

# Anti-biofouling organic-inorganic hybrid membrane for water treatment

Ajay K. Singh<sup>1</sup>, Priyanka Singh<sup>2</sup>, Sandhya Mishra<sup>2</sup>, Vinod K. Shahi<sup>\*1</sup>

<sup>1</sup> *Electro-Membrane Processes Division,*

<sup>2</sup> *Salt and Marine Chemicals Division,*

*Central Salt & Marine Chemicals Research Institute, Council of Scientific & Industrial Research (CSIR), G. B. Marg, Bhavnagar-364002 (Gujarat) INDIA*

*Tel: +91-278-2569445; Fax: +91-278-2567562/2566970; E-mail: [vkshahi@csmcri.org](mailto:vkshahi@csmcri.org);*

*[vinodshahi1@yahoo.com](mailto:vinodshahi1@yahoo.com)*

## **S1. Biosafety precautions during the antibacterial and antifungal activity:**

Bacteria/fungi are potentially hazardous and care should be taken while working with them. Standard bio safety lab techniques were followed while handling bacteria/fungi and various media. Gloves were used during all experimentation, and any accidental spills were immediately sterilized using 70 % isopropanol/water followed by bleach. The work area was also sterilized with 70 % isopropanol/water after completion of work. Unused media and bacterial suspensions were first deactivated with commercial bleach for 1 h before being disposed in bio safety bags. All material that had come in contact with bacteria (e.g., pipette tips, tubes, agar plates, etc.) was also thrown in biosafety bags in tightly closed bins. Bio safety bags were autoclaved for 2 h before final disposal.

## **S2. Water uptake measurements**

The swelling ratio ( $S_w$ ) for nanocomposite membranes was determined by water uptake measurement using following equation (1):

$$S_w(\%) = \frac{(m_s - m_D)}{m_D} \times 100 \quad (1)$$

Where  $m_D$  is weight of dry membrane and  $m_s$  is weight of wet membrane after wipe out surface water by absorbing paper.

### S3. Dimensional changes

Dimensional changes of the membranes were investigated by square pieces of the membrane was immersed in distilled water for 24 h, the surface was wiped and samples were dried at 70 °C for 12 h. The thicknesses of membranes were measured by the Mitutoyo digimatic micrometer. Length and width of membranes were measured by millimetre scale. Volume fraction ( $\phi$ ) of water was estimated by equation (2)

$$\phi = \frac{L_x L_y L_z - L_{x0} L_{y0} L_{z0}}{L_x L_y L_z} \quad (2)$$

Where,  $L_x, L_y, L_z$  may be the length/width/thickness of the swollen membrane and subscript 'o' represent the dimension in dry condition.

### S4. Ion exchange capacity, surface charge concentration and void porosity measurements

For determining ion exchange capacity (IEC), accurately weighted dry membrane was dipped in 1.0 mol/L HCl for 24 h. Afterward the membrane was washed with distil water and then immersed in 1.0 mol/L NaCl for 24 h. Exchanged  $H^+$  was titrated against 0.001 mol/L NaOH solution using phenolphthalein indicator. The IEC was calculated according to the equation (3).

$$IEC(\text{mequiv. g}^{-1} \text{ dry membrane}) = \frac{C_{Na^+} V_{sol}}{W_{dry}} \quad (3)$$

Where  $W_{dry}$  is the weight of the membrane sample under dry condition.

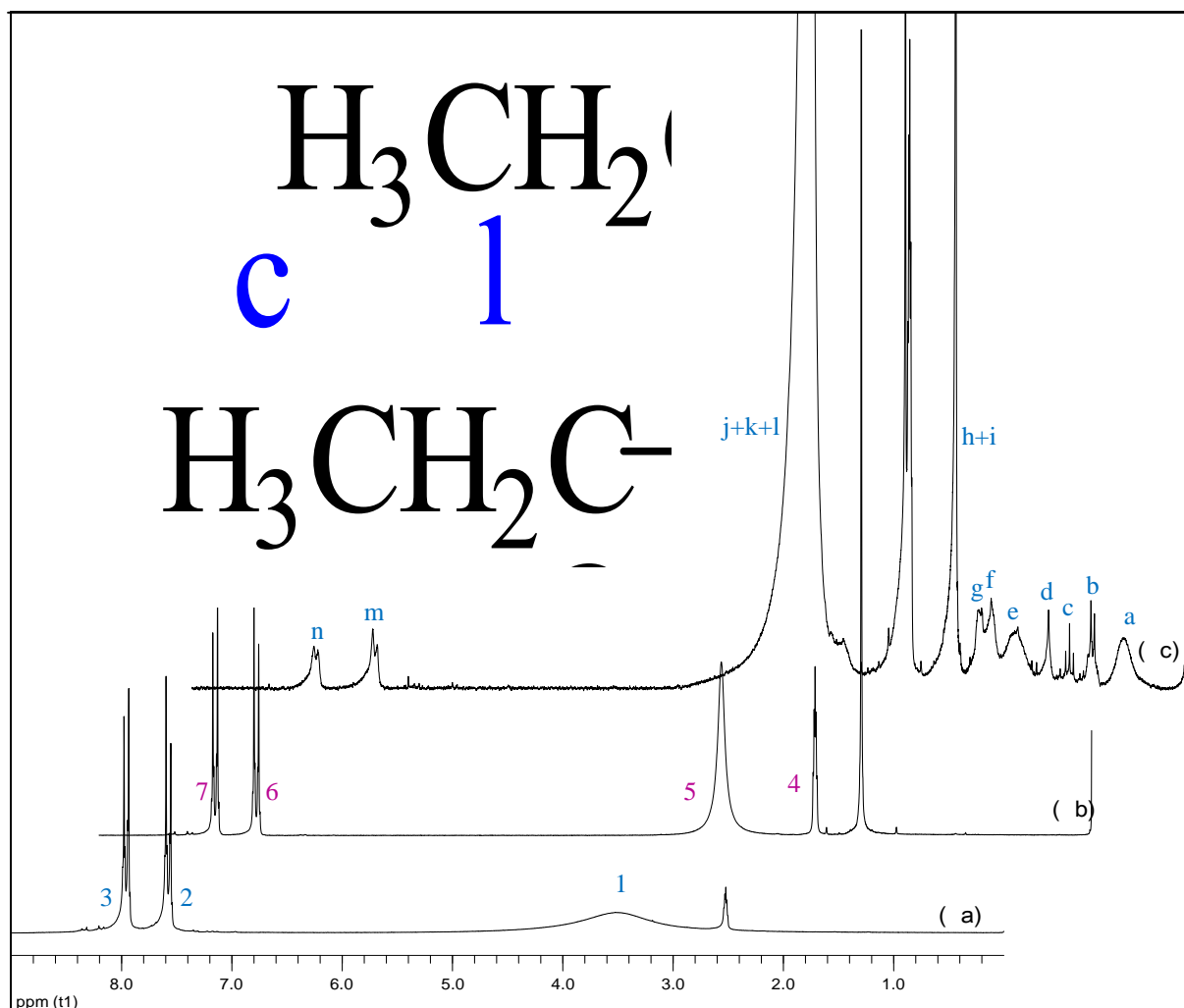
With the help of IEC and water uptake capability determined the net surface charge density ( $\chi^m$ ) in the membrane was determined in unit of (moles of ionic sites)/ (unit volume of wet membrane) by using the equation (4).

$$\chi^m = \tau(IEC) \frac{\rho_d}{\varphi_w} \quad (4)$$

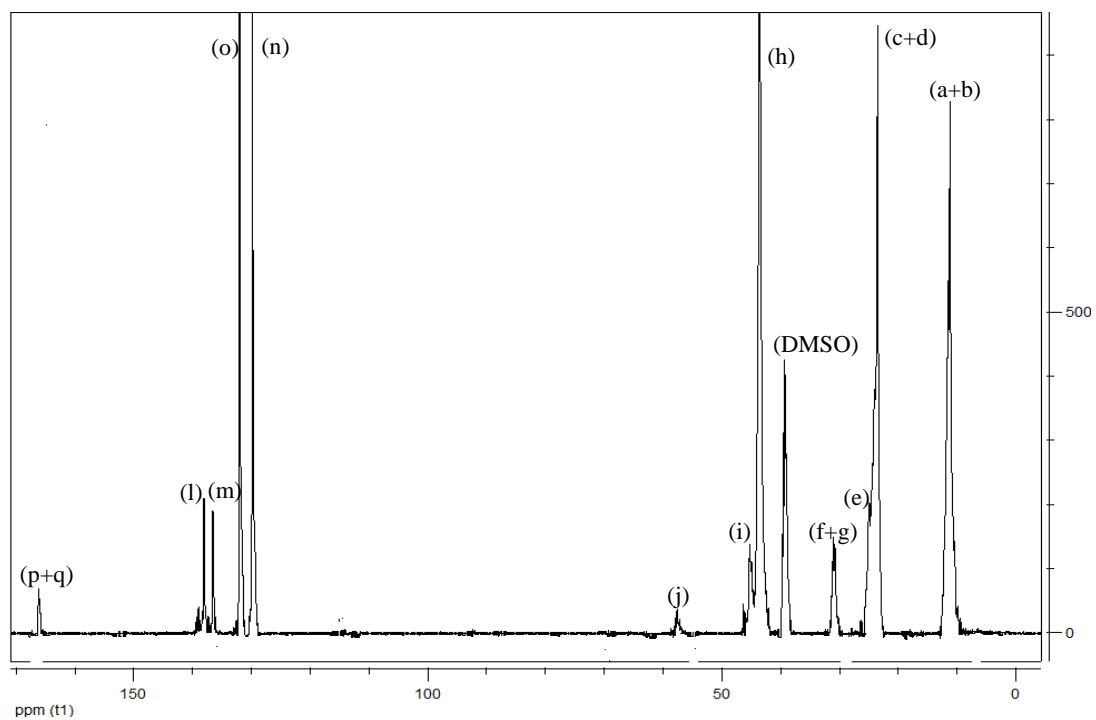
Where IEC is expressed in equivalent per gram of dry membrane,  $\rho_d$  the density of dry membrane and  $\tau$  denotes membrane voids porosity. Void porosity (volume of free water within membrane per unit volume of wet membrane) can be obtained by using the equation (5).

$$\tau = \frac{\varphi_w}{1 + \varphi_w} \quad (5)$$

**Fig. S1**  $^1\text{H}$  NMR spectra (a) (COT) 5-(4-chlorophenyl)-1,3,4-oxadiazole-2-thiol in  $d_6$ -DMSO; (b) 2-(2-chloroethylthio)-5-(4-chlorophenyl)-1,3,4-oxadiazole in  $d_6$ -DMSO; (c) APDSMO in  $d_6$ -DMSO.



**Fig. S2**  $^{13}\text{C}$  NMR spectra APDSMO in  $\text{D}_2\text{O}$ .



**Fig. S3** Synthesis route for hybrid membranes and TEM images of MO-6 membrane (a, b, and c) at different magnifications.

**(a)**

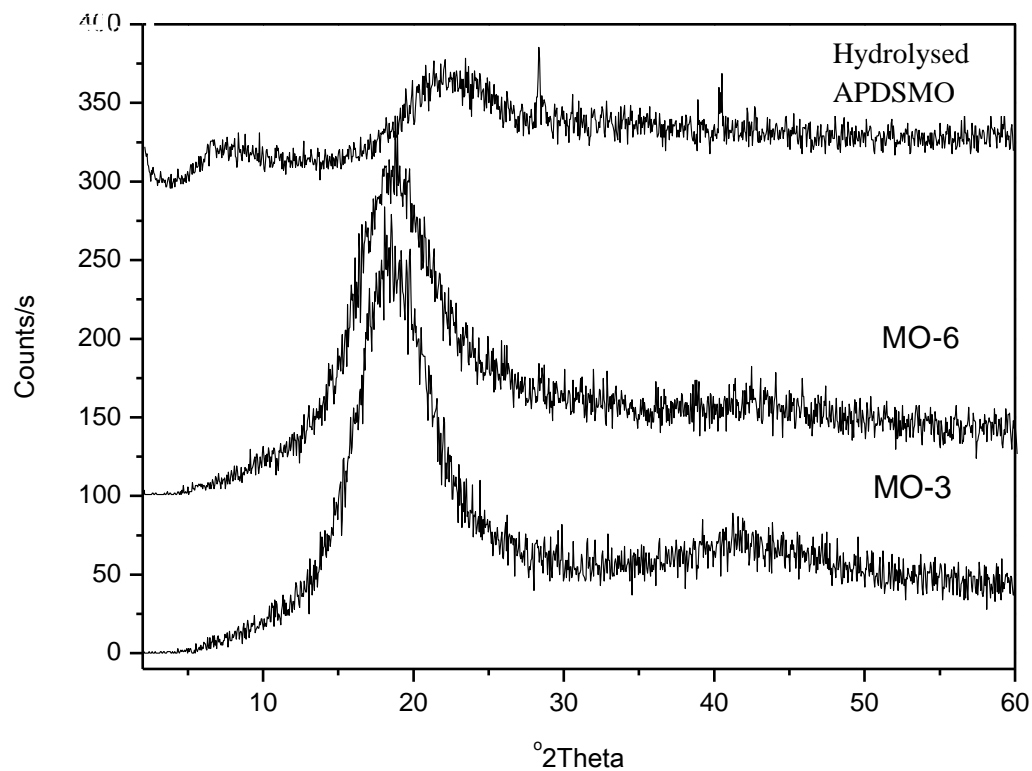
**(b)**

**2 nm**

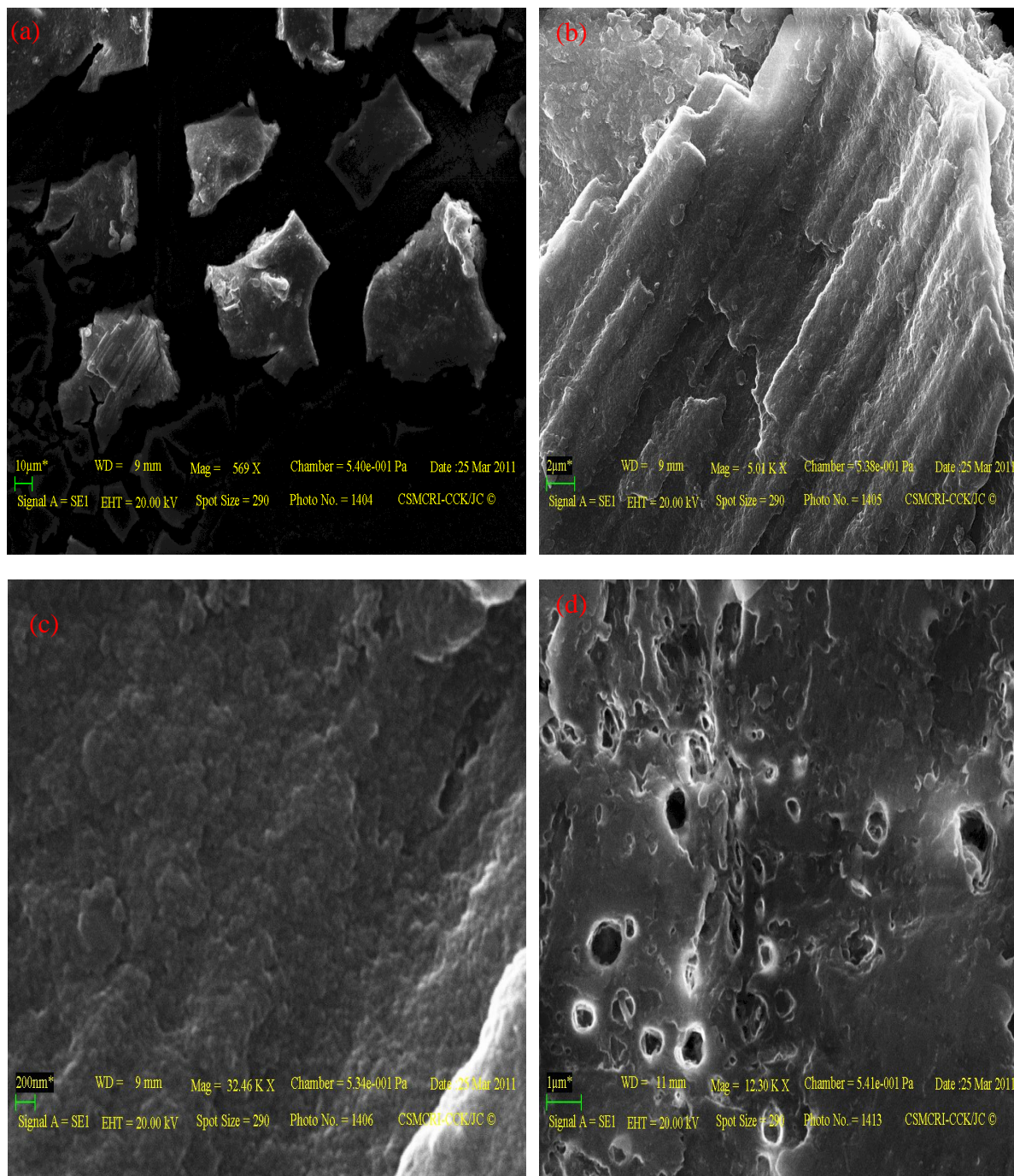
**5 nm**

**10 nm**

**Fig. S4** X-ray diffraction patterns for different hybrid membranes.

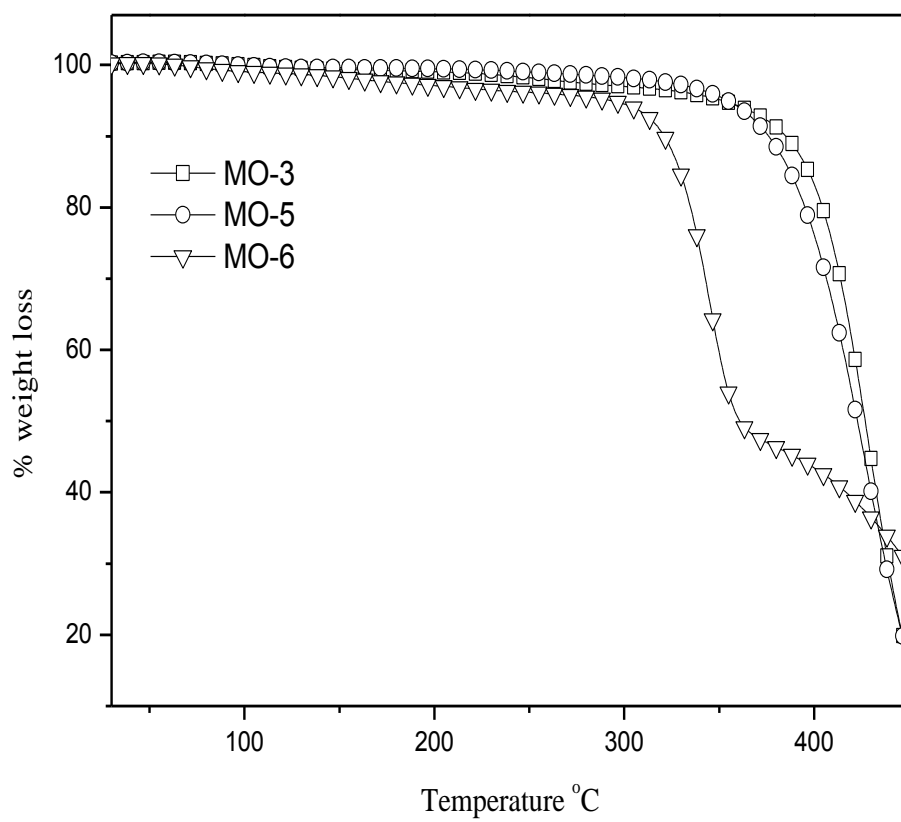


**Fig. S5** SEM image of (a-c) hydrolysed APSMO (low, medium and high resolution, respectively); (d) MO-5 membrane.

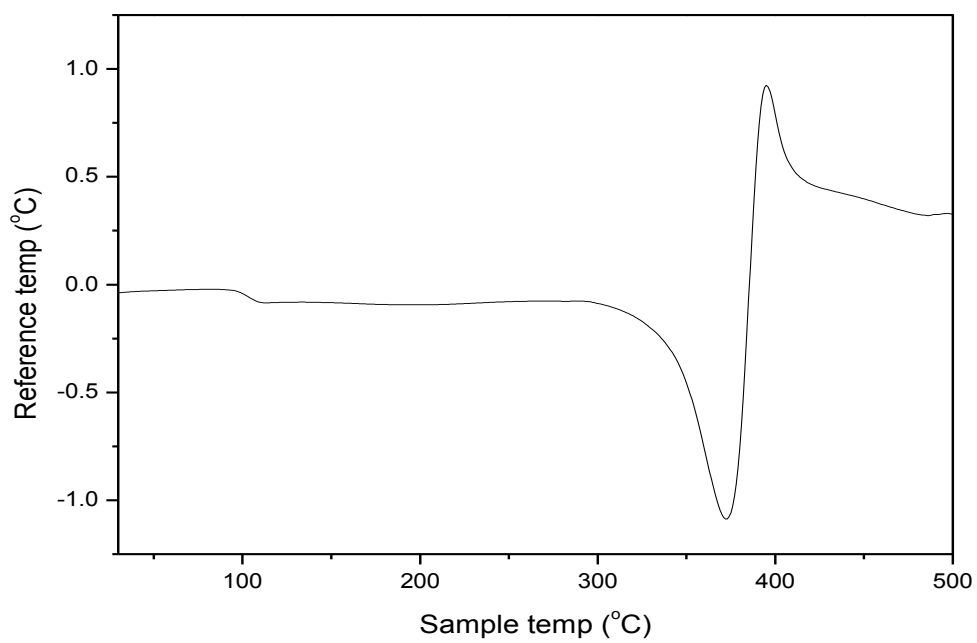




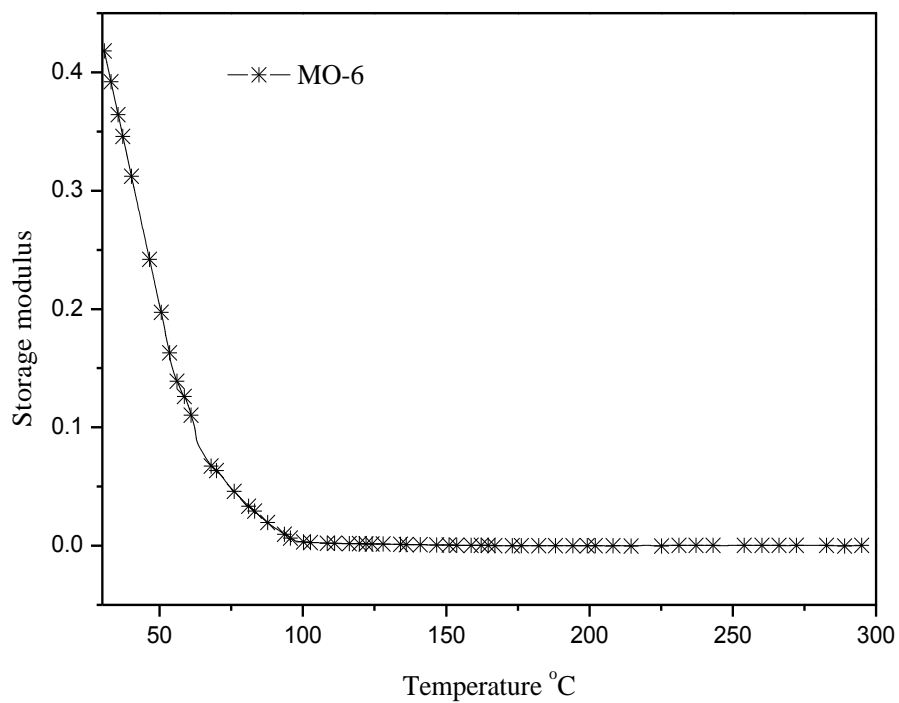
**Fig. S6** TGA curve of different hybrid membranes.



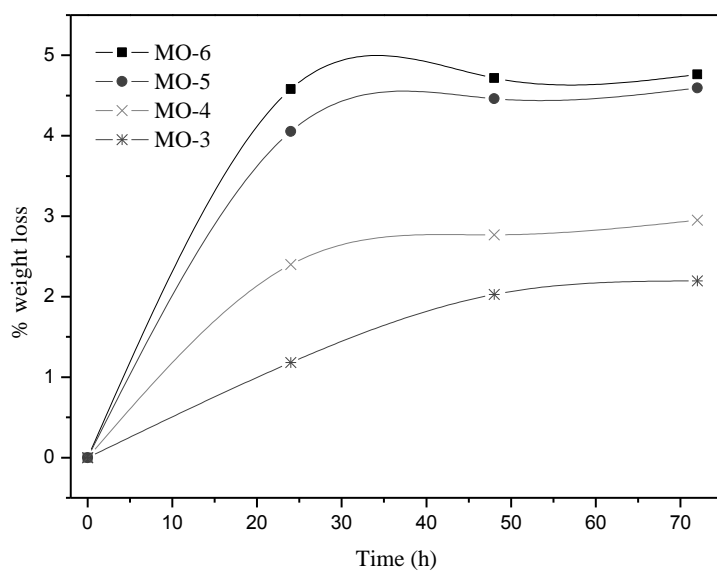
**Fig. S7** DSC spectra for MO-6 nanocomposite membranes.



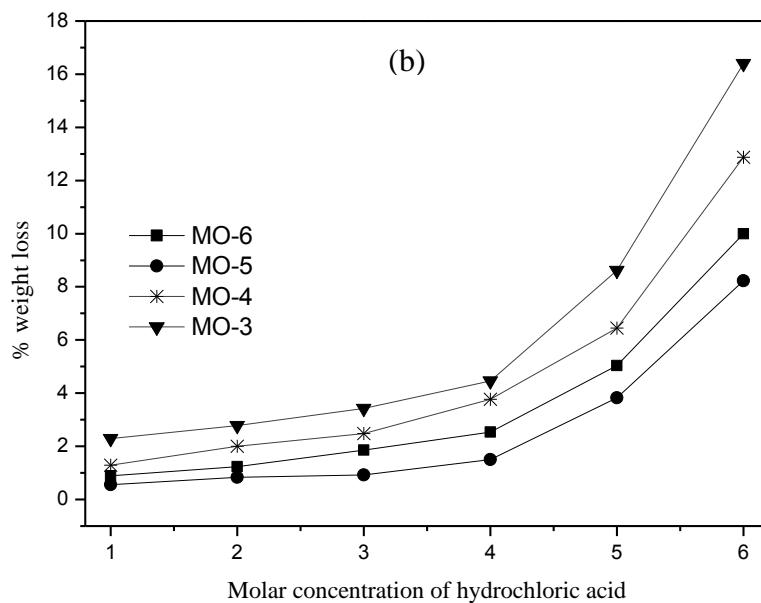
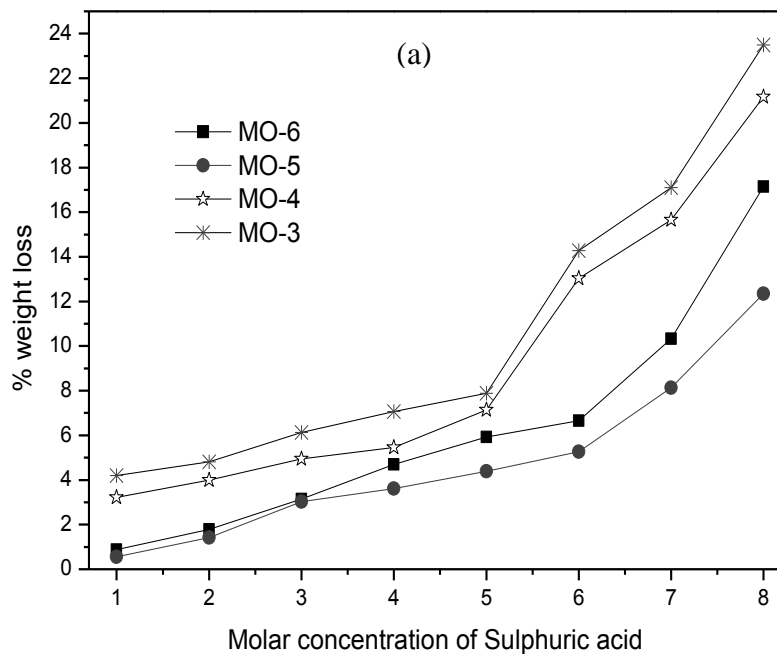
**Fig. S8** DMA thermogram for MO-6 membrane at 10 °C/ minute heating rate in N<sub>2</sub> atmosphere.



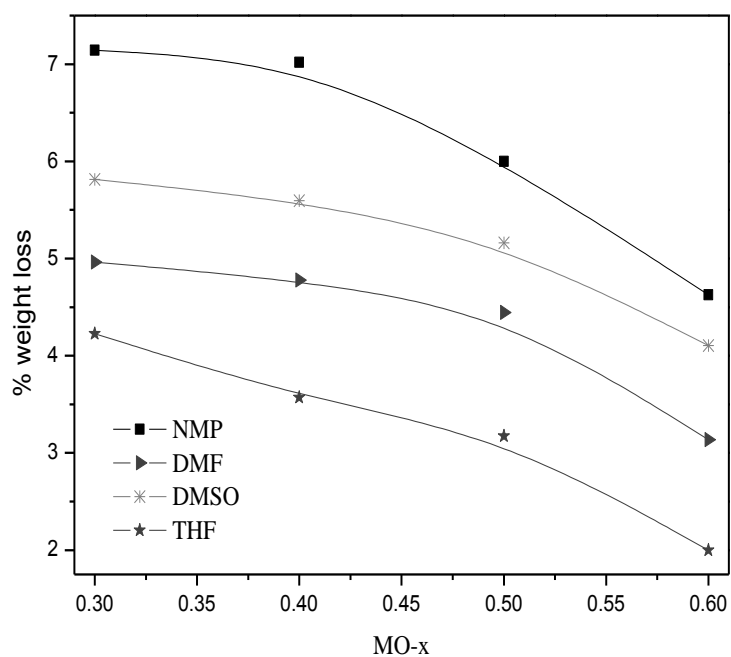
**Fig. S9** Weight loss (%) for different hybrid membranes after treatment in 5% aqueous NaOCl solution at 80 °C for different time intervals.



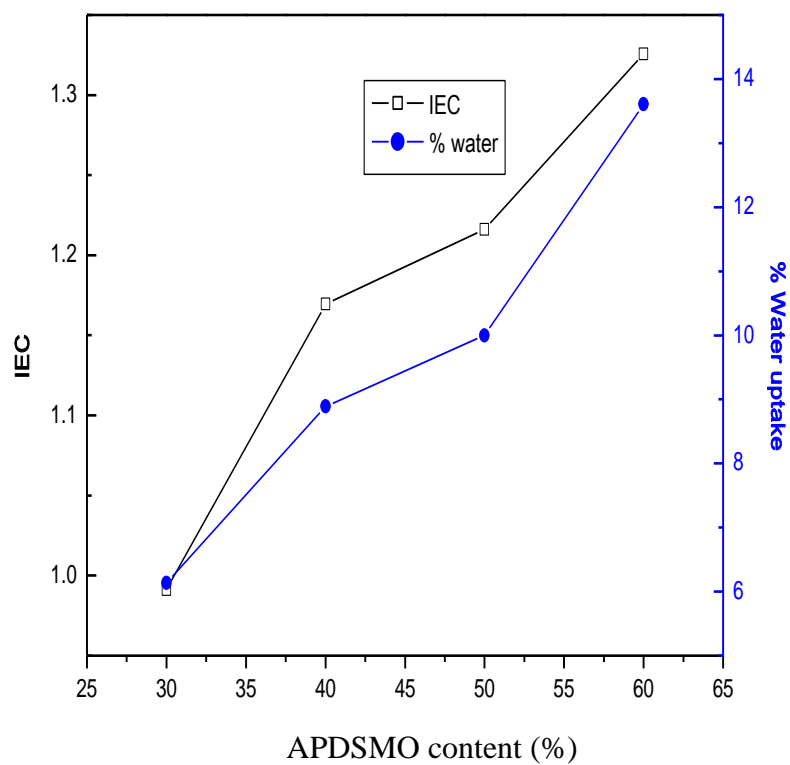
**Fig. S10** Weight loss (%) for different hybrid membranes after treatment with different concentrations of: (A) HCl and (B) H<sub>2</sub>SO<sub>4</sub> for 30 days.



**Fig. S11** Weight loss (%) for hybrid membranes in different organic solvents.



**Fig. S12** Ion exchange capacity (IEC) and water uptake values for different hybrid membranes.



**Fig. S13** 24 h grown bacteria for membrane antifouling application ( $OD_{600}=2.3299$ ).

