

*Electronic Supplementary Information*

**MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) modified  $\alpha$ -alumina membranes for efficient adsorption of dyes from organic solvents**

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## **S1 Experimental**

### **S1.2 Chemicals and materials**

All chemicals were purchased from Sigma-Aldrich, unless otherwise indicated. Aluminum (III) nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), terephthalic acid, 2-aminoterephthalic acid and acetic acid were used for the MOF preparation. All water used is Milli-Q water. N,N-Dimethylformamide (DMF) and methanol were used for washing the MOF powders. Rose Bengal ( $\text{C}_{20}\text{H}_2\text{Cl}_4\text{I}_4\text{Na}_2\text{O}_5$ ), methanol and iso-propanol were used for adsorption experiments. Flat disc-shaped  $\alpha$ -alumina membranes (having a diameter of 39 mm, a thickness of 2 mm, and a pore diameter of 80 nm) were purchased from Pervatech B.V., The Netherlands.

### **S1.3 Synthesis of MIL-53(Al) and $\text{NH}_2$ -MIL-53(Al) seeds**

The MIL-53 and  $\text{NH}_2$ -MIL-53 membranes were prepared on an  $\alpha$ -alumina support by the reactive seeding (RS) method, where the alumina support works as metal source reacted with organic ligand to growth a seed layer directly. A typical RS method contains two steps, (i) seed layer growth and (ii) secondary MOF layer growth. For the seed growth, 0.5 g of  $\text{H}_2\text{BDC}$  (3 mmol) or  $\text{NH}_2\text{-H}_2\text{BDC}$  (2.7 mmol), 55 ml water and 0.5 ml acetic acid were mixed and stirred vigorously for 15 min. The resulting mixture was further dispersed by sonication for 15 min. Then, the solution was transferred into a Teflon-lined stainless steel autoclave containing an  $\alpha$ -alumina support that was placed vertically. The autoclave was sealed and heated at 120 °C for two days and then cooled down to room temperature. The  $\alpha$ -alumina membrane reacted with the organic ligand and was rinsed with ethanol three times and dried in an oven at 60 °C for 24 h and further referred to as seed layer membrane.

### **S1.4 Synthesis of MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) membranes through secondary growth**

Secondary growth steps for the synthesis of the MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) membranes are slightly different. For the MIL-53(Al) membrane, typically 3.0 g (8.0 mmol) Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 0.72 g (4.3 mmol) H<sub>2</sub>BDC was dispersed in 55 ml water and then loaded into an autoclave, in which the seed layer membrane was fixed vertically and heated at 160 °C for 24 h. After cooling the autoclave, the MIL-53(Al) membrane was washed with ethanol three times and then dried at 90° C under vacuum.

For the synthesis of the NH<sub>2</sub>-MIL-53(Al) membrane, 2.0 g (5.3 mmol) Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 0.5 g (2.7 mmol) NH<sub>2</sub>-H<sub>2</sub>BDC were dispersed in 55 ml water. Again, the resulting mixture was loaded into an autoclave containing a seed layer membrane positioned vertically and was then heated at 80 °C for 72 h. The washing and drying steps are as reported for the MIL-53(Al) membrane.

In addition, the MOF powders synthesized during the second growth step were collected from the bottom of the autoclave. Subsequently, the powders were thoroughly activated in DMF at 140 °C K for 12 h and methanol at 90 °C K for 15 h. The powders were washed with acetone and dried at 120 °C under vacuum.

## **S2 Materials characterization**

### **S2.1 XRD, FE-SEM and TEM**

To confirm the formation of MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al), XRD measurements were carried out. The XRD patterns of the membranes and MOF powders were obtained with a Bruker D8 advance diffractometer by using Co-K $\alpha$  at room temperature. The measurement

covers a scan range of  $2\theta = 5^\circ$  to  $50^\circ$  with a scan speed of 0.2 s per step and step size of  $0.02^\circ$  in a continuous scanning mode. XRD peaks were assigned using Diamond Software (Diamond 4.5.2, Crystal Impact GbR, Bonn, Germany) and CCDC data from the Table S2. FE-SEM images were acquired to observe the morphology of MOF membranes and powders. The gold-coated samples were placed in a Nova NanoSEM 450 (Thermo Fisher Scientific) with an accelerating voltage of 10 kV. TEM analysis was carried out with JEOL JEM-2010 microscope operated at 200 kV.

## **S2.2 N<sub>2</sub> and CO<sub>2</sub> adsorption-desorption experiments**

N<sub>2</sub> and CO<sub>2</sub> adsorption isotherms of MOFs particles and membranes were recorded with a Tristar II 3020 (Micromeritics) setup at 77 and 295 K, respectively. Prior to the measurements, at least 150 mg of MOF powder was degassed at 423 K under vacuum for 16 h and subsequently used for adsorption measurements.

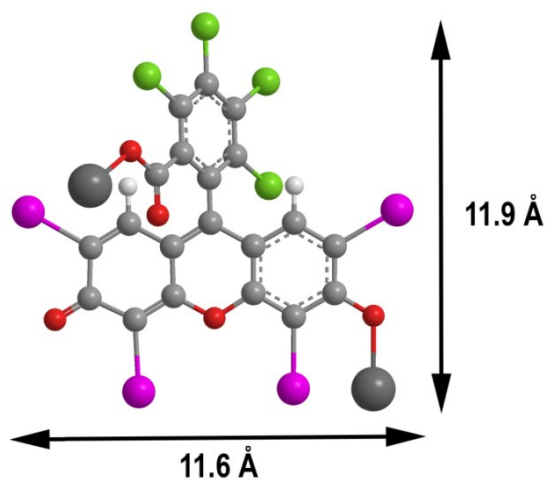
## **S2.3 Dye adsorption performance of MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) membranes**

Membrane performance was tested in a typical stainless steel dead-end pressure cell at a transmembrane pressure (TMP) of 6 bar at room temperature. The system is pressurized using inert argon. During the filtration, the feed solution was stirred at 100 rpm using a magnet stirrer. The membrane cell was filled with 240 ml of feed solution per membrane and different samples of 10 ml were collected for each membrane at the permeate side. The membrane permeability was calculated according to Equation <sup>1</sup>,

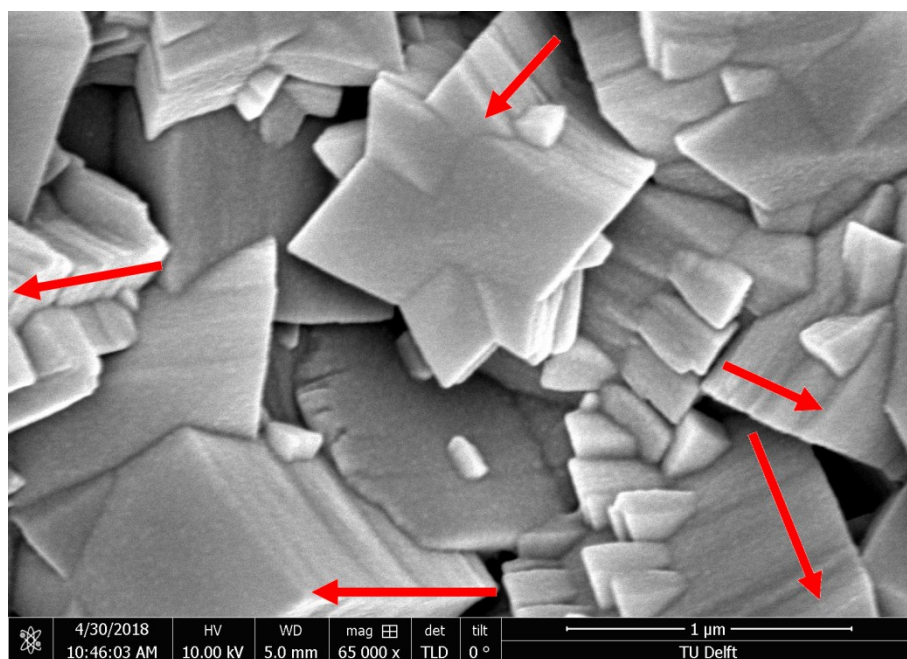
$$\text{Permeability} = \frac{J}{\Delta P} = \frac{V}{\Delta P A t} = [L m^{-2} h^{-1} bar^{-1}] \quad (1)$$

where  $J$  is the solvent flux [ $\text{L m}^{-2} \text{ h}^{-1}$ ],  $\Delta P$  is the applied pressure across the membrane [bar],  $V$  is the permeate volume [L],  $A$  is the effective membrane surface area [ $\text{m}^2$ ] and  $t$  is the collecting permeate sample time [h]. The solutes concentration in the permeate ( $C_{\text{permeate}}$ ) and initial concentration in the feed ( $C_{\text{feed}}$ ) were measured using a double-beam UV-Vis spectrophotometer (Shimadzu, UV-1800).

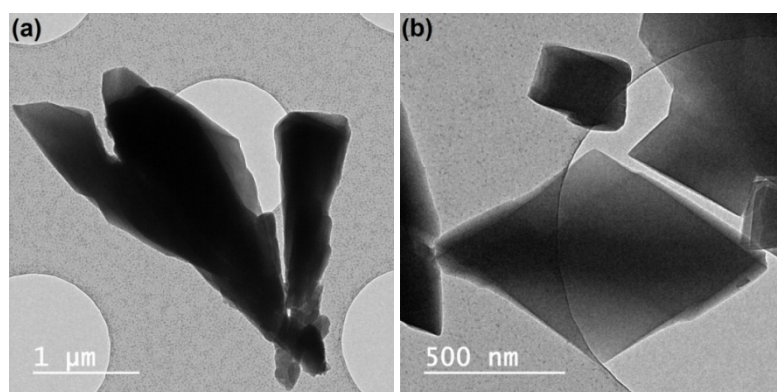
## S2.3 Figures and tables



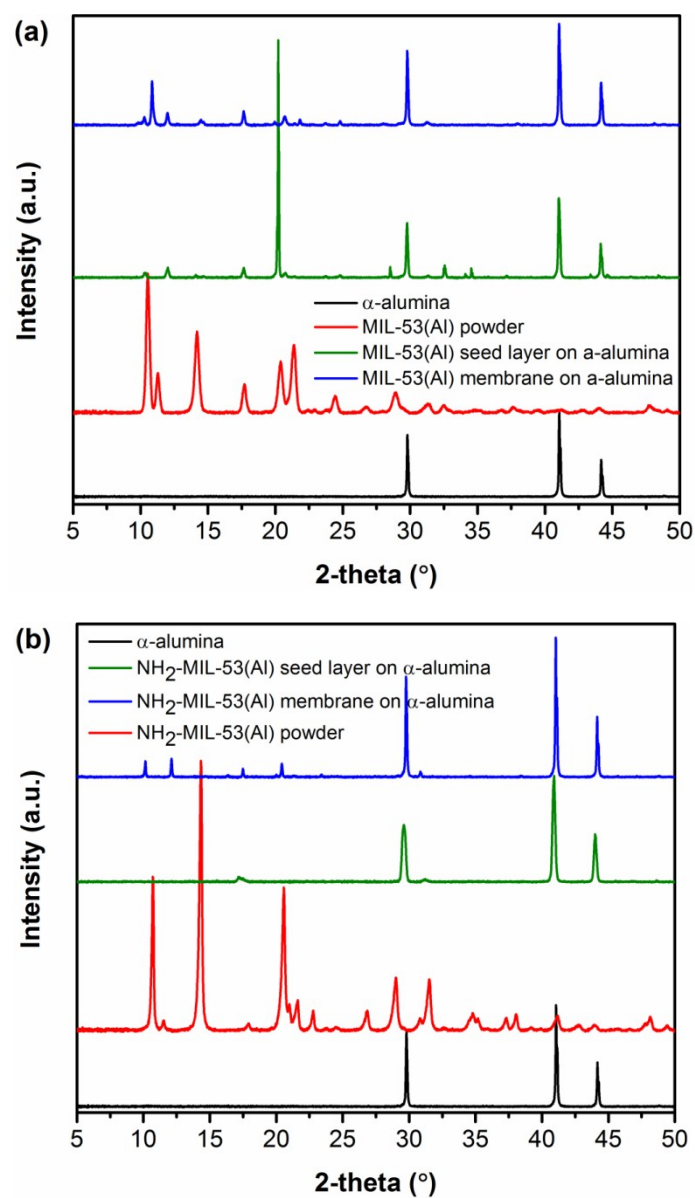
**Scheme S1.** Molecular structure of Rose Bengal (RB) and its overall dimensions.



**Figure S1.** High magnification FE-SEM surface images of NH<sub>2</sub>-MIL-53(Al) membranes. Arrows indicate the growing directions.



**Figure S2.** TEM images of (a) MIL-53(Al) and (b) NH<sub>2</sub>-MIL-53(Al) particles collected from the autoclave.

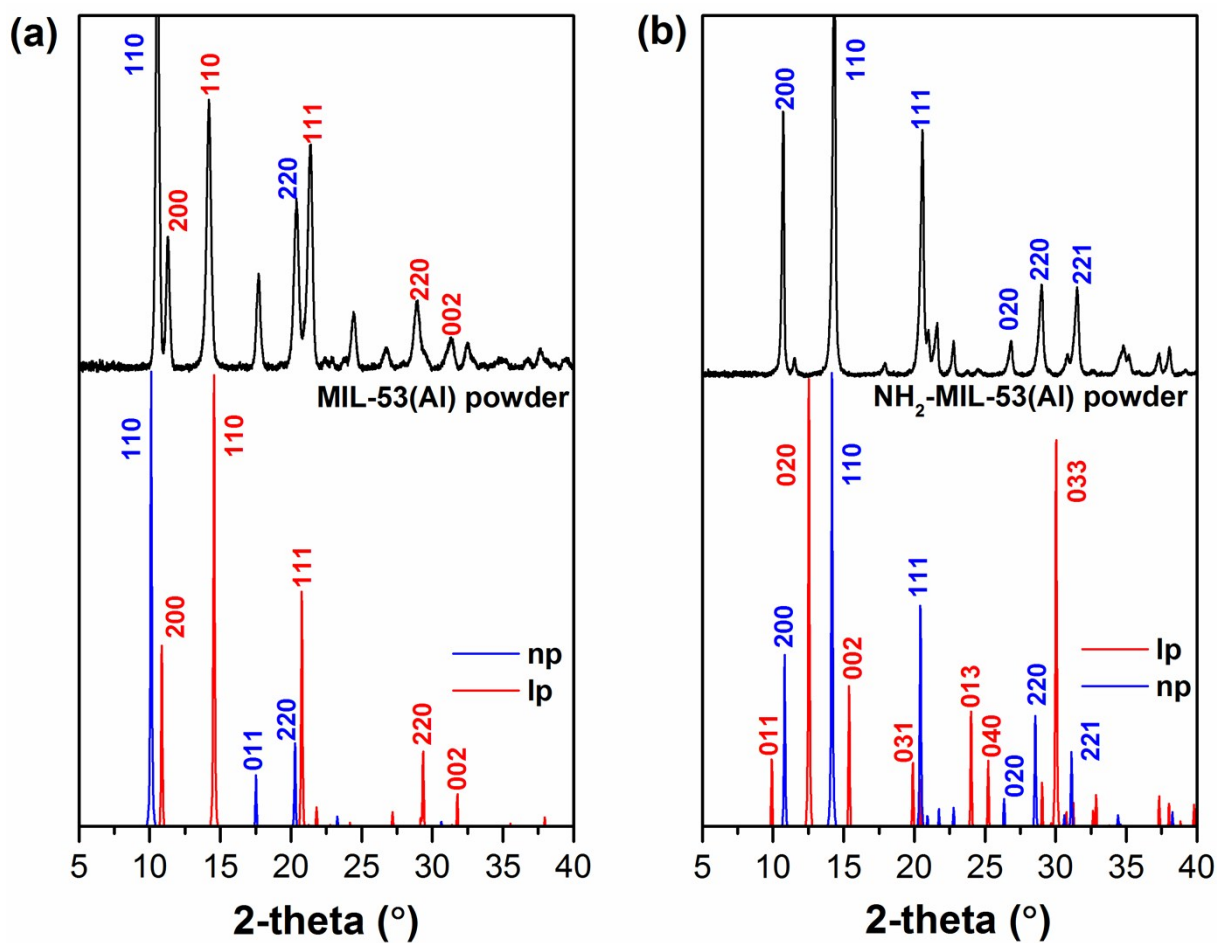


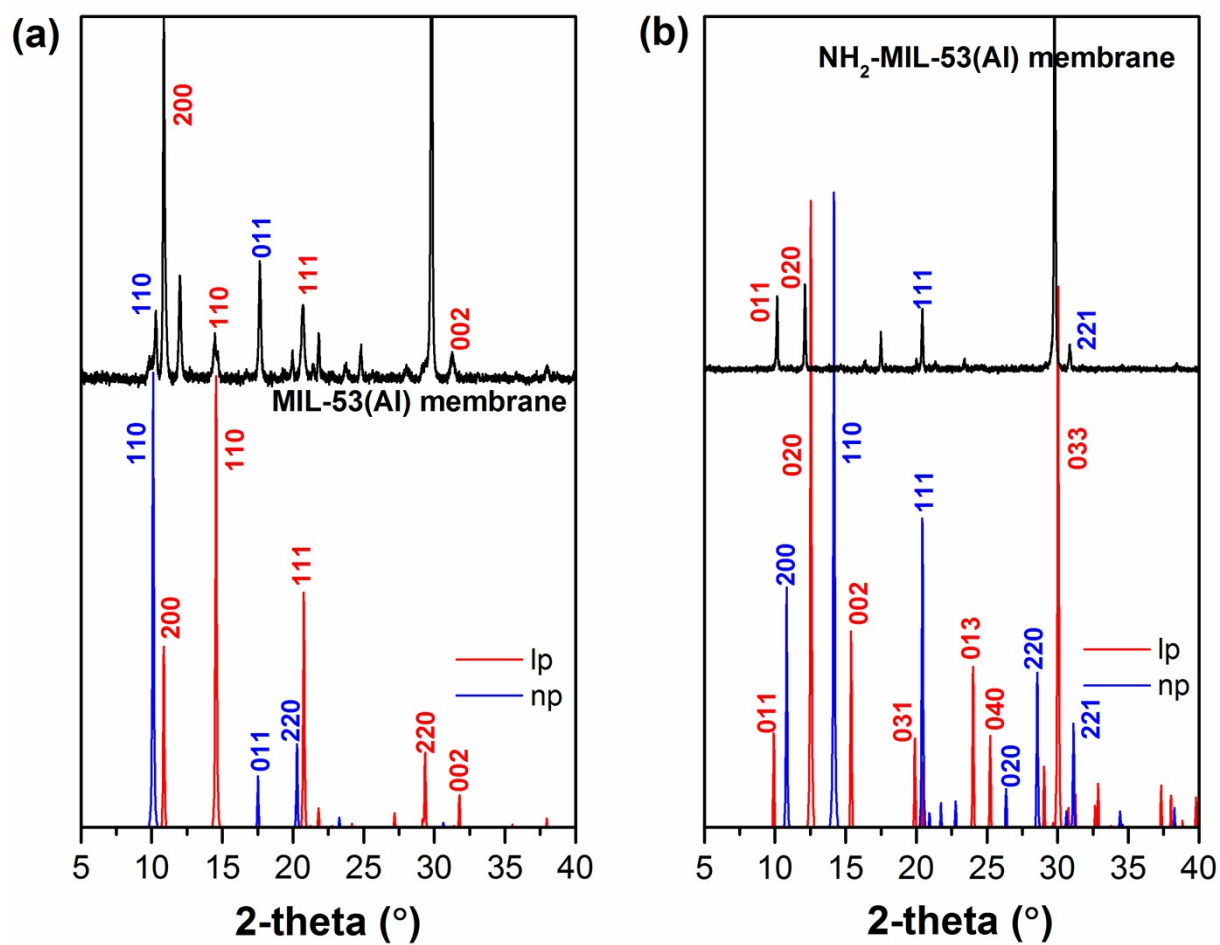
**Figure S3.** XRD patterns of (a) MIL-53(Al) and (b) NH<sub>2</sub>-MIL-53(Al) powders and membranes.



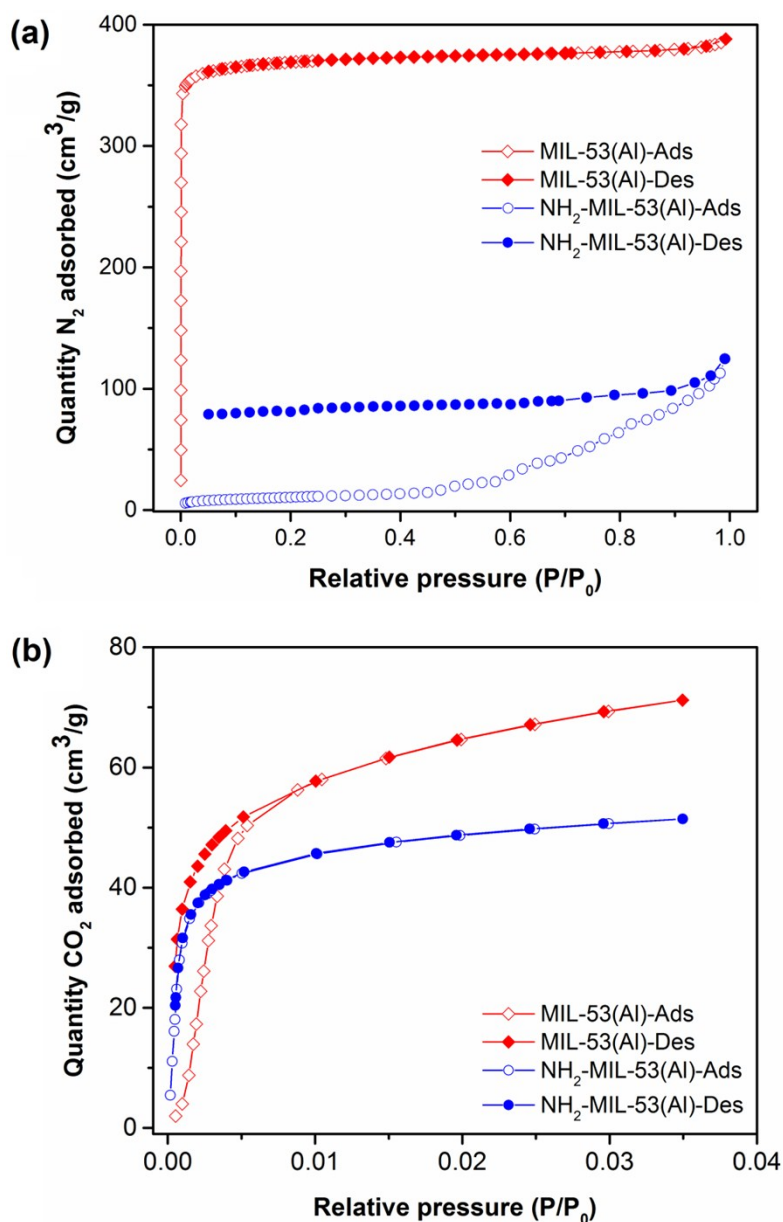
**Table S2.** CCDC codes of MOFs used in this study.

MOF	Chemical formula	CCDC	Ref.
MIL-53(Al)	$\text{Al}(\text{OH})[\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2]$	lp: 220477, np: 220476	<sup>2</sup>
$\text{NH}_2$ -MIL-53(Al)	$\text{Al}(\text{OH})[\text{O}_2\text{C}-\text{C}_6\text{H}_3\text{NH}_2-\text{CO}_2]$	lp: 847255, np: 847256	<sup>3</sup>

**Figure S4.** Experimental and simulated XRD patterns of (a) MIL-53(Al) and (b)  $\text{NH}_2$ -MIL-53(Al) powders.

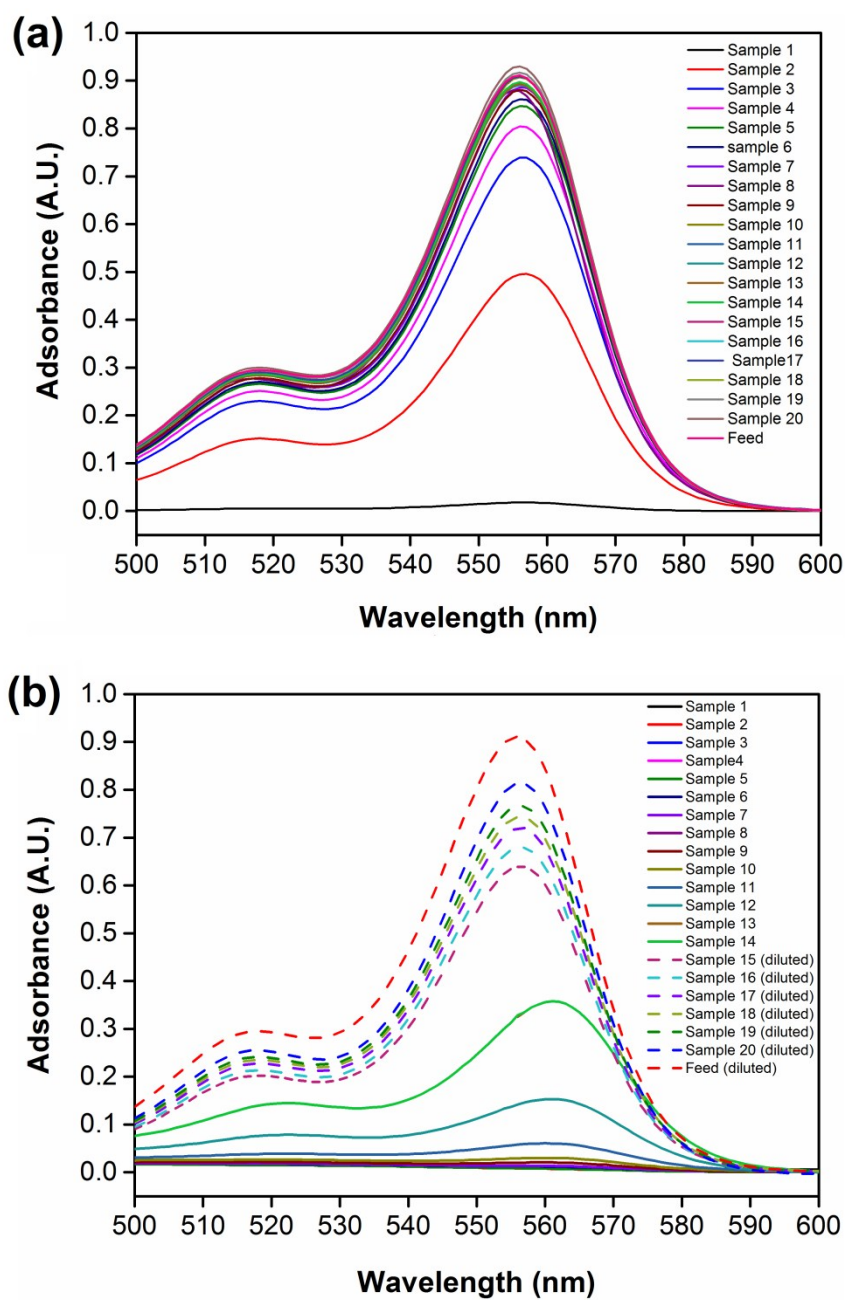


**Figure S5.** Experimental and simulated XRD patterns of (a) MIL-53(Al) and (b) NH<sub>2</sub>-MIL-53(Al) membrane.



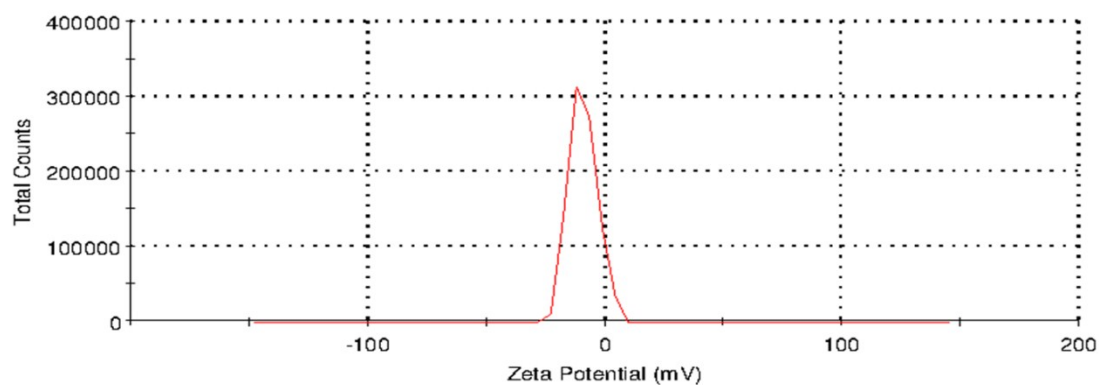
**Figure S6.** Experimental  $N_2$  (a) and  $CO_2$  (b) adsorption (open symbols) and desorption (solid symbols) of MIL-53(Al) and  $NH_2$ -MIL-53(Al).

$N_2$  and  $CO_2$  adsorption-desorption isotherms of MIL-53(Al) and  $NH_2$ -MIL-53(Al) powders are presented in Figure S6. MIL-53(Al) exhibits a reversible, Type-I  $N_2$  isotherm (Figure 6S a), indicating the microporous nature of this material.  $N_2$  could not adsorb in the  $NH_2$ -MIL-53(Al) powders as it presents in the np form (Figure S4 b)<sup>4, 5</sup>.  $CO_2$  adsorption-desorption isotherms of MI-53(Al) and  $NH_2$ -MIL-53(Al) powders at low pressure are in agreement with literature<sup>5</sup>.

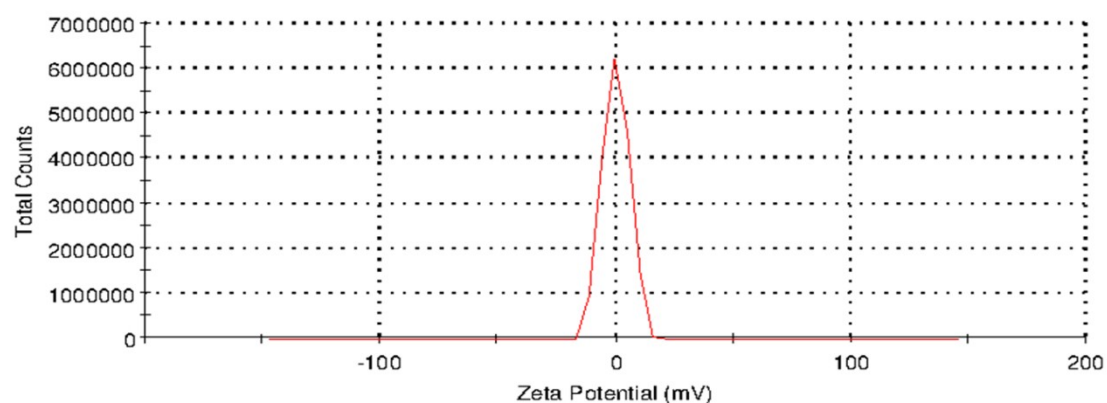


**Figure S7.** UV-vis absorption spectra of RB in methanol of different 10 ml batches of permeate collected for (a) bare  $\alpha$ -alumina support and (b)  $\text{NH}_2$ -MIL-53(Al) membrane. The model feed solution was a 250 ml mixture of RB ( $200 \text{ mg L}^{-1}$ ) in methanol. The feed solution and all collected samples and feed were diluted 20 times in Figure S6a while feed solution and samples 15-20 were diluted 20 times in the Figure S6b.

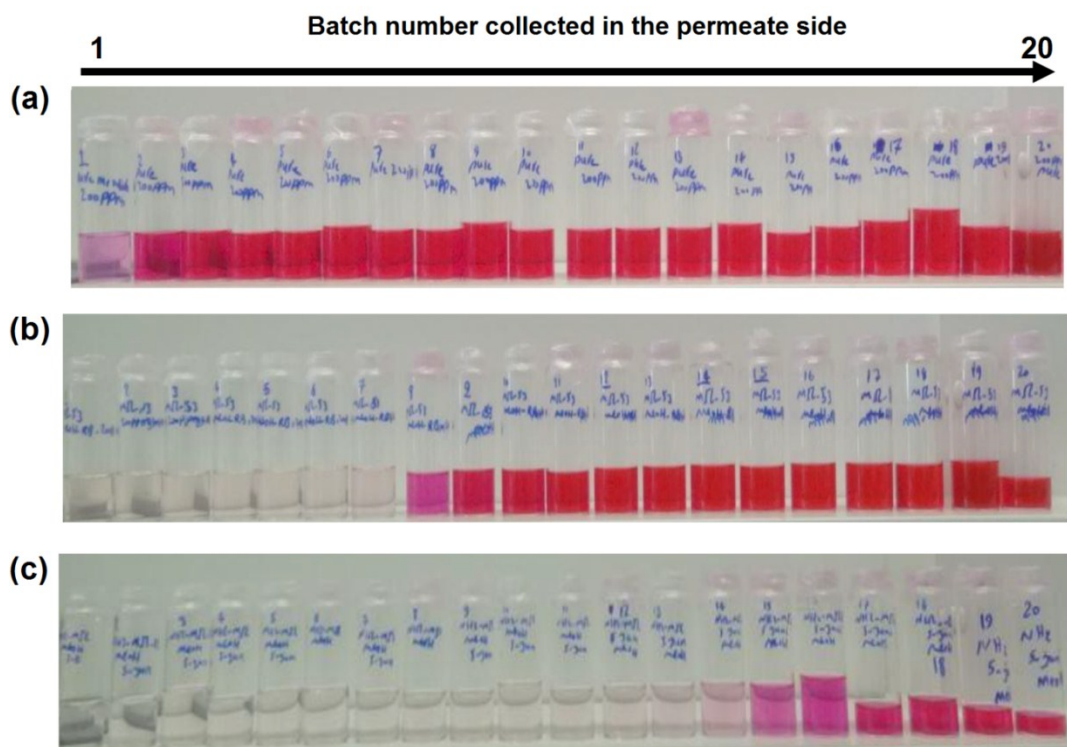
(a)	Mean (mV)	Area (%)	Width (mV)
<b>Zeta Potential (mV): -9,25</b>	<b>Peak 1: -9,25</b>	100,0	5,80
<b>Zeta Deviation (mV): 5,80</b>	<b>Peak 2: 0,00</b>	0,0	0,00
<b>Conductivity (mS/cm): 0,00462</b>	<b>Peak 3: 0,00</b>	0,0	0,00



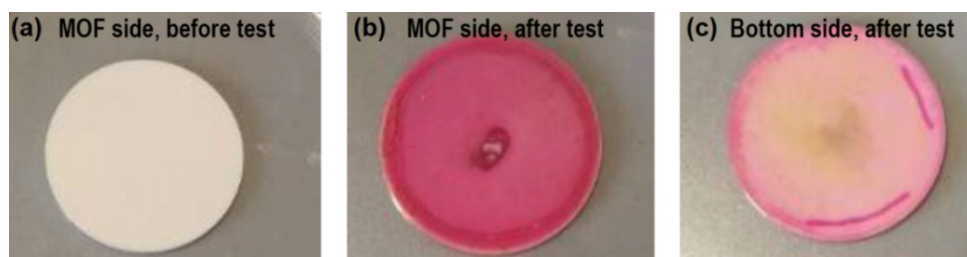
(b)	Mean (mV)	Area (%)	Width (mV)
<b>Zeta Potential (mV): 0,0302</b>	<b>Peak 1: 0,0302</b>	100,0	5,60
<b>Zeta Deviation (mV): 5,60</b>	<b>Peak 2: 0,00</b>	0,0	0,00
<b>Conductivity (mS/cm): 6,59e-4</b>	<b>Peak 3: 0,00</b>	0,0	0,00



**Figure S8.** The zeta-potential distribution of (a) MIL-53 and (b) NH<sub>2</sub>-MIL-53 powders in methanol.



**Figure S9.** Photographs of collected samples at the permeate side of (a) bare  $\alpha$ -alumina, (b) MIL-53(Al) and  $\text{NH}_2$ -MIL-53(Al) membranes tested with RB in methanol ( $200 \text{ mg L}^{-1}$ ).



**Figure S10.** Photographs of the  $\text{NH}_2$ -MIL-53(Al) membrane before and after the filtration test RB in methanol ( $200 \text{ mg L}^{-1}$ ).

### S3 References

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