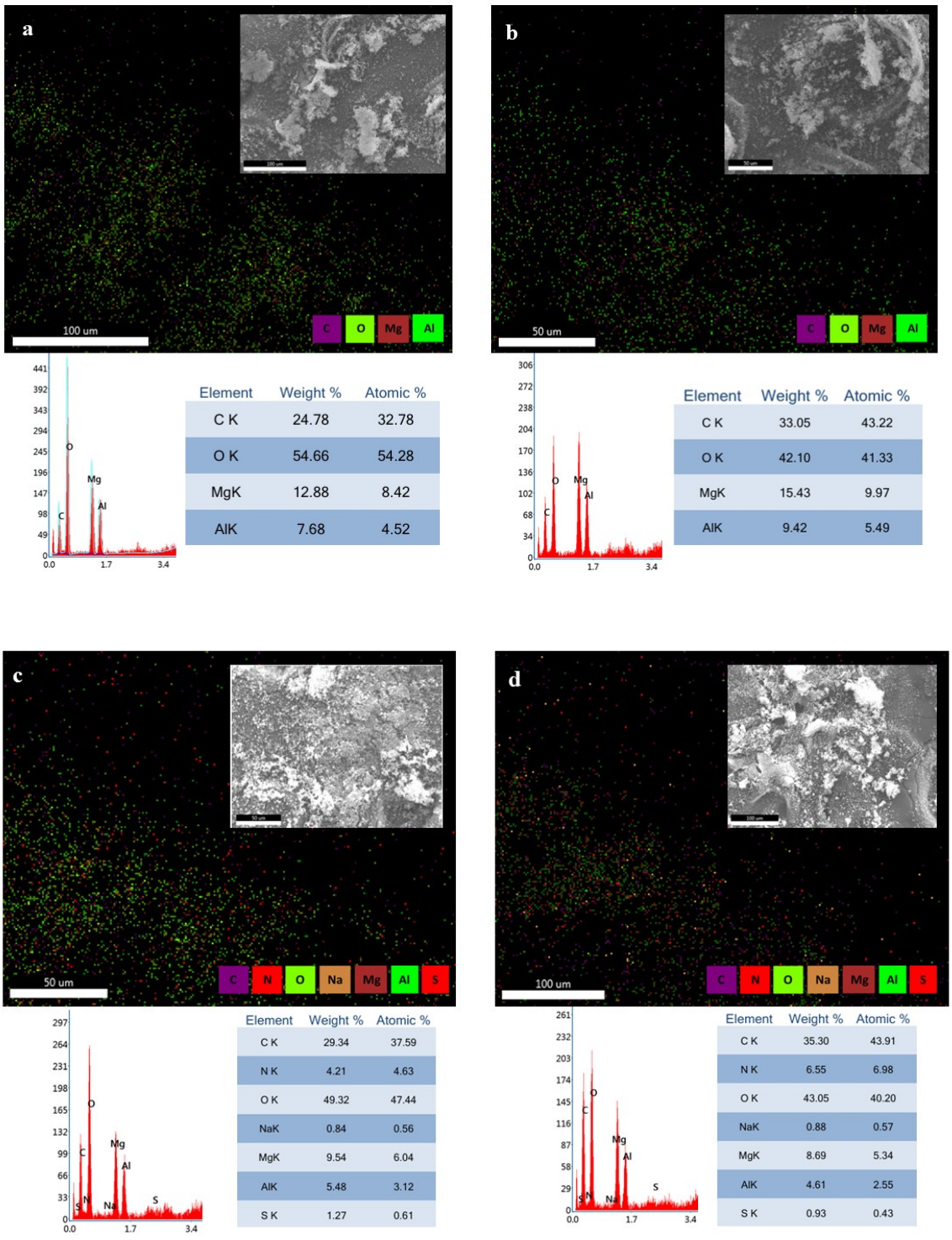


Figure S10. EDX mapping of nanocomposites before and after adsorption of MO dye

(a) MAH and (b) MAO (c) MO-MAH and MO-MAO

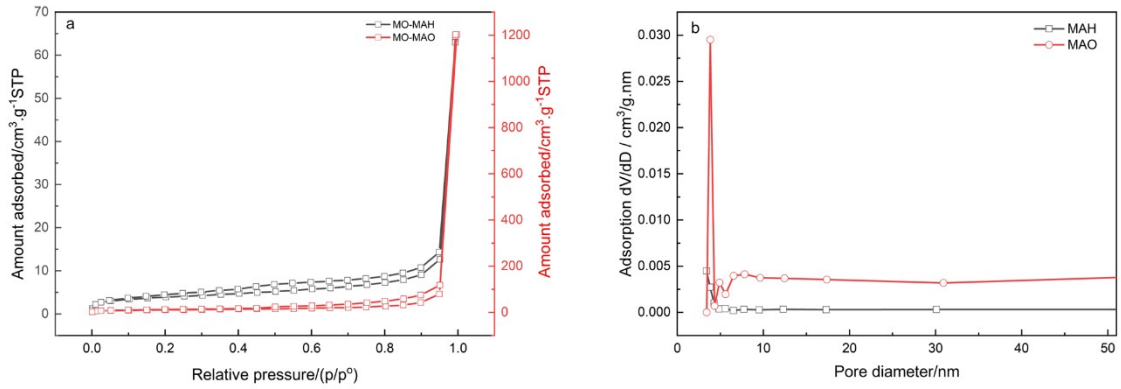


Figure S11. (a) N_2 Adsorption -desorption isotherm and (b) pore size distribution curve of MAH and MAO after MO dye adsorption

Adsorbent	BET Surface Area (m^2/g)	Average Pore Diameter (nm)
MO-MAH	13.844	3.4
MO-MAO	38.180	3.827

Table S3. Textural properties of the material after adsorption

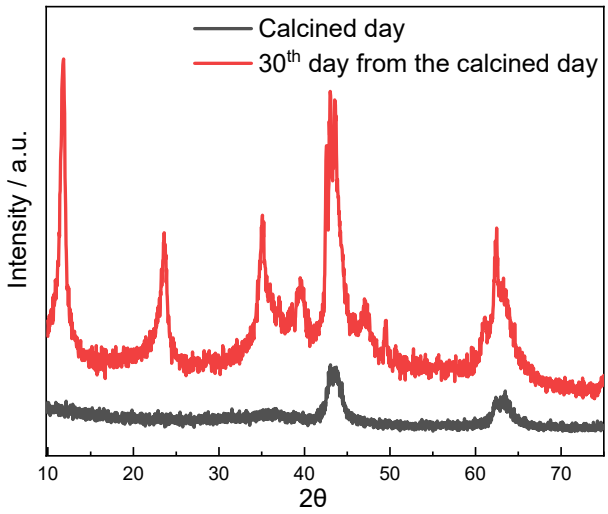


Figure S12. XRD patterns of MAO recorded immediately and 30 days after calcination.

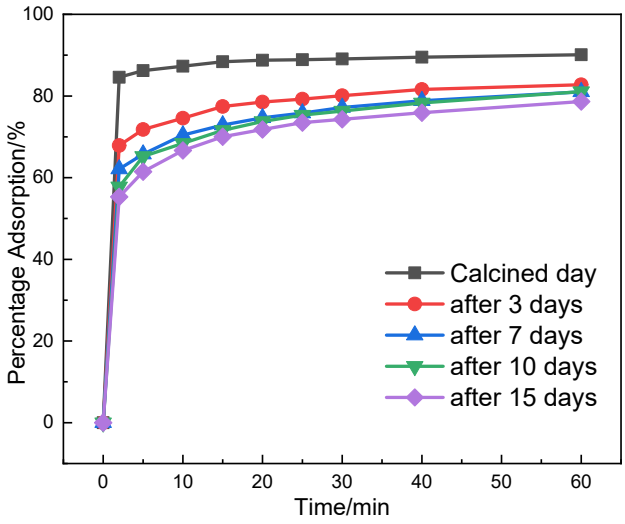


Figure S13. Percentage adsorption of MO dye by MAO measured over different days from the calcination day (Day 1 to Day 15). Experimental conditions: dye concentration = 200 mg/L, adsorbent dose = 30 mg, contact time = 1 hour, temperature = 30 °C.

References

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