# Supplementary Information

## Durable and Recyclable MOF@Polycaprolactone Mixed-Matrix Membrane with Hierarchical Porosity for Wastewater Treatment

*Amal Hani, Rana R. Haikal*, Worood A. El-Mehalmey, Youssef Safwat, and Mohamed H. Alkordi*

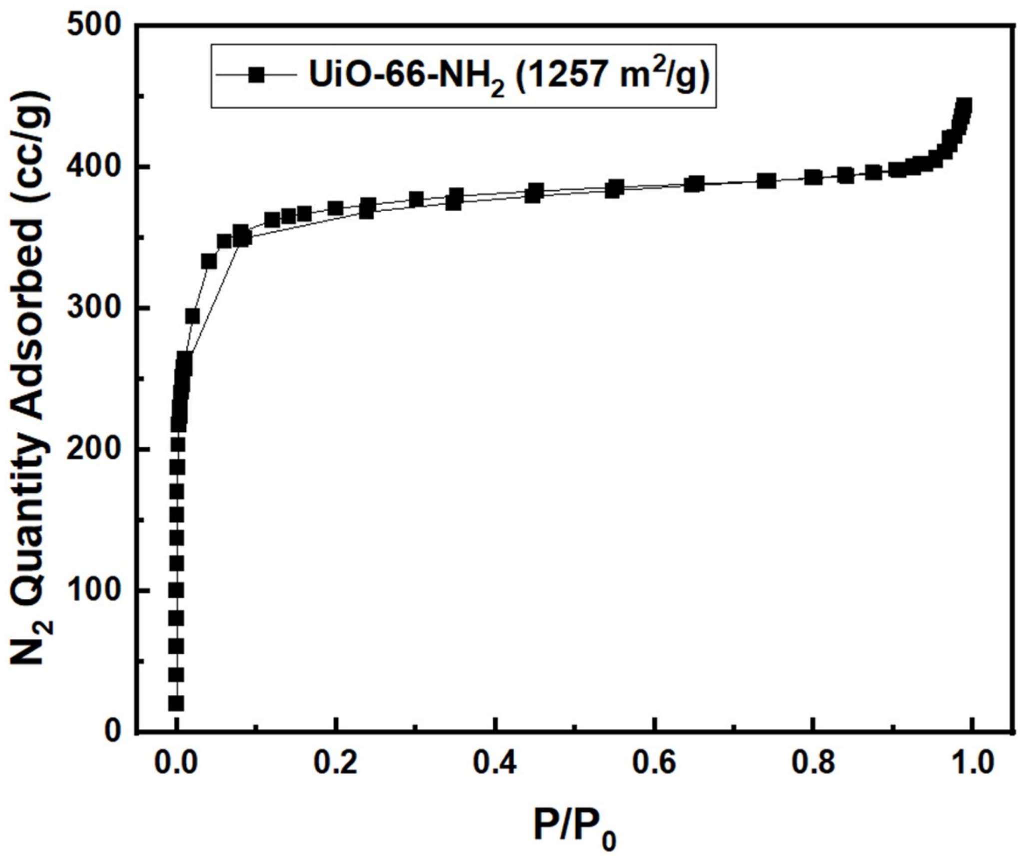
Center for Materials Science, Zewail City of Science and Technology, Ahmed Zewail road, October Gardens, 6th of October City, Giza, Egypt

* rraouf@zewailcity.edu.eg

## Methods

### Synthesis of UiO-66-$NH_2$

In a clean vial, 2-aminoterephthalic acid (**271.5 mg**) was sonicated in 10 ml DMF for 10 minutes to which was then added a separately prepared solution of $ZrCl_4$ (**251.3 mg)** in 10 ml DMF and 2 ml conc. HCl 37 %. The vial was capped and the mixture was left in oven at 80°C for 24 h. The solid was then filtered under vacuum through a membrane filter and washed with ACN, then exchanged in ACN at 80°C for 24 hrs. The solid was then filtered under vacuum and dried in oven at 80°C for 24 hrs. **(Yield = 192 mg, Yellow Solid)**. Successful synthesis was confirmed via FTIR spectroscopy, XRD powder diffraction, as well as $N_2$ adsorption isotherm measurement and BET surface area calculation (Figure below).




### Preparation of PCL Control Membranes

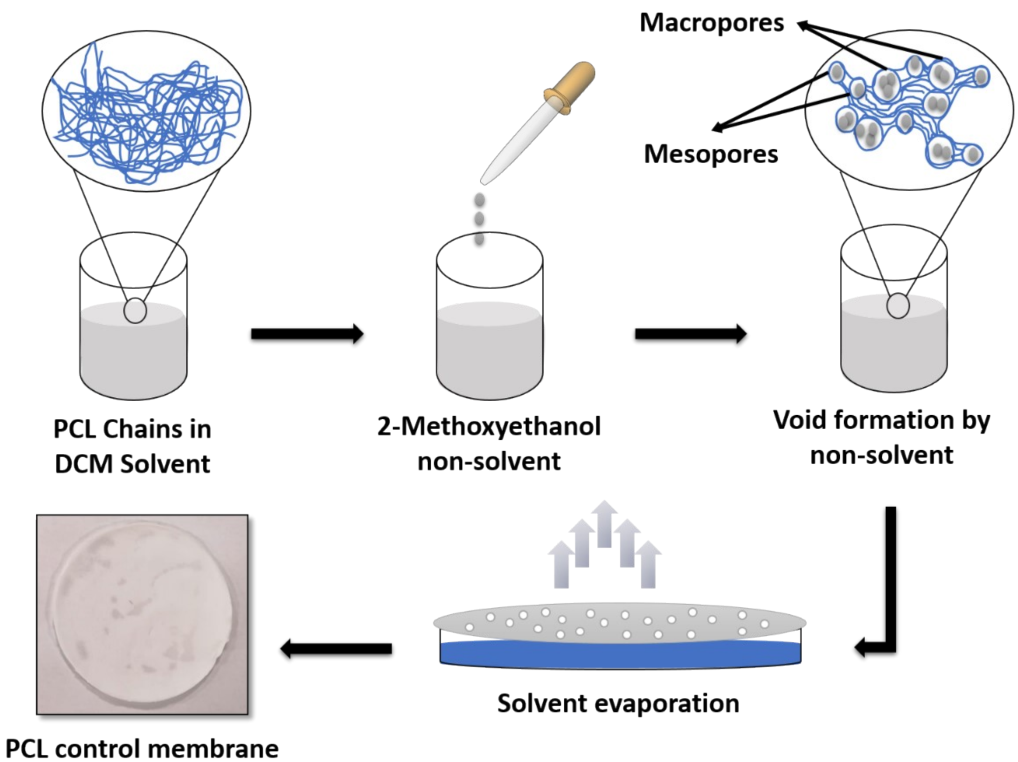
In a vial, 10 wt% of PCL was added to DCM: 2-MethoxyEtOH solvent mixture and left to stir at rt overnight. The solution was casted onto a petri dish and covered with perforated parafilm and left to dry slowly at rt overnight. The formed membrane was cut into pieces and dried under vacuum for 30 min for further characterization. Different ratios of the DCM: 2-MethoxyEtOH solvent mixture were prepared according to **Table S1.**

**Table S1.** Preparation of PCL control membranes with different solvent:non-solvent ratio of DCM: 2-MethoxyEtOH solvent mixture.

| DCM: 2-MethoxyEtOH | DCM Volume (mL) | 2-MethoxyEtOH Volume (mL) | Weight of PCL (mg) |
|---|---|---|---|
| **100:0** | 10 | 0 | |
| **70:30** | 7 | 3 | |
| **50:50** | 5 | 5 | 1000 |
| **30:70** | 3 | 7 | |
| **0:100** | 0 | 10 | |

**Due uptake and recyclability study of 5% MOF@PCL MMM using filtration setup**

This study was performed using a stainless steel membrane filtration setup with an automated syringe pump at a fixed flow rate of 1 mL/min. The membrane is fitted into the filtration setup, where it is pre-treated with 5 mL of distilled water, followed by 5 mL of MOF activation solution (NaOH pH ~ 10 for MB and 0.1 M HCl pH ~ 1.5 for MO), then finally washed with another 5 mL of distilled water. Immediately, 5 mL of respective dye solution was passed through the membrane at a flow rate of 1 mL/min. The effluent was then collected and its concentration was determined using UV-Vis spectrophotometry. Initial concentrations of standard dyes were measured and designated cycle 0, after which concentrations of filtrate solution was employed. For breakthrough experiments, similar procedure was employed using dye solutions of 5 ppm concentration and flow rate of 0.5 mL/min. Regeneration of 5% MOF@PCL MMM was carried out via a washing step between consecutive cycles by passing 5 mL of MOF activation solution followed by 5 mL of distilled water. This process was repeated for 10 cycles, where the concentration of remaining dye in the filtrate was measured after each cycle using UV-Vis spectrophotometry.




**Scheme S1.** Preparation of porous PCL control membranes.

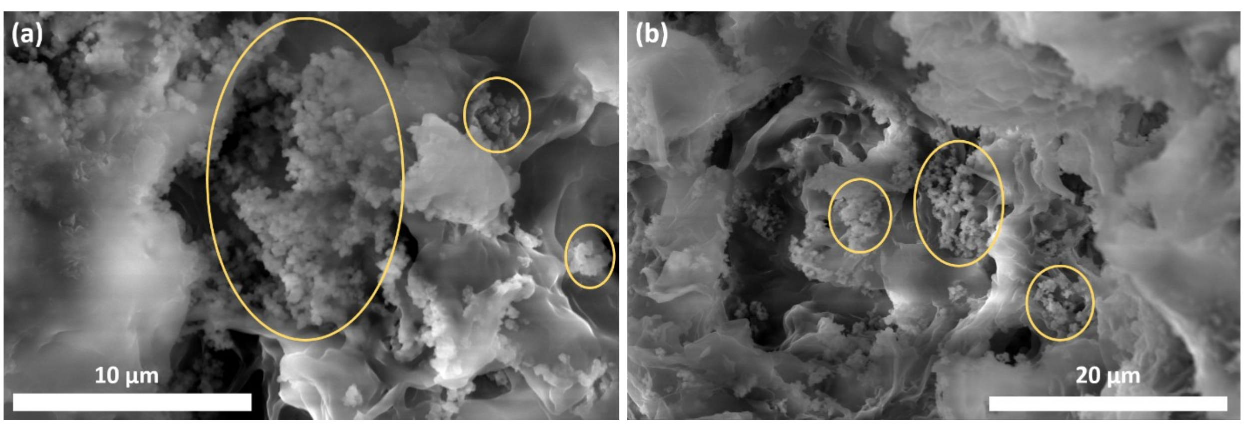



**Figure S1.** SEM images of 10 wt% MOF@PCL from the top view (a) and cross-sectional view (b) demonstrating the inhomogeneous distribution and aggregation of MOF NPs (yellow circles) within the PCL polymeric matrix.

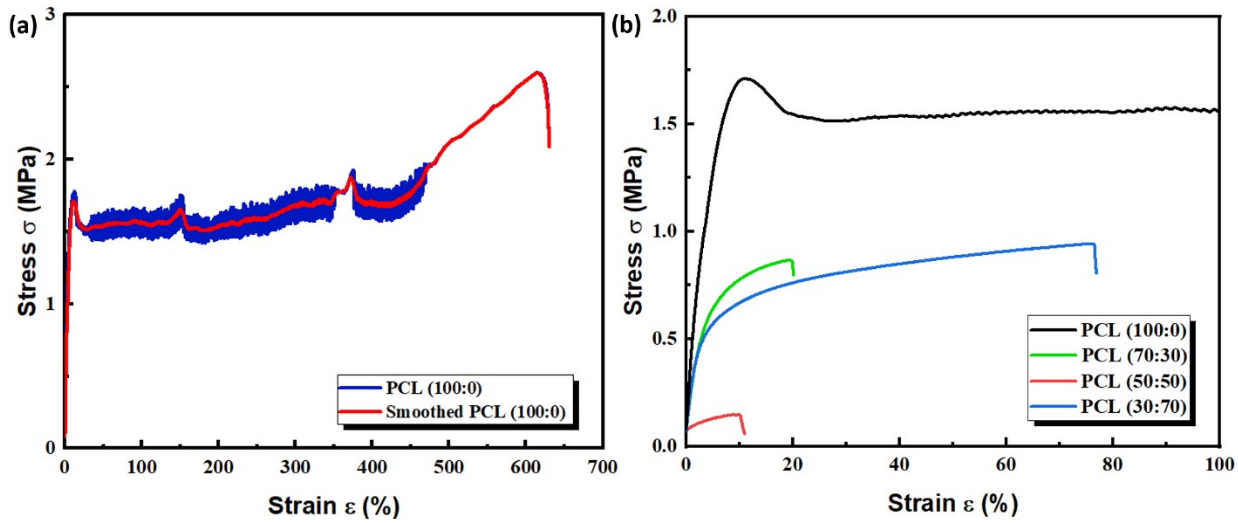



**Figure S2.** (a) Stress-strain curve of PCL(100:0) before and after smoothing, and (b) Stress-strain curves of PCL membranes fabricated using different ratios of DCM:2-methoxyethanol solvent:non-solvent mixture.

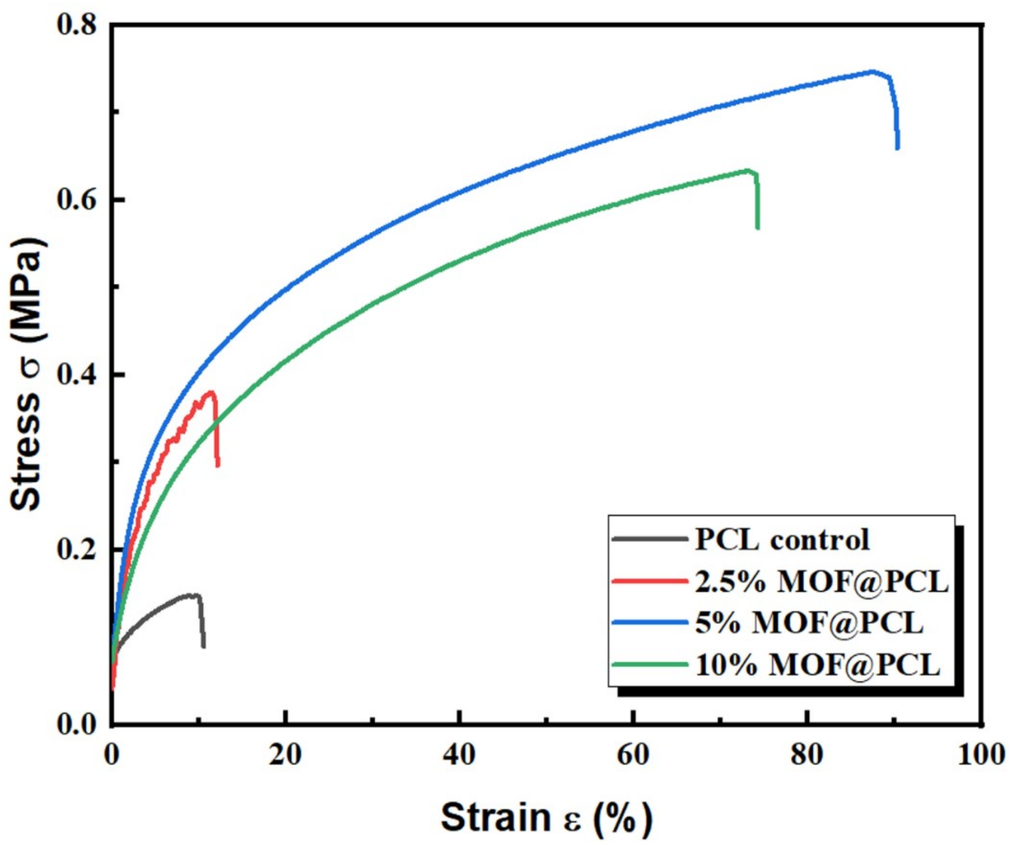



**Figure S3.** Stress-strain curves of PCL control membrane and MOF@PCL MMMs.

**Table S2.** Average densities and porosity values of prepared PCL control membranes. Density of PCL ($\rho_0$) was taken to be 1.145 g/cm$^3$.

| | | Density, $\rho$ (g/cm$^3$) | Porosity %, $\varepsilon$ |
|---|---|---|---|
| **PCL control membranes** | 100:0 | 1.127 | 1.6 |
| | 70:30 | 0.311 | 72.9 |
| | 50:50 | 0.209 | 81.7 |
| | 30:70 | 0.947 | 17.3 |

**Table S3.** Tensile properties of PCL control membranes with different solvent:non-solvent ratio of DCM:2-methoxyethanol solvent mixture and MOF@PCL MMMs with different MOF wt%.

| | | Break stress (MPa) | Maximum elongation % | Young's modulus (MPa) |
|---|---|---|---|---|
| **PCL control membranes** | 100:0 | 2.596 | 615 | 0.3467 |
| | 70:30 | 0.866 | 19 | 0.2123 |
| | 50:50 | 0.148 | 10 | 0.0337 |
| | 30:70 | 0.943 | 76 | 0.2634 |
| **MOF@PCL MMMs** | 2.5 wt% | 0.380 | 11 | 0.0933 |
| | 5 wt% | 0.746 | 88 | 0.0955 |
| | 10 wt% | 0.633 | 73 | 0.0588 |

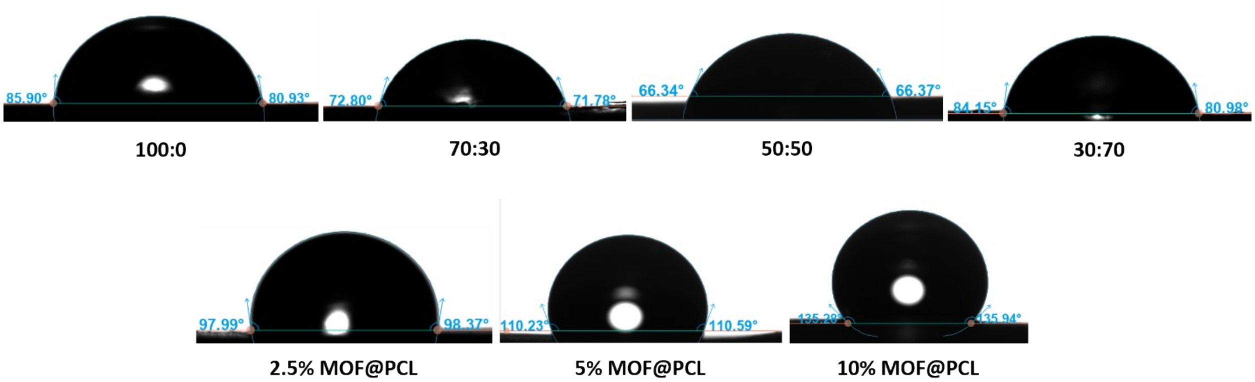



**Figure S4.** Water contact angle images of PCL membranes with different DCM: 2-MethoxyEtOH ratios and MOF@PCL MMMs with different MOF wt%.

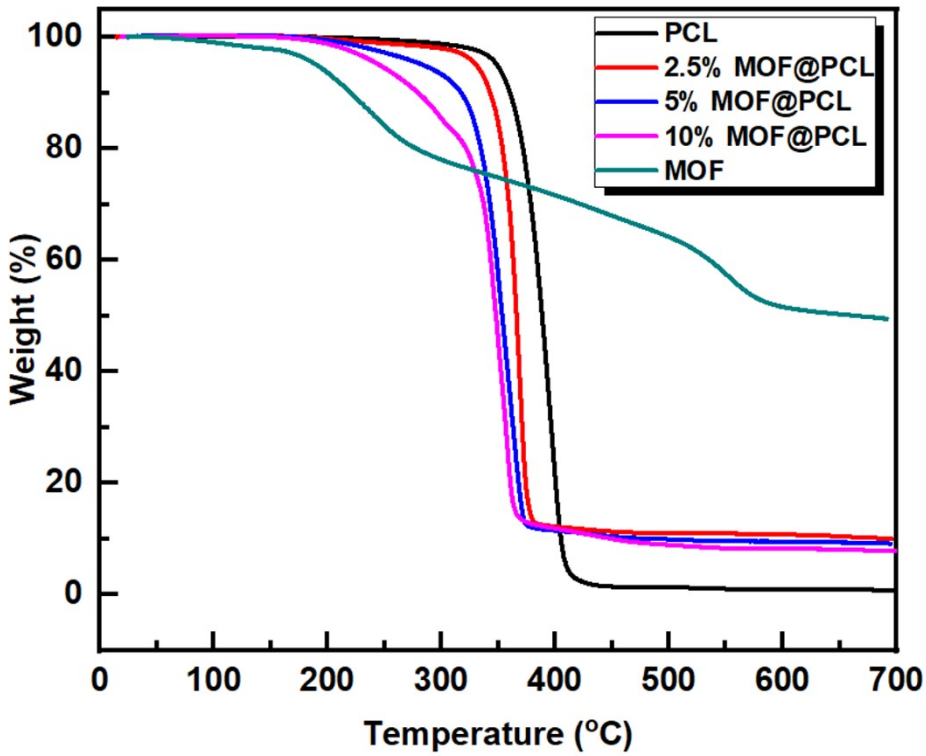



**Figure S5.** TGA profiles of PCL control membrane, UiO-66-$NH_2$ MOF, and MOF@PCL MMMs with different MOF wt%

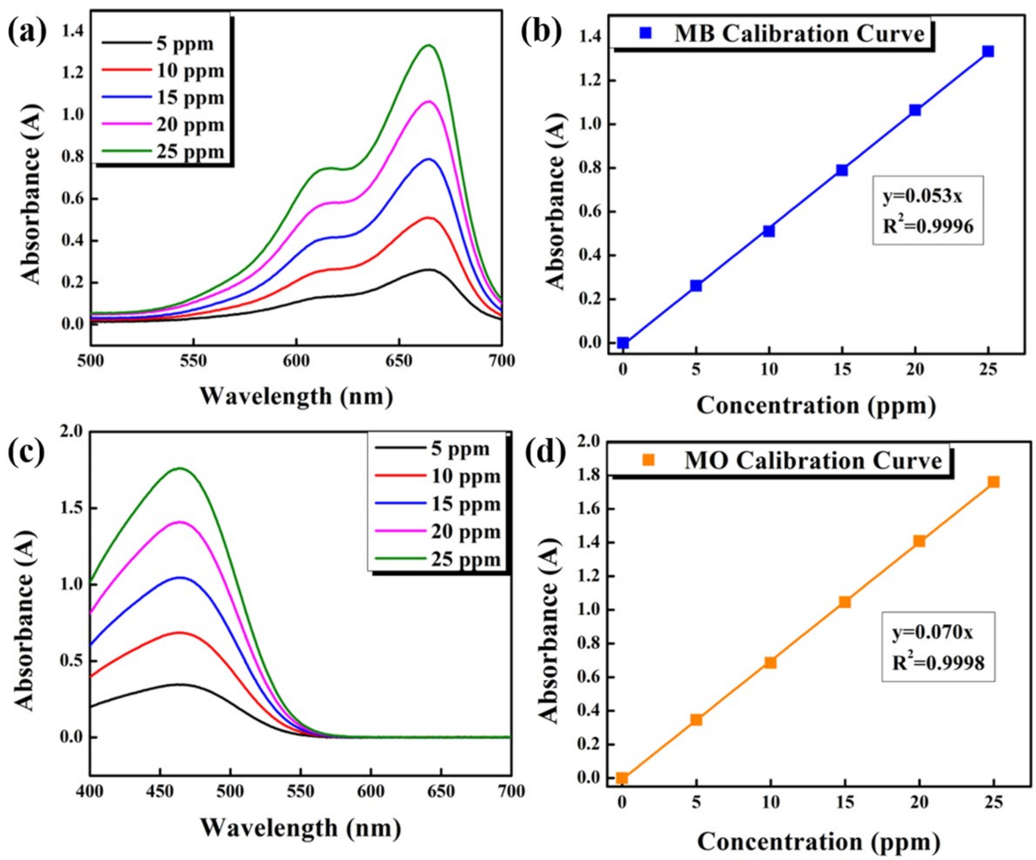



**Figure S6.** (a and b) UV-Vis spectra and calibration curve for MB (at pH = 11), respectively and (c and d) UV-Vis spectra and calibration curve for MO (at pH = 7), respectively.

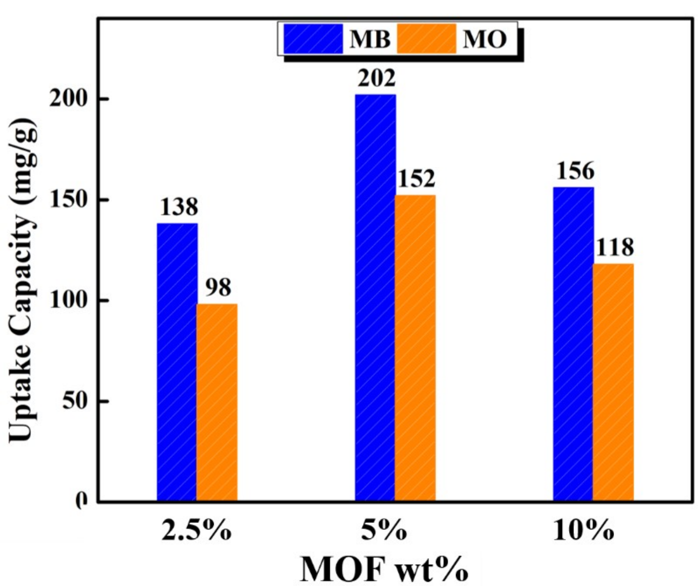



**Figure S7.** Adsorption capacities of MOF@PCL MMMs with different MOF wt% for MB and MO after passing dye solution of 600 ppm concentration.

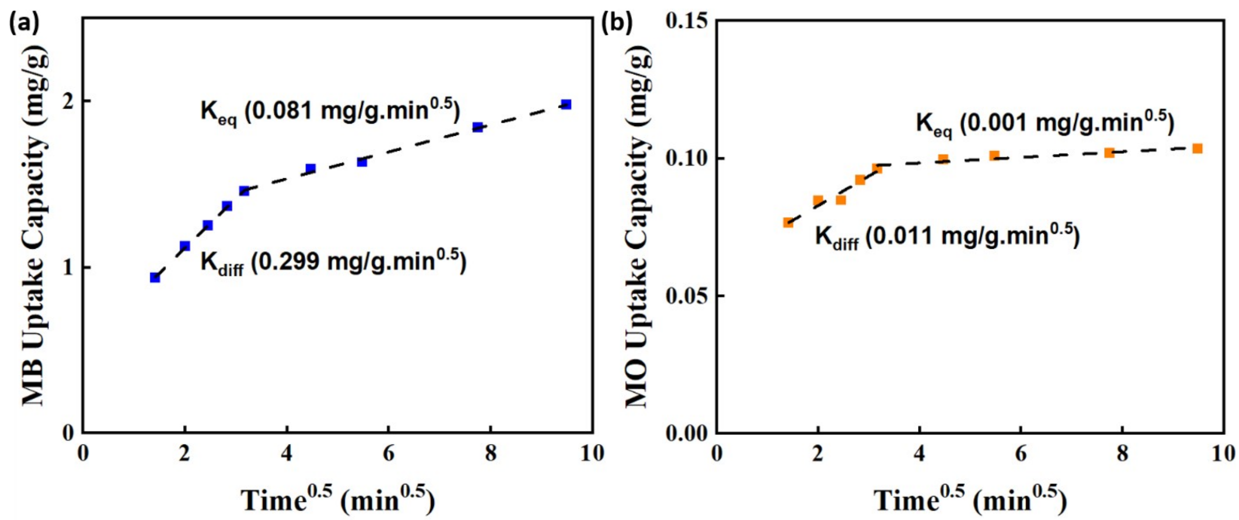



**Figure S8.** Intraparticle diffusion plots of MB (a) and MO (b) adsorption by PCL control membrane at 298 K.

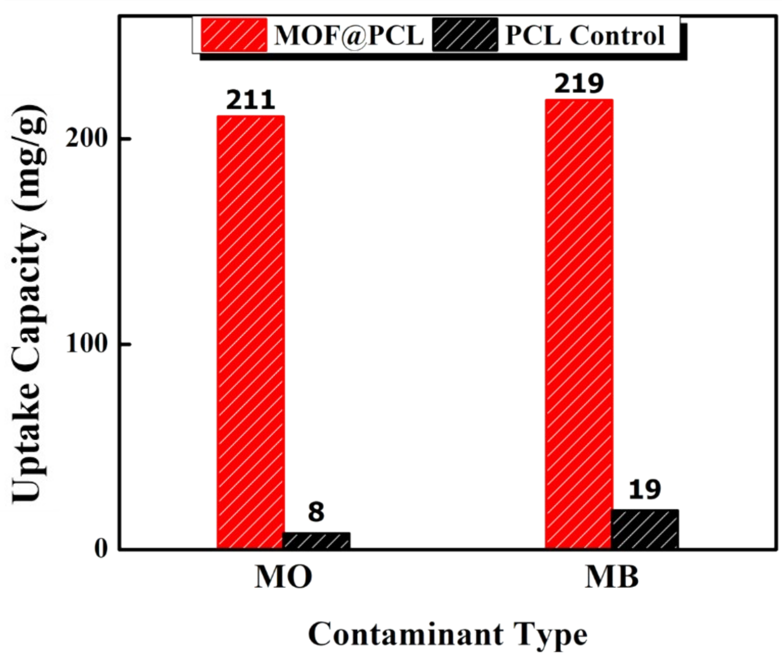



**Figure S9.** Comparison of maximum adsorption capacities of 5% MOF@PCL MMM and PCL control membrane for MB and MO.

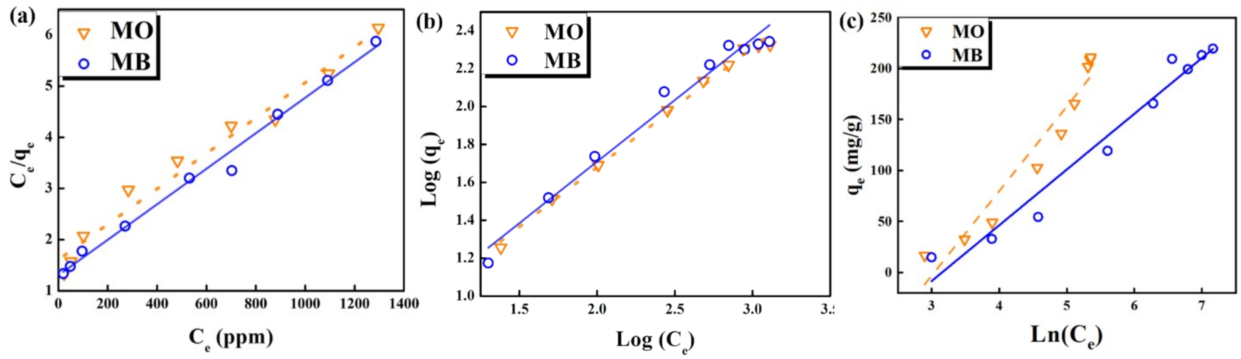



**Figure S10.** Linear adsorption isotherm plots fitted by (a) Langmuir, (b) Freundlich, and (c) Temkin models to investigate uptake behavior of 5% MOF@PCL MMM towards MB and MO.

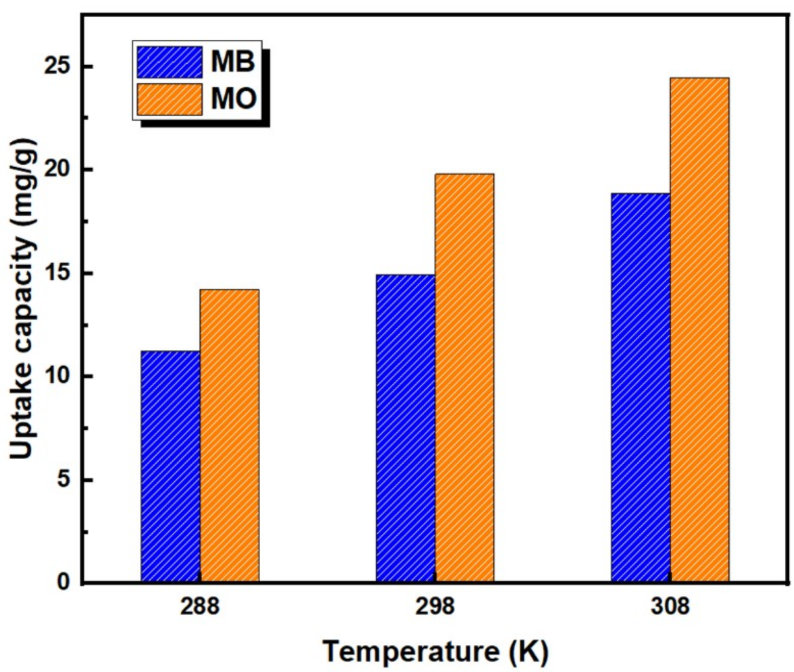



**Figure S11.** Uptake capacities of MB and MO by 5% MOF@PCL MMM at different temperatures using 25 ppm initial dye concentration.

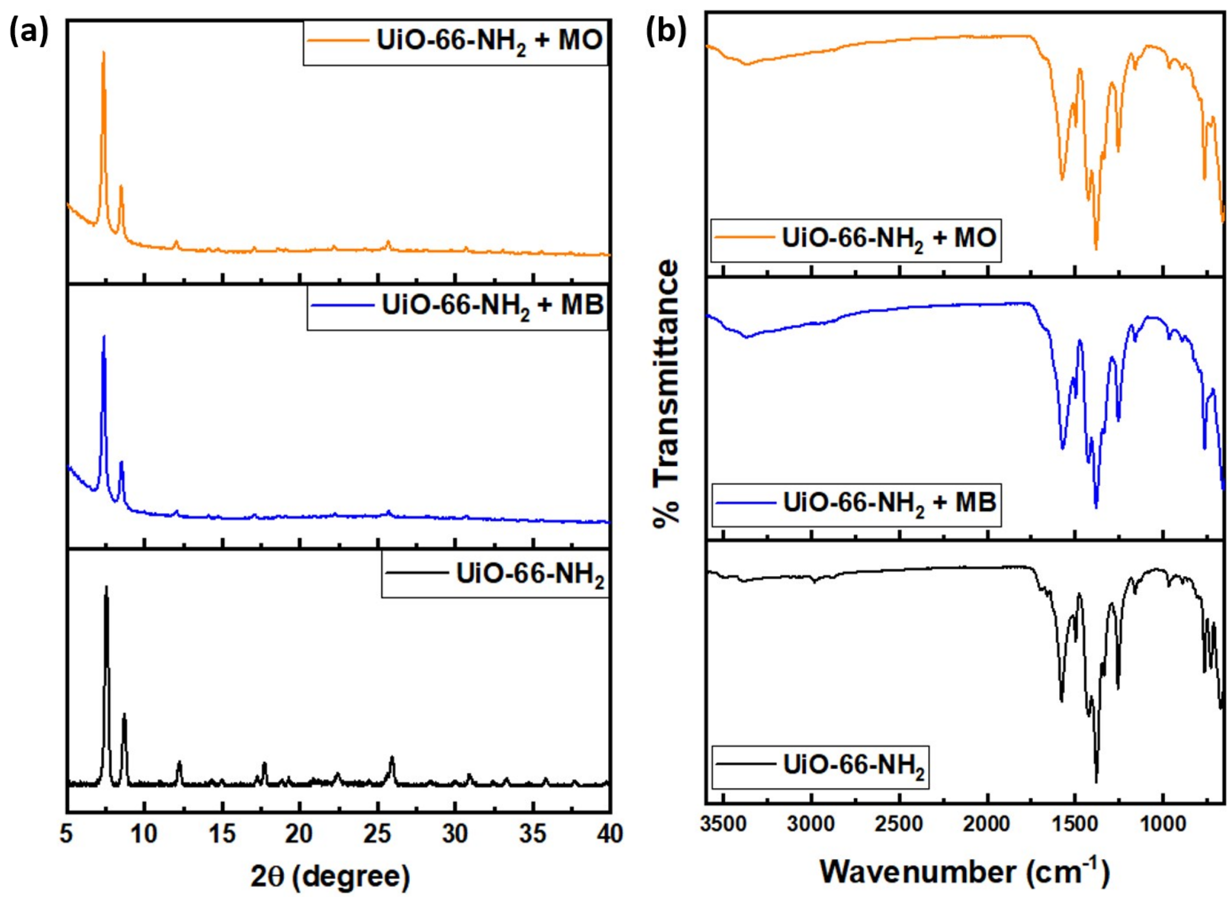



**Figure S12.** XRD patterns (a) and FTIR spectra (b) of UiO-66-$NH_2$ before and after dye uptake.

**Table S4.** Adsorption capacities for dye removal by MOF-polymer MMMs.

| MOF-polymer MMM | MOF wt% | Adsorption capacity (mg/g) | | Ref. |
|---|---|---|---|---|
| | | MB | MO | |
| UiO-66@PSF | 9 | 86 | 94 | [1] |
| UiO-66-$NH_2$@CA | 10 | 345 | 587 | [2] |
| UiO-66@PANI | 10 | - | 432 | [3] |
| Chitosan@UiO-66 | 95 | - | 370 | [4] |
| MIL-140C-2NMe$^+$@PVDF | 67 | - | 300 | [5] |
| MIL-68(Al)@PVDF | 6 | 74[a] | - | [6] |
| PDA/ZIF-67@PP | - | 92.3%[b] | 99.5%[b] | [7] |
| **UiO-66-$NH_2$@PCL** | **5** | **309** | **208** | **This work** |

[a] Units in μg/cm$^2$, [b] Dye removal % values were reported rather than adsorption capacities

## References

[1] S. Ahmadipouya, S.A. Mousavi, A. Shokrgozar, D.V. Mousavi, Improving dye removal and antifouling performance of polysulfone nanofiltration membranes by incorporation of UiO-66 metal-organic framework, Journal of Environmental Chemical Engineering 10(3) (2022) 107535. https://doi.org/https://doi.org/10.1016/j.jece.2022.107535.
[2] W.A. El-Mehalmey, Y. Safwat, M. Bassyouni, M.H. Alkordi, Strong Interplay between Polymer Surface Charge and MOF Cage Chemistry in Mixed-Matrix Membrane for Water Treatment Applications, ACS Applied Materials & Interfaces 12(24) (2020) 27625-27631. https://doi.org/10.1021/acsami.0c06399.
[3] K. Mirzaei, E. Jafarpour, A. Shojaei, H. Molavi, Facile Synthesis of Polyaniline@UiO-66 Nanohybrids for Efficient and Rapid Adsorption of Methyl Orange from Aqueous Media, Industrial & Engineering Chemistry Research 61(32) (2022) 11735-11746. https://doi.org/10.1021/acs.iecr.2c00919.
[4] R. Ediati, W. Aulia, B.A. Nikmatin, A.R.P. Hidayat, U.M. Fitriana, C. Muarifah, D.O. Sulistiono, F. Martak, D. Prasetyoko, Chitosan/UiO-66 composites as high-performance adsorbents for the removal of methyl orange in aqueous solution, Materials Today Chemistry 21 (2021) 100533. https://doi.org/https://doi.org/10.1016/j.mtchem.2021.100533.
[5] J. Liu, K. Yu, X. Han, J. Yu, W. Xiang, D. Zhao, B. Chen, Cationic Zr-based metal-organic framework via post-synthetic alkylation for selective adsorption and separation of anionic dyes, Materials Today Chemistry 24 (2022) 100897. https://doi.org/10.1016/j.mtchem.2022.100897.
[6] Y. Tan, Z. Sun, H. Meng, Y. Han, J. Wu, J. Xu, Y. Xu, X. Zhang, A new MOFs/polymer hybrid membrane: MIL-68(Al)/PVDF, fabrication and application in high-efficient removal of p-nitrophenol and methylene blue, Separation and Purification Technology 215 (2019) 217-226. https://doi.org/https://doi.org/10.1016/j.seppur.2019.01.008.
[7] N. Li, G. Chen, J. Zhao, B. Yan, Z. Cheng, L. Meng, V. Chen, Self-cleaning PDA/ZIF-67@PP membrane for dye wastewater remediation with peroxymonosulfate and visible light activation, Journal of Membrane Science 591 (2019) 117341. https://doi.org/https://doi.org/10.1016/j.memsci.2019.117341.