Supporting information

**Influence of carbohydrate polymer shaping on organic dye adsorption by a metal-organic framework in water**

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S1. XRF spectra

**Fig. S1** XRF spectra of dried MIL-alg. The molar ratio of Fe and Ca in dried MIL-alg was calculated from calibration curves, which were obtained using standard samples, iron oxide (Fe$_2$O$_3$) and calcium sulfate dihydrate (CaSO$_4$·2H$_2$O), to be Fe:Ca = 1:1.64.
S2. Elemental analysis

**Table S1.** Observed weight percentage of elements in MIL, dried alg and dried MIL-alg.

| Sample  | C (%)  | H (%)  | N (%) | Cl (%) | Others (%) |
|---------|--------|--------|-------|--------|------------|
| MIL     | 33.52  | 2.16   | 0.6   | -      | 63.73      |
| MIL-alg | 32.72  | 3.98   | -     | 0      | 63.34      |
| alg     | 33.52  | 4.27   | -     | -      | 62.24      |

From the results of elemental analysis, the formulas of MIL and dried alg were calculated to be \([\text{Fe}_3\text{O(H}_2\text{O)}_2\text{(OH)}_{0.7}\text{(NO}_3)_{0.3}\text{(1,3,5-benzenetricarboxylate)_2}]\) (C 32.54, H 1.62 and N 0.63 %) and \({\left[\text{Ca(C}_6\text{H}_7\text{O}_6\right]_2}\cdot\text{2H}_2\text{O}\} \) (C 33.81 and H 4.26 %). It was confirmed that dried MIL-alg is free from CaCl\(_2\) and therefore consists of MIL and alg. In addition, nitrogen was not observed in MIL-alg, suggesting that NO\(_3\) anions in MIL are replaced by OH anions during the preparation of MIL-alg beads. Using the composition ratio of Fe:Ca = 1:1.64 (mol) obtained by XRF analysis and the formula of MIL (\([\text{Fe}_3\text{O(H}_2\text{O)}_2\text{(OH)}(1,3,5\text{-benzenetricarboxylate)_2}]\)) and alg (\([\text{Ca(C}_6\text{H}_7\text{O}_6}\right]_2\)), the formula of dried MIL-alg was calculated to be \((\text{MIL})(\text{alg})_{4.92}\text{(H}_2\text{O)}_{14}\) (C 32.77 and H 3.85 %). High hydrophilicity of alginate beads causes rapid uptake of atmospheric water during handling of dried MIL-alg in the atmosphere.
S3. Thermogravimetric curve

Fig. S2 Thermogravimetric curves of (a) MIL, (b) sodium alginate, (c) one MIL-alg (hydrogel) bead and one alg (hydrogel) bead, and (d) enlarged view of Fig. S2(c). The water content in sodium alginate was calculated from the thermogravimetric curve to be 18.02 %, indicating the formula of [Na(C₆H₇O₆)]·2.5H₂O. The amount of MIL included in one MIL-alg bead was calculated from the thermogravimetric curve and the chemical composition of MIL-alg (MIL:alg = 1:4.92) to be 0.15 mg.
S4. N$_2$ adsorption/desorption isotherm and $t$-plot

**Fig. S3** N$_2$ adsorption (closed symbol)/desorption (open symbol) isotherm of MIL at 77 K.

**Fig. S4** N$_2$ adsorption (closed symbols)/desorption (open symbols) isotherms of Orange II adsorbed MIL (red circle) and Rhodamine B adsorbed MIL (purple circle) at 77 K.
The theoretical micropore volumes of dye adsorbed MIL assuming that all dye molecules are adsorbed to the outer surface of MIL were calculated using the following equation,

$$V_{\text{theor}} = \frac{V_{\text{MIL}}}{1 + m_{\text{dye}}}$$

where $V_{\text{theor}}$ is the theoretical micropore volume of dye adsorbed MIL ($\text{cm}^3/\text{g}$), $V_{\text{MIL}}$ is the observed micropore volume in MIL ($\text{cm}^3/\text{g}$) and $m_{\text{dye}}$ is the mass of adsorbed dye (g). The adsorption amounts of dyes were determined in the same procedure described in the main text. $V_{\text{exp}}$, which is the experimental micropore volume ($\text{cm}^3/\text{g}$), was calculated from $t$-plots (Fig. S5). The theoretical dye adsorption amounts were calculated using $V_{\text{theor}}$ and the dimensions of dye molecules shown in Fig. 5.
Theoretical dye adsorption amounts (see Table S2) were lower than the experimental values (424 and 164 mg/g for Orange II and Rhodamine B, respectively) probably because of overestimated molecular dimensions of dyes and removal of adsorbed dyes during the washing process.

The external surface area of MIL was calculated from the \( t \)-plot. The theoretical monolayer adsorption amounts of dyes on external surface of MIL were calculated using the external surface area and maximum cross-sectional areas of dye molecules estimated from the dimensions in Fig. 5.

Table S2: Micropore volumes, theoretical micropore volumes and theoretical dye adsorption amounts.

|                          | MIL     | Orange II adsorbed | Rhodamine B adsorbed |
|--------------------------|---------|--------------------|----------------------|
| Micropore volume (cm\(^3\)/g) | 0.55    | 0.19               | 0.28                 |
| Theoretical micropore volume (cm\(^3\)/g) | -       | 0.37               | 0.48                 |
| Theoretical dye adsorption amount (mg/g) | -       | 277                | 100                  |

Theoretical monolayer adsorption amounts of dyes on external surface of MIL.

Table S3: External surface area of MIL and theoretical monolayer adsorption amounts of dyes on external surface of MIL.

| External surface area (m\(^2\)/g) | Theoretical monolayer adsorption amount of Orange II (mg/g) | Theoretical monolayer adsorption amount of Rhodamine B (mg/g) |
|----------------------------------|-----------------------------------------------------------|-------------------------------------------------------------|
| 73.57                            | 29.15                                                     | 23.90                                                       |
S5. SEM-EDX analysis

Fig. S6 (a) SEM image and (b-e) EDX maps ((b) C, (c) Fe, (d) O and (e) Ca) of dried MIL-alg.

Table S4. Weight percentage data obtained from the EDX analysis (Fig. S6).

|       | C (%) | O (%) | Ca (%) | Fe (%) |
|-------|-------|-------|--------|--------|
| MIL-alg | 33.89 | 37.32 | 16.48  | 12.3   |
Table S5. Weight percentage data obtained from the point analysis (Fig. S7).

| Point | C (%) | O (%) | Ca (%) | Fe (%) |
|-------|-------|-------|--------|--------|
| 1     | 42.92 | 40.08 | 13.07  | 3.94   |
| 2     | 40.33 | 38.57 | 7.60   | 13.51  |
| 3     | 38.92 | 34.65 | 20.14  | 6.29   |
| 4     | 33.06 | 35.61 | 23.74  | 7.59   |
| 5     | 30.74 | 32.09 | 27.51  | 9.65   |
| 6     | 32.63 | 36.79 | 24.79  | 5.80   |
S6. UV-vis absorption spectra

**Fig. S8** UV-vis spectral change of aqueous Orange II solution (15 mg/L) in the presence of (a) alg (10 beads), (b) MIL-alg (10 beads) and (c) MIL (10 mg).
Fig. S9 UV-vis spectral change of aqueous Rhodamine B solution (15 mg /L) in the presence of (a) alg (10 beads), (b) MIL-alg (10 beads) and (c) MIL (10 mg).
### S7. Comparison of adsorption amounts on various adsorbents for Orange II and Rhodamine B

#### Table S6. Orange II and Rhodamine B adsorption amounts on previously reported adsorbents.

| Dye          | Adsorbent                              | Surface area (m²/g) | Adsorption amount (mg/g) | Temperature (°C) | pH | Reference |
|--------------|----------------------------------------|---------------------|--------------------------|------------------|----|-----------|
| Orange II    | [Cu(4,4'-bipyridine)Cl]₂               | 6.8                 | 921                      | 27               | —  | (51)      |
|              | [Cu(4,4'-bipyridine)(SO₄)]₂            | 5.3                 | 3308                     | 27               | —  | (51)      |
|              | Hexadecyltrimethylammonium              | —                   | 38.96                    | 30               | 10 | (52)      |
|              | bromide-coated zoelite                  | —                   | 105.9                    | 25               | 20 | (52)      |
|              | Polyamine/bentonite nanocomposite       | 7.5                 | 152.7                    | 30               | 20 | (53)      |
|              | Zirconium-based chitosan microcomposite | 6.24                | 920                      | 30               | 20 | (54)      |
|              | Cationic surfactant modified biochar    | —                   | 29.1                     | 35               | 70 | (55)      |
|              | pyrolyzed from cornstalk                | —                   | 182.7                    | 30               | 70 | (56)      |
|              | Kapok fiber oriented polyamine          | 21.9                | 82.93                    | 30               | 7  | (57)      |
|              | Aluminum oxide nanoparticle              | 82.91               | 97.0                     | 30               | —  | (58)      |
|              | MIL-100(Fe)                            | 2037                | 410                      | 25               | 3.0| (59)      |
|              | MIL                                      | 1286                | 424                      | 30               | 6.9| This work|
|              | MIL-alg                                 | —                   | 541                      | 30               | 6.9| This work|
| Rhodamine B  | Waste of seeds of Aleurites Moluccana   | —                   | 82                       | 25               | 6  | (59)      |
|              | Treated rice husk-based activated carbon| 892                 | 478.5                    | 30               | —  | (60)      |
|              | Graphite oxide                          | 71.5                | 576                      | 30               | —  | (61)      |
|              | MnFe₂O₄ nanoparticles                   | 52.99               | 9.3                      | 25               | 10.5| (62)   |
|              | MIL-68(Al)                              | 97/6                | 1111.1                   | —                | —  | (63)      |
|              | Modified zeolite                        | —                   | 4.41                     | 30               | 7  | (64)      |
|              | Nanoscale MIL-100(Fe)                   | 1.24                | 73                       | 35               | —  | (65)      |
|              | Hierarchical SnS₂ nanosheet             | 43.6                | 200                      | 25               | —  | (66)      |
|              | MIL                                      | 1286                | 164                      | 30               | 5.5| This work|
|              | MIL-alg                                 | —                   | 161                      | 30               | 5.5| This work|
S8. XPS analysis

**Fig. S10** XPS spectra of (a) Fe $2p_{3/2}$ in MIL, Orange II adsorbed MIL and Rhodamine B adsorbed MIL and (b) Fe $2p_{3/2}$ in MIL-alg, Orange II adsorbed MIL-alg and Rhodamine B adsorbed MIL-alg.
S9. Pseudo first-order, pseudo second-order and pseudo $n$th-order model analysis for dye adsorption on MIL and MIL-alg
**Fig. S11** Pseudo first-order, pseudo second-order and pseudo nth-order model analysis for dye adsorption at 30 °C. (a) Orange II adsorption on MIL, (b) Orange II adsorption on MIL-alg, (c) Rhodamine B adsorption on MIL and (d) Rhodamine B adsorption on MIL-alg. The red, blue and green lines represent fitting curves for the pseudo first-order, pseudo second-order and pseudo nth-order models, respectively.
S10. Adsorption isotherm models, affinity distribution function and adsorption kinetic models

The adsorption isotherms were fitting using the Langmuir-Freundlich (LF) model (equation S1),\(^\text{17,18}\)

\[
q_e = \frac{q_m a C_e^n}{1 + a C_e^n} \quad (S1)
\]

where \(q_e\) is the adsorption amount (mg/g), \(q_m\) is the theoretical maximum adsorption amount (mg/g), \(a\) is the affinity constant and \(n\) is the heterogeneity parameter with the range from 0 to 1 and \(C_e\) is the equilibrium concentration (mg/L).

The affinity distribution analysis based on the LF model was performed using the equation S2,\(^\text{17,18}\)

\[
N_i = q_m a n (1/K_i)^n \times \frac{(1 + 2a(1/K_i)^n + a^2(1/K_i)^{2n} + 4a(1/K_i)^n n^2 - a^2(1/K_i)^{2n} n^2 - n^2)}{(1 + a(1/K_i)^n)^4} \quad (S2)
\]

where \(N_i\) is the number of adsorption sites and \(K_i\) is the association constant. \(K_i\) has the range between \(K_{\text{max}} = 1/C_{\text{min}}\) and \(K_{\text{min}} = 1/C_{\text{max}}\), in which \(C_{\text{min}}\) and \(C_{\text{max}}\) are the maximum and minimum equilibrium concentrations, respectively.

The adsorption kinetic analysis was performed using the following pseudo first-order (eq S3), pseudo second-order (equation S4) and pseudo nth-order (equation S5) models,\(^\text{19,20}\)

\[
q_t = q_e [1 - \exp (- k_1 t)] \quad (S3)
\]

\[
q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (S4)
\]

\[
q_t = q_e - [(n - 1)kt + q_e^{(1-n)}]^{1/(1-n)} \quad (S5)
\]

where \(q_t\) is the adsorption amount at time \(t\) (mg/g), \(q_e\) is the equilibrium adsorption amount (mg/g), \(k_1\), \(k_2\) and \(k\) are the kinetic rate constants and \(n\) is the reaction order.

The adsorption kinetic data were also analyzed using the following two-compartment kinetic model (equation S6),\(^\text{21}\)

\[\text{16}\]
\[ q_e = q_{fast} \left[ 1 - \exp(-k_{fast}t) \right] + q_{slow} \left[ 1 - \exp(-k_{slow}t) \right] \]  

(S6)

where \( q_{fast} \) and \( q_{slow} \) are the adsorption amounts of dye per gram of MIL (mg/g) at time \( t \) (min) of fast and slow adsorption, respectively, and \( k_{fast} \) and \( k_{slow} \) are the adsorption rate constants (1/min).
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