A highly permeable Zinc-based MOF/ polyphenylsulfone composite membrane with elevated antifouling properties

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Experiments

Zn-MOF was synthesized by the chemical route using polyethylene terephthalate as an organic linker and $Zn(NO_3)_2 \cdot 6H_2O$ as a metal based. The Zn-based MOF shows a needle/hexagonal structure in scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) images (Fig. S1) and the elemental composition and particle size distribution of Zn-MOF were determined from energy-dispersive X-ray spectroscopy (EDS) patterns (Fig. S2 and S3) and Z-average value was 932 nm (Fig.S4). The resulting membranes were fabricated by a wet phase inversion method using a dope solution including 17 wt% PPSU (Ultrason P3010; BASF; Germany) as the base polymer material and 83 wt% N, N-dimethylformamide as solvent, with different concentration of Zn-MOF (0.1 wt%,0.5 wt% and 1.0 wt%) material as an additive. To analyze the topography and cross-sectional morphology of membranes, atomic force microscopy (AFM; Veeco NanoScope V MultiMode software) and SEM-EDS (JEOL; Japan) were performed. The surface charge of the membranes was investigated by an electrokinetic analyzer (Anton Paar SurPASS; GmbH; Austria). The surface hydrophilicity of the membranes was characterized by a water contact angle measurement technique (Attension T330; Biolin Scientific; Netherlands).

The membrane overall porosity was determined by the gravimetric method, as defined in the following Eq.:

$$Porosity(\%) = \left(W_W - W_D / \rho \, . \, A \, . \, l_m \right) \times 100 \qquad (1)$$

where, W_W: weight of the wet membrane, W_D: weight of the dry membrane, A: membrane effective area (m^2), ρ: water density (0.998 gcm^{-3}) and l_m: membrane thickness (m).

The membrane mechanical strength was studied using tensile tests. The tensile strength at break of the membranes sample (25 mm gauge length and 10 mm width) was determined on the LR5K Plus tensile test machine (Lloyd Instruments Ltd., United Kingdom) with a deformation speed of 10 mm/min at room temperature. Each dumbbell-shaped membrane samples were tested triplicate and the average results were reported using NEXYGEN Plus software.

The membrane performance was determined by water hydraulic permeability measurements by a pressure-driven cross-flow filtration module (CF042; Sterlitech Corporation; USA) (see Fig.S5) and calculated according to Eq. (1):

$$Hydraulic\ Permeability = J_v/\Delta P \qquad\qquad (2)$$

where, , J_v: water volumetric flux, and ΔP : transmembrane pressure driving force. The rejection of prepared membranes was evaluated using 1000 mg/L bovine serum albumin (BSA) (Sigma-Aldrich, USA) as feed solutions prepared in a phosphate buffer (0.1 mol/L, pH 7). The rejection experiments were performed at 2 bar pressures under room temperature. After filtration study, the membranes rejection was calculated by following Eq.:

$$Protein\ rejection\ (\%) = \left[(C_f - C_p)/C_f\right] \times 100 \qquad\qquad (3)$$

where, C_f : concentration of the feed, C_p : concentration of permeate. The concentration of BSA in feed and permeate were determined using a UV spectrophotometer (Agilent Technologies, Cary 60 UV–Vis)

Furthermore, the membrane fouling studies were carried out three cycles of experiments using the following procedure: the initial water volumetric flux was measured at 2 bar pressure for 150 min under room temperature. Afterward, the feed solution was changed from deionized water (Milli-Q system, Millipore, USA) to the model fouling protein BSA solution (1000 mg/L in 0.1 mol/L phosphate buffer, pH 7.0) and the water flux was recorded for 300 min under the above-mentioned condition. Subsequently filtration of the protein solutions, the fouled membrane was washed again fresh deionized water and the final water volumetric flux was measured for 150 min. The achieved time-dependent fluxes were normalized to clearly observe the variation in water flux behavior. The antifouling properties of the membranes were evaluated by the flux recovery ratio using the following Eq.:

$$Flux\ recovery\ ratio(\%) = \left[J_{v2}/J_{v1} \right] \times 100 \qquad\qquad (4)$$

where, J_{v1} : initial water volumetric flux and J_{v2} :final water volumetric flux.
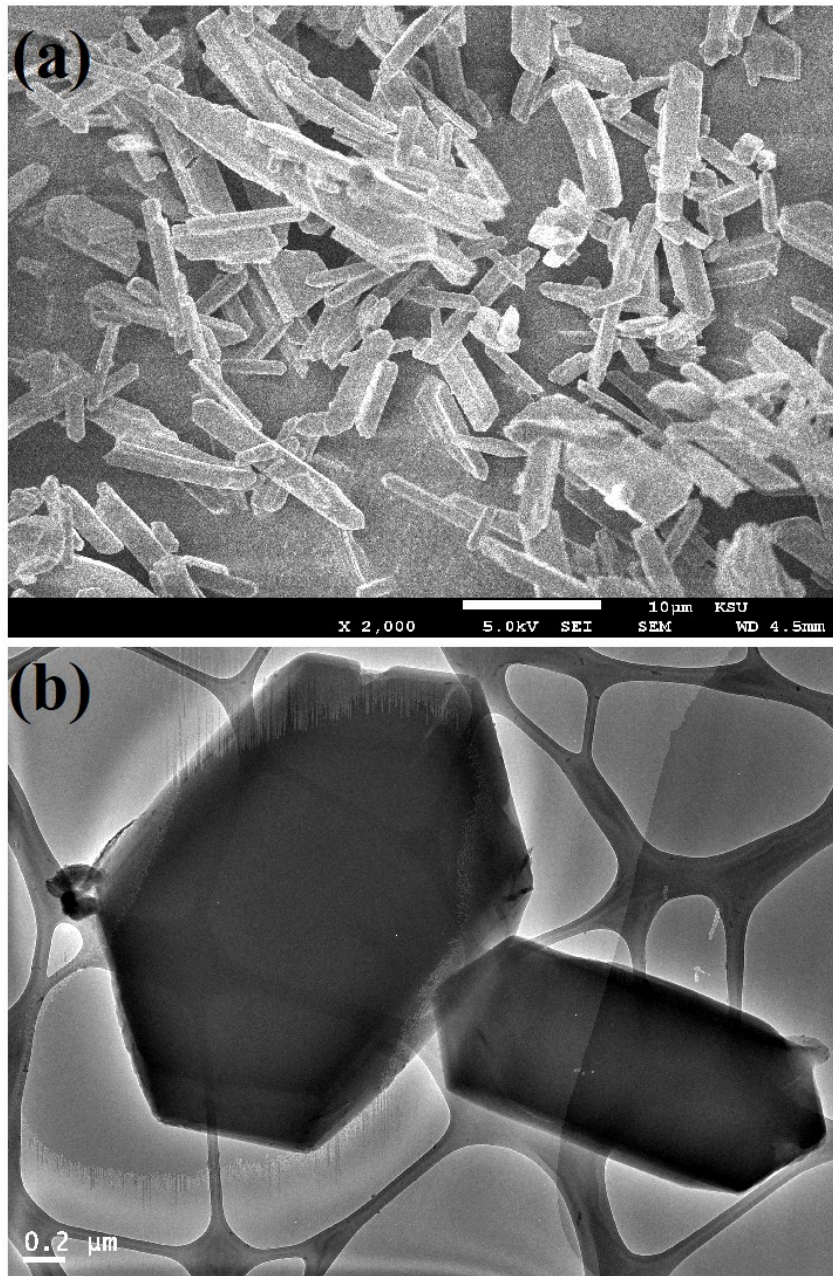
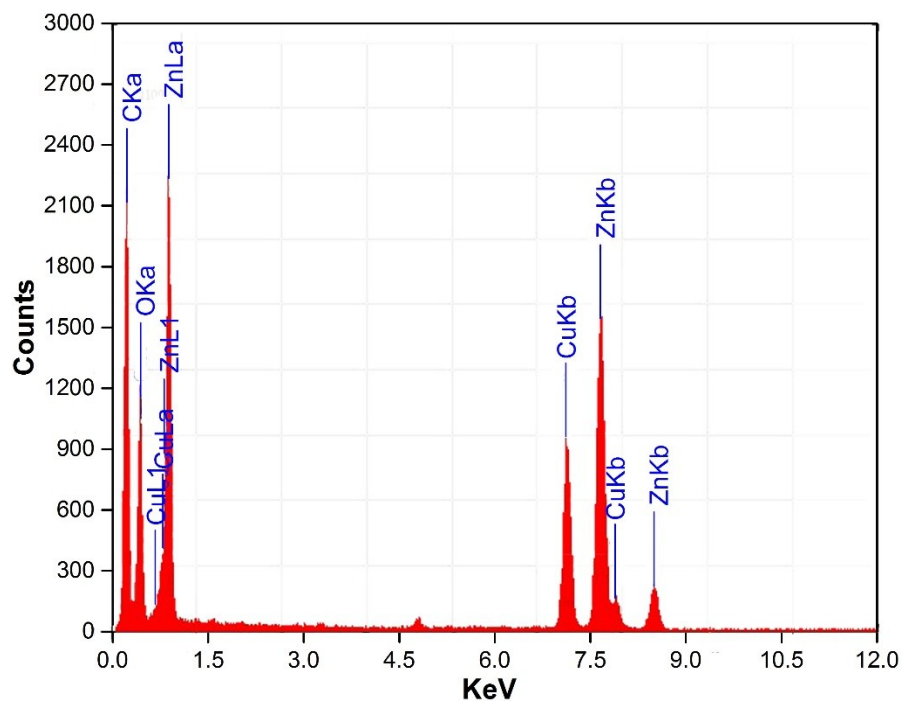**Figure S1**. (a) SEM and (b) TEM images of Zn-MOF.

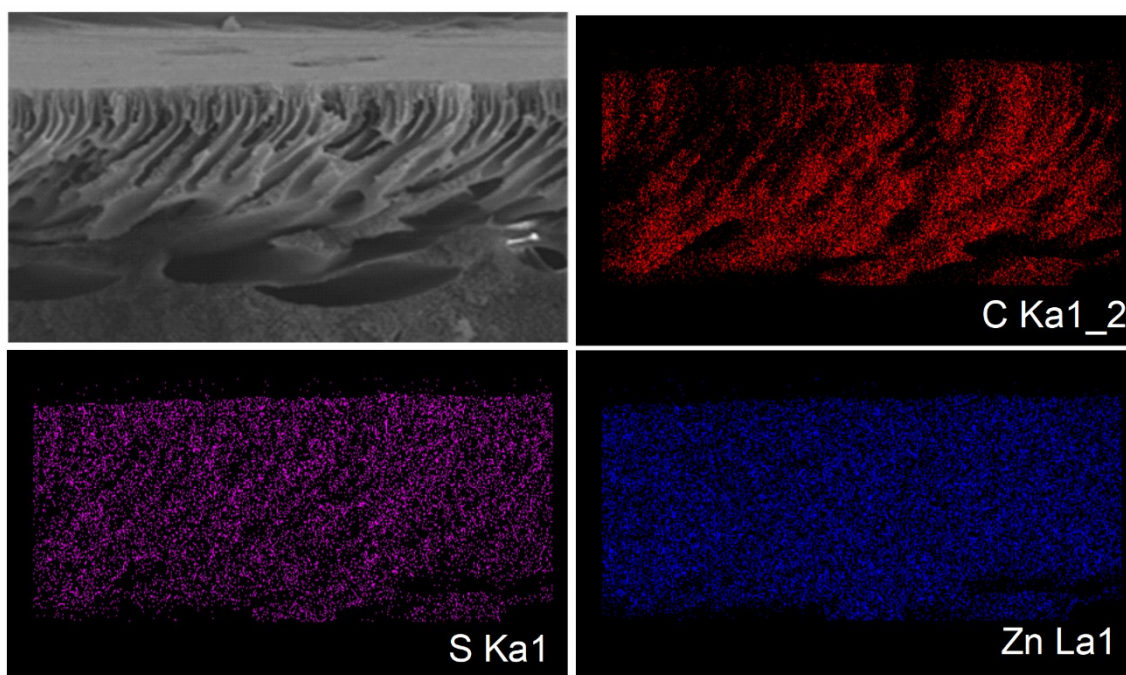**Figure S2.** TEM EDS spectrum of Zn-MOF.

Figure S3. SEM image elemental mapping analysis of prepared Zn-MOF composite membrane.
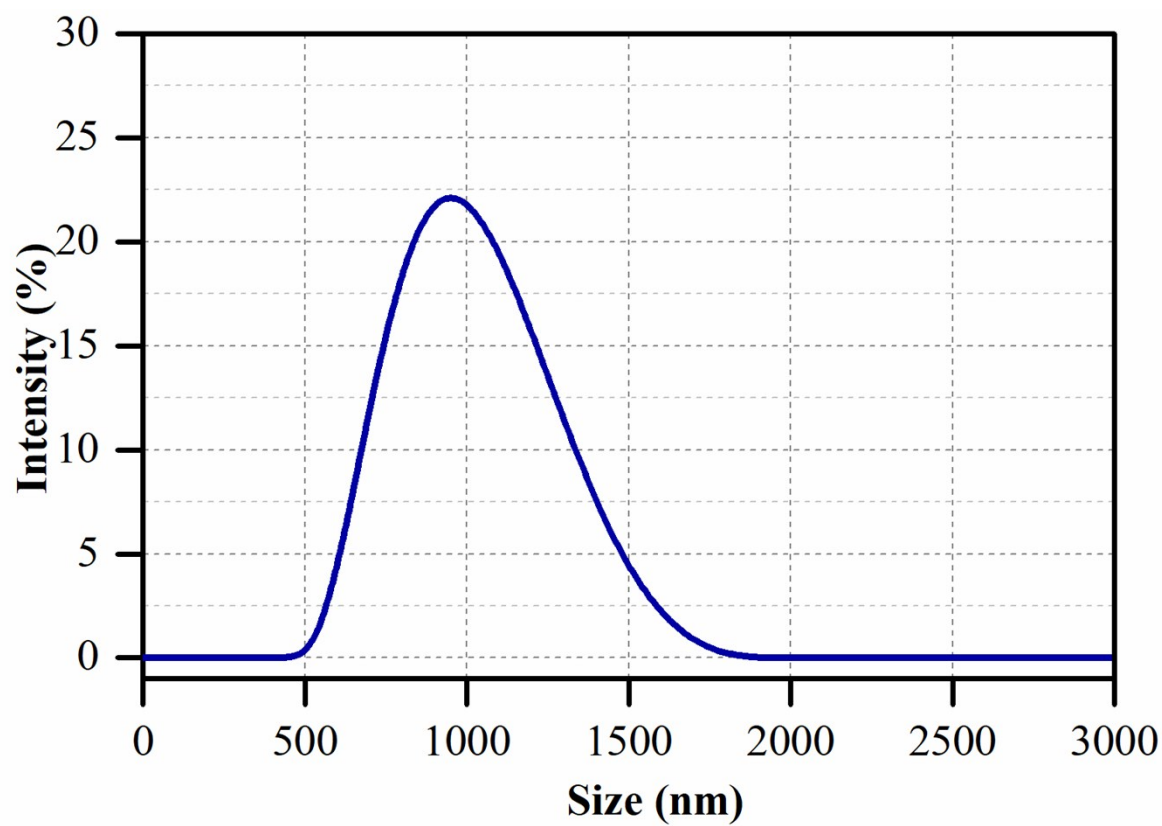
Figure S4. Particle size distribution of Zn-MOF.

Fig. S5. Schematic illustration of filtration experiment through the cross-flow CF042 cell.