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Removal of hazardous material from wastewater by using metal organic framework (MOF) embedded polymeric membranes

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1 **Removal of Hazardous Material from Wastewater by using Metal Organic Framework**
2
3 **(MOFs) Embedded Polymeric Membranes**

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13 **ABSTRACT**

14 Heavy metals in wastewater can cause acute and chronic toxicity which leads to learning
15 disabilities, cancer, and even death. In present work, Zn based MOF (MOF-5) was prepared,
16 and it is characterized by FT-IR, XRD, and SEM Analysis. MOF-5 incorporated polymeric
17 membranes (PES, CA and PVDF) prepared by phase inversion method. The morphology,
18 hydrophilicity, porosity, permeation performance, antifouling properties and the rejection of
19 Cu (II) and Co (II) metal ions of the membranes were significantly improved with the addition
20 MOF-5. Higher rejection efficiency for Co (II) in PES/MOF-5 and CA/MOF-5 was found to
21 be 74.40 % and 77 % respectively.

22 **Keywords:** Heavy metal ions, Metal-organic frameworks (MOFs), Composite membranes,
23 Nanofiltration (NF).

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Introduction

36 Increasing contamination of industrial wastewater by heavy metal ions found to be
37 significant global concern. The primary source of heavy metal ions are industries like
38 electroplating, battery manufacturing, metallurgical, tannery, and metal finishing.^[1,2] Unlike
39 organic contaminants, heavy metal ions are non-biodegradable in nature and likely to cause
40 healthy risk by entering into the human food chain through marine animals.^[3,4] Over the years,
41 numerous techniques have been studied for the removal of heavy metal from wastewater
42 namely adsorption, precipitation, ion exchange, membrane separation, electro dialysis, and
43 photocatalysis.^[5] Nanofiltration (NF) membrane was proven to be a very potential method for
44 removal of heavy metals because of its low cost and high effectiveness.^[6] A comparative study
45 of copper and cadmium removal from wastewater using NF has been investigated.^[7] NF
46 membranes were shown to be capable of removing 96% of copper and 97% of cadmium ions.
47 However, the difficulties to achieve both high water permeability and rejection simultaneously
48 limits the performance of NF membranes.

49 Metal-organic frameworks (MOFs) are proven to be a promising material to overcome
50 the above mentioned drawback. MOFs offers highly tunable pore structure, along with an
51 enormous variability and chemical functionality.^[8] MOFs can be synthesised by combination
52 of metallic and organic linkers namely benzenedicarboxylates (BDC) and benzenetricarboxylates
53 (BTC) via chemical or physical techniques. The incorporation of MOFs on polymer matrix has
54 been reported for the removal of dye and heavy metals using nanofiltration.^[9,10] Thin film
55 nanocomposite membranes were developed by embedding MOFs on Polyimide support shows
56 increased permeability of solvent due to increase in porosity and hydrophilicity.^[9] UiO-
57 66@GO/PES composite membranes has been reported with enhanced antifouling property.
58 The pure water flux of MOFs incorporated composite membrane was increased by 351%

59 compared to that of neat PES membrane, together with increased rejection ratio to organic
60 dyes. ^[11] The MOFs were used for the removal of heavy metal ions from aqueous solution.
61 Bakhtiari ^[2] and Rivera *et al.*, ^[12] proven that MOF-5 can be an effective adsorbent for the
62 removal of heavy metal ions like copper and lead from aqueous medium. Therefore, research
63 on MOF embedded polymeric membrane is highly desirable, especially for the application of
64 water purification. ^[10] Despite these considerable advantages, limited structural stability of
65 MOFs when exposure to water remains a point of concern. The water stability of MOFs related
66 to composition of metal sites and structure of metal clusters. ^[13] Polymer and MOFs is
67 controlled by weak interactions such as Hydrogen bond, van der Waals forces, and π - π
68 stacking. MOFs introduces free volume and active porous sites on the membrane will be
69 favourable for gas and liquid separation. ^[14] Herein, we report MOF-5 embedded membranes
70 with three different polymers namely Cellulose acetate (CA), Polyethersulfone (PES), and
71 Polyvinylidene fluoride (PVDF). MOF-5, a prototypical Zn based MOF with cubical structure
72 have been used to achieve the high water purification performance for the removal of copper
73 and cobalt ions (hazardous materials) from wastewater. The schematic representation of
74 removal of heavy metal ion from aqueous solution by MOF-5 incorporated polymeric
75 membranes Nanofiltration is shown in Scheme. 1.

76 **Experimental**

77 ***Materials***

78 N, N-dimethylformamide (DMF, Merck), Terephthalic acid (SRL Pvt Ltd., India), Zinc nitrate
79 hexahydrate (Loba Chemie Pvt Ltd. India) were employed to prepare the MOF material. All
80 chemicals used were of analytical grade. Copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), Cobalt
81 sulfate hexahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) were purchased from Merck specialties Pvt Ltd., India.
82 Polyethersulfone (PES, veradel 13000 p), Polyvinylidene fluoride (PVDF, Solef® 6010) was
83 procured from Solvay Solexis Ltd., India. Cellulose Acetate (CA) were purchased from Mysore

84 Acetate and Chemicals Company Ltd., India. Ultrapure water was produced in the laboratory
85 using millipore pilot plant.

86 ***Preparation and characterization of MOF-5***

87 MOF-5 was synthesized in a glass reactor equipped with reflux condenser following the
88 procedure reported in the literature.^[9,15] 2 g of terephthalic acid and 9.31 g of zinc nitrate
89 hexahydrate were dissolved in 60 ml of DMF solution under stirring at atmospheric conditions
90 and heated up to 150°C for 4h. After 2 hr, white crystals of MOF-5 was formed, and the product
91 was cooled down to room temperature. The white crystals were separated by filtration and
92 washed with 100 ml acetone, and finally, solid crystals were dried at 60°C for 3 hr in a vacuum
93 oven. Fourier transform infrared (FTIR) spectroscopy of MOF-5 (Thermo Scientific Nicolet
94 iS5 FT-IR spectrometer) was analysed in the spectral region of wavenumbers from 400 to 4000
95 cm^{-1} . The crystalline structure of MOF-5 was studied using X-ray diffractometer (Model
96 Rigaku Ultima III) using a monochromatic source of Cu $K\alpha$ radiation with the range of 2θ
97 with an angle of 5° to 80° and with an operating voltage of 40 kV. The surface morphology of
98 prepared MOF-5 was studied using Scanning Electron Microscope equipped with Energy
99 Dispersive X-ray (Quanta 250 FEG).

100 ***Fabrication of MOF incorporated polymeric membranes***

101 The neat and MOF-5 embedded PES, CA, PVDF membranes were prepared by phase inversion
102 induced by immersion precipitation method.^[8] MOF-5 loading was kept at 0.5% of the
103 polymers. The casting solutions contain 17.5% of polymers (PES, CA, and PVDF) and 21.7
104 ml of DMF solvent. The composition of casting solutions for all the membranes is shown in
105 Table 1. MOF-5 (0.5%) was added into 21.7ml of DMF and dispersed well by sonication for 1
106 hr to improve the homogeneity using Ultrasonicator. After dispersing MOF-5 in DMF,
107 polymers were dissolved in the dope solution by mechanical stirring for about 3 hr. The

108 complete dispersion of Polymer/MOF-5 was again confirmed using ultrasonication for 30 min
109 before casting. After removing air bubbles, homogenous casting solution was cast onto a finely
110 levelled glass plate with 400 μm thickness. Subsequently, the film was then immersed in the
111 distilled water which is maintained at 10°C , and then membranes were soaked in fresh distilled
112 water for 24 hr to ensure the complete phase inversion.

113 *Membrane Characterisation*

114 The functional group of neat and MOF-5 incorporated polymeric membranes (PES, CA and
115 PVDF) were investigated by ATR interfaced Fourier transform infrared (FTIR)
116 spectrophotometer (Thermo Scientific Nicolet iS5 FT-IR spectrometer, India). The range of
117 wavenumbers were analysed between 400 to 4000 cm^{-1} . The XRD pattern of membranes were
118 analysed by X-ray diffractometer (Model Rigaku Ultima III) using a monochromatic source of
119 $\text{Cu K}\alpha$ radiation with the range of 2θ with an angle of 5° to 80° and with an operating voltage
120 of 40kV. The surface morphology of neat polymer and composite Polymer/MOF-5 membranes
121 were studied using Scanning Electron Microscope equipped with Energy Dispersive X-ray
122 (VEGA 3, TESCAN, USA). The membrane samples were fractured in liquid nitrogen, and gold
123 coated by sputtering to make them conductive. The MOF-5 distribution on the surface of the
124 composite membrane has been analysed by Energy Dispersion of X-ray (EDX).

125 Hydrophilicity of membranes were measured using contact angle measurement. Goniometer
126 (model 250-F1 Rame-Hart Instruments, Succasunna, NJ) used for the determination of Contact
127 angle for membranes by sessile drop method using. About $5\ \mu\text{L}$ drop of water is injected on a
128 dry membrane surface at five different locations through a micro syringe. The average of
129 contact angle value was measured from the individual droplets in the five regions which
130 determine the hydrophilicity of membrane.

131 *Permeation and rejection studies*

132 The permeability of neat and MOF-5 incorporated polymeric membranes were studied by using
133 pure distilled water and aqueous solutions of Cu (II), Co (II) at a concentration of 1000 ppm.
134 The permeation studies were conducted by using a dead end stirred NF cell with an active
135 membrane area of 14.6 cm². The water was pressurized by supplying nitrogen gas to the NF
136 cell, and then membranes were compacted for 30 min at 10 bar pressure to minimize the
137 compaction effects. At steady state conditions, the water permeated for 10 min at 25°C were
138 noted down, and the permeate flux (J_w) of each membrane was quantified based on the
139 following Eq. (1).

$$140 \quad J_w = \frac{V}{A \times \Delta t} \quad (1)$$

141 where J_w is the permeate flux (kg/m²hr), V is permeate volume (m³), A is effective membrane
142 area (m²), and Δt is permeation time (hr).

143 The performance of neat and composite membranes was evaluated using percentage rejection
144 of heavy metal ions from aqueous medium. The concentration of permeate solutions was
145 determined by using Atomic absorption spectrophotometer (Perkin Elmer, Analyst 4000,
146 USA). The measured value of permeate (C_p) and feed concentration (C_f) was used to calculate
147 observed rejection percentage (R_{obs} %) by following the Eq. (2).

$$148 \quad R_{obs}(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

149 ***Membrane Resistance (R_m)***

150 The resistance to the feed flow of neat and MOF-5 incorporated polymeric membrane has been
151 calculated by Eq. (3).

$$152 \quad R_m = \left(\frac{\Delta P}{\eta_w \times J_w}\right) \quad (3)$$

153 Where,

154 ΔP - Transmembrane Pressure.

155 η_w - Viscosity of the feed.

156 ***Membrane porosity and pore size***

157 To measure the membranes porosity, samples were cut into specific sizes and then mopped
158 with filter paper. After noting their wet weight, the samples are dried in an oven at 60°C for 24
159 hr. The porosity (ϵ) and mean pore radius of the membranes were calculated by [Eqn. 1], and
160 [Eqn. 2] respectively in the Supporting Information.

161 ***Determination of Mass Transfer Coefficient and Diffusion Coefficient***

162 Due to concentration polarisation, the solute concentration at membrane surface (C_m) is higher
163 than that of the bulk solution concentration (C_f). This leads to additional resistance to the
164 permeate flux (J_v), and it can be expressed based on the Concentration Polarisation Model
165 described in the Supporting Information [Eqn. 3]. Correlation for the mass-transfer coefficient
166 can be obtained based on the diffusive transport of the heavy metal ions described in the
167 Supporting Information [Eqn. 4]. The diffusivity of an aqueous solution of Cu (II) and Co (II)
168 was found to be $4.335 \times 10^{-9} \text{ m}^2/\text{s}$, $4.182 \times 10^{-9} \text{ m}^2/\text{s}$ respectively, and listed in Table 2. Observed
169 rejection efficiency of heavy metal ions were affected by the concentration polarisation, and
170 hence, the real rejection percentage of the membranes can be calculated using the concentration
171 at the surface of the membrane (C_m) by [Eqn. 6], in the Supporting Information.

172 **Results and Discussion**

173 ***FTIR characterization of MOF-5***

174 The FTIR spectra of MOF-5 shown in Fig. 1. Asymmetric stretching of C-O bonded to Zn has
175 been identified by the attachment of carboxylate ligand to Zn_4O centre were indicated in the
176 peaks of 1381 And 1573 cm^{-1} . The peak values between the range of 900 to 1250 cm^{-1} has
177 various small peaks are appeared to indicate the C-H stretching of benzene dicarboxylate

178 linker. The broad peak occurred in the range of 3161 cm^{-1} shows the O-H group IR bands at
179 1502 , and 653 cm^{-1} indicated random dimethylformamide (DMF) distribution in the MOF-5
180 framework structure. ^[17]

181 ***XRD analysis of MOF-5***

182 X-ray diffraction analysis of MOF-5 shown in Fig. 2. The peaks at 6.8° , 9.7° , 14° and 15.8° in
183 2θ which indicates the formation of a crystalline structure. ^[17] The inconsistency peaks appear
184 due to the framework interpenetration and pore occupation. The intensities of the two peaks
185 were overturned that can be attributed to some alterations of atomic orientations in the crystal
186 planes by absorbed species (solvent and water molecules), unreacted zinc centers and
187 framework interpenetration.

188 ***Surface Morphology of MOF-5***

189 Surface morphology of MOF-5 have shown using SEM images in Fig. 3. Irregularly shaped,
190 the majority had the cubic shape with crystals structure and porous nature, its present in the
191 (Fig. 3a and 3d). ^[17] The cubical structure has occurred more, and some cluster-like
192 arrangement also present which shows the adsorption property of MOF-5, its shows in the (Fig.
193 3b and 3c). The organic cluster and inorganic moiety interaction have occurred in MOF-5.

194 ***Energy Dispersive X-ray Spectroscopy of MOF-5***

195 The elemental composition of the MOF-5 was characterized by EDX (Fig. S1, Supporting
196 Information) revealing the expected elemental constituents (C, Zn, and O) are detected. The
197 peak appearance indicate the Zn metal ion attach with carboxylate ligand and it proves the
198 formation of MOF-5 by the interaction of metal ion and organic cluster. ^[17]

199 ***FTIR characterisation of membranes***

200 The FTIR spectra of neat and MOF-5 incorporated polymeric membranes namely PES/MOF-
201 5, CA/MOF-5, and PVDF/MOF-5 were illustrated in Fig. 4. The spectral features of neat PES,
202 CA and PVDF membranes are repeated in composite CA/MOF-5, PES/MOF-5 and
203 PVDF/MOF-5 membrane spectra, in which peaks corresponding to MOF-5 were also
204 observed. The peak values for both neat PES and PES/MOF-5 at 1240, 1485, and 1578 cm^{-1}
205 have identified the bands of aromatic ether, C=C bond stretch and aromatic bands of the
206 benzene ring respectively which confirms the characteristic peaks of PES. The presence of the
207 peak value at 3370 cm^{-1} in PES/MOF-5 membranes indicates the (O-H) stretching of MOF-5
208 in the PES membranes. ^[18] In case of neat CA and CA/MOF-5 membranes the peak at 1746
209 cm^{-1} was identified the stretching of carbonyl group has been present in both membranes and
210 for composite CA/MOF-5 membrane the peak occurred in the range of 3460 cm^{-1} shows the
211 O-H stretching which indicates the presence of MOF-5 in the membranes. ^[19] Band at
212 wavenumbers 1396 cm^{-1} and 1175 cm^{-1} is due to CH stretching vibration and C-F stretching
213 vibration in PVDF and PVDF/MOF-5 membranes. The broad peaks occurred at 3429 cm^{-1} in
214 FTIR spectra of PVDF/MOF-5 could be assigned to O-H stretching. ^[20] From these functional
215 group identification, confirms MOF-5 is embedded into membranes and create a polymeric
216 structure as an integral part, could be enhancing the hydrophilic nature compared with neat
217 membranes.

218 *XRD analysis of membranes*

219 The XRD diffraction patterns of MOF-5, neat and MOF-5 incorporated polymeric membranes
220 were shown in Fig. 5. The XRD spectra of MOF-5 had two peaks at 9.8° 2 θ and 15.8° 2 θ ,
221 which confirm the crystallinity of MOF-5 particles. The peak occurrence of little shift at 9.8°
222 2 θ in the composite PES/MOF-5, CA/MOF-5 and PVDF/MOF-5 membranes in the dispersion
223 peak of PES, CA and PVDF membranes due to the low addition of MOF-5. It's indicated that
224 the slight interaction between MOF-5 and polymeric membranes. ^[21] It is confirmed that the

225 synthesized MOF-5 improve the stability, hydrophilicity and antifouling properties of
226 composite polymeric/MOF-5 membranes. [21,22] XRD analysis indicate that the MOF-5
227 presence in the Polymeric membrane matrix

228 *Surface morphology of membranes*

229 The surface morphology of the neat and MOF-5 embedded CA, PES, PVDF membranes was
230 monitored by SEM images. The cross-sectional view of neat and modified PES membrane is
231 shown in Fig. 6. It is well known that the skin layer and porous sublayer in the membrane
232 determine the water permeation rate and separation factor. [23] The thick and dense asymmetric
233 structures were observed on neat PES membrane such morphology was responsible for the
234 lower pore radius and membrane permeability. In case of modified PES membrane, the
235 interconnection between skin top layer and substructure (bottom layer) were improved. Finger-
236 like substructures and thin skin layer were observed. Subsequently, increase in pore radius and
237 decreased macro voids were found with the addition of 0.5 wt. % of MOF-5.

238 The asymmetry structure of sponge-like cross-section, finger-like and highly porous structure
239 was observed in the surface morphology of neat CA and CA/MOF-5 in Fig. 7. The MOF-5 has
240 been uniformly dispersed in the polymeric membranes, and the structure of the MOF-5
241 incorporated membranes does not differ from the neat membranes due to the low-level loading
242 0.5 wt. % of MOF-5 into the membranes. Defective pore structure has been occurred due to
243 the interfacial stresses of MOF-5 and membranes. [22] The increase in the pore size indicated
244 the increased hydrophilicity and permeability for CA/MOF-5 which improves the membrane
245 to be a perfect membrane for the removal of heavy metal ions. Fig. 8 shows the cross sectional
246 view of neat PVDF and PVDF/MOF-5 membranes. An asymmetric structure consisting of a
247 dense top layer, a porous sublayer (support), and a sponge-like structure in the bottom layer. It
248 seems that the support layer begins with finger-like cavities underneath the dense top layer
249 ending up in large voids near the bottom layer. In the pristine membrane, a significant portion

250 of sublayer is made of a spongy structure consisting of small cellular pores, and only little
251 finger-like voids were observed underneath the top surface. While the addition of 0.5 wt. % of
252 MOF-5 into the PVDF casting solution the finger-like voids have been developed nearly up to
253 the membrane bottom, and the share of spongy pores is lower by increasing the hydrophilicity
254 of PVDF membranes. Porosity was enhanced by the addition of MOF-5 in the casting solutions
255 of PVDF membrane. [24] This trend can be interpreted and explained by membrane formation
256 mechanism during phase inversion process into the coagulation bath. MOF-5 in the casting
257 solution increases the penetration of nonsolvent (water) into the casting solution.

258 *Energy Dispersive X-ray Spectroscopy of membranes*

259 The presence of organic elements in both neat and MOF-5 incorporated Polymeric membranes,
260 indicates that the presence of MOF-5 does not affect the asymmetric membrane structures. The
261 MOF-5 embedded polymeric membranes shows only minor percentage of Zn elements could
262 be due to the low percentage loading of MOF-5 (Fig. S2, Fig. S3, and Fig. S4, Supporting
263 Information). The presence of Zn element in the MOF-5 incorporated polymeric membranes
264 confirms the presence of MOF-5 in the polymeric matrix. [25]

265 *The Porosity and Average Pore Radius of Membranes*

266 The porosity and mean pore radius values were shown in Table. 3. The average pore radius of
267 PES/MOF-5 membrane has been increased from 5.62 nm to 6.97 nm, and the porosity (%)
268 value also increase from 70 % to 78 % due to the addition of MOF-5 into the PES casting
269 solution and its obviously shows that MOF-5 has improved the hydrophilicity of PES. [26] The
270 average pore radius of CA/ MOF-5 membrane has been increased from the range of 5.57 nm
271 to 9.09 nm due to the addition of MOF-5 which improve the hydrophilicity of CA membranes
272 and porosity (%) also increased from 72 to 81 %. [22] The average pore radius of PVDF/MOF-
273 5 has been raised from the range of 3.92 nm to 4.3 nm with the addition of MOF-5. [26]

274 ***Hydrophilicity Measurement***

275 The hydrophilicity of the membranes characterized by the contact angle measurement and the
276 contact angle data are listed in the Table. 4. The contact angle falls with the addition of MOF-
277 5, and this could be due to fact that contact angle is a function of surface roughness. The contact
278 angle of PES membranes decreased from 86.075° to 76.42°, with the addition of MOF-5 which
279 shows that the hydrophilicity PES/MOF-5 membranes significantly superior to neat PES
280 membranes. [27] In case of CA, PVDF membranes contact angle was decreased from 75.03° to
281 70.68° and 80.47° to 72.975 ° respectively, which proves that hydrophilicity has been increased
282 because of the addition of MOF-5. [19,24]

283 ***Membrane Resistance and Permeability***

284 The pure water flux of neat and MOF-5 embedded PES, CA and PVDF membranes can be
285 used to determine the hydraulic permeability and membrane resistance. The pure water flux of
286 neat and MOF-5 incorporated polymeric membranes is shown in Fig. 9. The membrane
287 permeability is inversely proportional to the membrane resistance. The membrane permeability
288 and membrane resistance was calculated from Eq. (1), and Eq. (3) respectively and listed in
289 Table.5. The neat PES, CA and PVDF membranes were having higher membrane resistance
290 compared with PES/MOF-5, CA/MOF-5 and PVDF/MOF-5 could be due to the increase in
291 hydrophilicity of membranes by addition of MOF-5. [27] For PES membrane, the permeability
292 has been increased from 29.52 ±1.6 L/m² hr to 53.31± 1.6 L/m² hr and consequently membrane
293 resistance was decreased from 13 ×10¹³ m⁻¹ to 7.4×10¹³ m⁻¹. In case of CA/MOF-5
294 permeability was increased from 41.01±1.2 L/m² hr to 69.72± 1.4 L/m² hr and the hydraulic
295 resistance was reduced from 9.6×10¹³ m⁻¹ to 5.6×10¹³ m⁻¹ which indicates that the
296 hydrophilicity of CA/MOF-5 membrane has been improved. [19,22] The PVDF/MOF-5 have
297 higher water flux compared to neat PVDF membrane, and hydraulic resistance value was

298 reduced from $17 \times 10^{13} \text{ m}^{-1}$ to $11 \times 10^{13} \text{ m}^{-1}$. [24] CA/MOF-5 has shown higher water flux
299 compared to all other membranes, possibly due to the higher porosity of the CA membranes as
300 observed in Table 3. In all cases, MOF-5 incorporated membranes exhibited higher fluxes than
301 their corresponding neat membranes. The addition of MOF-5 particles to membranes enhances
302 the pure water flux through them, due to the increased hydrophilic character of the membranes.
303 Increase in hydrophilicity could be due to the higher affinity of metal cluster of MOFs for water
304 and consequently the pure water flux also increased.

305 ***Heavy Metal Ions Permeability of Membranes***

306 Experiments were carried out for the removal of copper Cu (II) and cobalt Co (II) metal ions
307 from water to study the influence of MOF-5. Fig. 10 and Fig. 11 illustrates the variation of the
308 rejection of neat and composite MOF-5 membranes for the metal ion aqueous solutions
309 containing Cu (II) and Co (II) respectively. CA/MOF-5, PES/MOF-5, and PVDF/MOF-5
310 membranes has higher permeability flux of $59 \pm 1.2 \text{ L/m}^2 \text{ hr}$, $41 \pm 1.6 \text{ L/m}^2 \text{ hr}$ and $27 \pm 1.4 \text{ L/m}^2$
311 hr respectively for Cu(II) solution when compared to neat CA, PES, and PVDF membranes. In
312 case of Co (II) solutions, similar higher permeability flux of $47 \pm 1.2 \text{ L/m}^2 \text{ hr}$, $40 \pm 1.4 \text{ L/m}^2 \text{ hr}$
313 and $24 \pm 1.2 \text{ L/m}^2 \text{ hr}$ observed for MOF-5 blend polymeric membranes CA/MOF-5, PES/MOF-
314 5, and PVDF/MOF-5 respectively, which proves that the MOF-5 enhance the hydrophilicity
315 and reducing the fouling flux. [28,29] CA/MOF-5 membranes has higher permeability compared
316 with all other membranes.

317 ***Performance of Composite Polymer/MOF-5 Membranes on heavy Metal ion rejection***

318 The effect of MOF-5 on the percentage rejection of metal ions for membranes is shown in
319 Table 6. The rejection capability of the prepared composite PES/MOF-5, CA/MOF-5
320 PVDF/MOF-5 membranes was comparatively higher than the neat membranes. The observed
321 rejection of Cu (II) in neat CA and CA/MOF-5 is found to be 50.8% and 53.3% respectively.

322 For PVDF and PVDF/MOF-5 observed rejection was 54.3% and 52.3%. The highest observed
323 rejection of Cu (II) is obtained in CA/MOF-5 membranes which is due to the higher affinity of
324 MOF-5 with the CA membrane. The Co (II) rejection is shown in Table.7. Rejection
325 performance of prepared membranes for Co (II) is much higher than that of Cu (II). Higher
326 rejection efficiency for Co (II) in PES/MOF-5 and CA/MOF-5 was found to be 74.40% and
327 77.0% respectively, which shows that membranes selectivity was not compromised with that
328 of the flux. Hence both the rejection and the permeability flux of composite PES/MOF-5,
329 CA/MOF-5, and PVDF/MOF-5 membranes remains higher than those of the neat polymeric
330 membranes. [27] The real rejection efficiencies (R_{real}) of the heavy metal ions were calculated
331 for both neat and Composite PES/MOF-5, CA/MOF-5, and PVDF/MOF-5 membranes. It was
332 implied that R_{real} values of both neat and Composite PES/MOF-5, CA/MOF-5, and
333 PVDF/MOF-5 membranes, remained higher than the R_{obs} values. [28] This is due to
334 concentration polarisation, and it remains higher for dead-end NF cell.

335 **Conclusion**

336 The MOF-5 synthesized by simple Solvothermal method and characterised by FTIR, XRD
337 analysis, SEM with EDX. Surface morphology reveals the formation of cubical structure of
338 MOF-5 and its useful properties for the removal of heavy metal ions from wastewater. The
339 MOF-5 particles incorporated into the three different polymers namely PES, CA and PVDF.
340 The addition of MOF-5 in polymeric membranes influenced porosity and surface mean pore
341 size of the prepared composite membranes. Further, the hydrophilic properties and
342 performance of composite membranes enhanced by the incorporation of MOF-5 due to the
343 metal clusters of MOF-5. The incorporation of MOF-5 has offered increased hydrophilicity of
344 polymeric membranes and is confirmed by the 70%, 80.58% and 46.47% improvement in
345 permeability for CA, PES and PVDF membranes respectively with 0.5 wt. % loading of MOF-
346 5. The MOF-5 incorporated polymeric membranes (PES/MOF-5, CA/MOF-5, and

347 PVDF/MOF-5) has higher rejection efficiency of Cu (II) and Co (II) ions compared to neat
348 polymeric membranes.

349

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439 **Table caption**

440 Table 1. Composition of casting solution for the preparation of composite membranes

441 Table 2. Mass transfer coefficient (K) and diffusion coefficient (D)

442 Table 3. Porosity and mean pore radius of membranes

443 Table 4. Contact angle measurement

444 Table 5. Membrane resistance and pure water flux

445 Table 6. Cu (II) rejection of membranes

446 Table 7. Co (II) rejection of membranes

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TABLES

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Membrane type	Composition of casting solutions			466
	Polymer	MOF-5	DMF solvent	467
	(g)	(g)	(ml)	468
Neat PES	4.375	-	21.7	469
PES+ 0.5% MOF-5	4.353	0.022	21.7	470
Neat PVDF	4.375	-	21.7	471
PVDF+0.5% MOF-5	4.353	0.022	21.7	472
Neat CA	4.375	-	21.7	473
CA+ 0.5% MOF-5	4.353	0.022	21.7	474
				475
				476

477 Table 1. Composition of casting solution for the preparation of composite membranes

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Feed solution	K	D	481
Copper solution	5.78×10^{-5} m/s	4.335×10^{-9} m ² /s	
Cobalt solution	4.22×10^{-5} m/s	4.182×10^{-9} m ² /s	482

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Table 2. Mass transfer coefficient (K) and diffusion coefficient (D)

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Membranes	Porosity (%)	Mean Pore radius (nm)
PES	70.50	5.62
PES/MOF-5	78.94	6.97
CA	72.50	5.57
CA/MOF-5	81.26	9.09
PVDF	65.32	3.92
PVDF/MOF-5	74.40	4.30

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489 Table 3. Porosity and mean pore radius of membranes

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Membranes	Contact Angle (°)
PES/MOF-5	76.42
CA/MOF-5	70.68
PVDF/MOF-5	72.975
PES	86.075
CA	75.03
PVDF	80.47

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492 Table 4. Contact angle measurement

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Membrane Type	Membranes Resistance, R_m (m^{-1})	Pure water flux (L/m^2 hr)
PES	13×10^{13}	29.52±1.6
PES/MOF-5	7.4×10^{13}	53.31±1.6
CA	9.6×10^{13}	41.01±1.2
CA/MOF-5	5.6×10^{13}	69.72±1.4
PVDF	17×10^{13}	22.96±1.4
PVDF/MOF-5	11×10^{13}	33.63±1.2

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Table 5. Membrane resistance and pure water flux

Membrane Type	C_m (ppm)	Rejection percentage (%)		498
		R_{obs}	R_{real}	499
PES	1178.14	30.5	35.35	500
PES/MOF-5	1075.12	51.4	58.74	501
CA	1111.97	50.8	52.39	502
CA/MOF-5	1033.57	53.3	58.00	503
PVDF	1072.63	52.3	55.52	504
PVDF/MOF-5	1039.91	54.3	56.05	504

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Table 6. Cu (II) rejection of membranes

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Membranes type	C_m (ppm)	Rejection Efficiency %	
		R_{obs} (%)	R_{real} (%)
PES	1084.29	58.35	61.58
PES/MOF-5	1225.31	74.40	79.10
CA	1079.60	45.30	49.34
CA/MOF-5	1353.49	77.0	83.00
PVDF	1040.16	41.8	44.04
PVDF/MOF-5	1116.93	64.20	67.94

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Table 7. Co (II) rejection of membranes

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523 **Figure caption**

524 Scheme. 1. Schematic representation of removal of heavy metal ions from aqueous solution by
525 MOF-5 incorporated membranes Nanofiltration.

526 Figure 1. FTIR spectra of MOF-5

527 Figure 2. XRD image of MOF-5

528 Figure 3. SEM image of MOF-5

529 Figure 4. FT-IR spectra of MOF-5, neat and MOF-5 incorporated membranes

530 Figure 5. XRD analysis of MOF-5, neat and MOF-5 incorporated membranes

531 Figure 6. Cross-sectional view of (a) neat PES and (b) PES/MOF-5

532 Figure 7. Cross-sectional view of (c) neat CA and (d) CA/MOF-5

533 Figure 8. Cross-sectional Image of (e) neat PVDF and (f) PVDF/MOF-5

534 Figure 9. Pure water flux of membranes

535 Figure 10. Flux of copper feed solution for membranes

536 Figure 11. Flux of cobalt feed solution for membranes

537 **Scheme**

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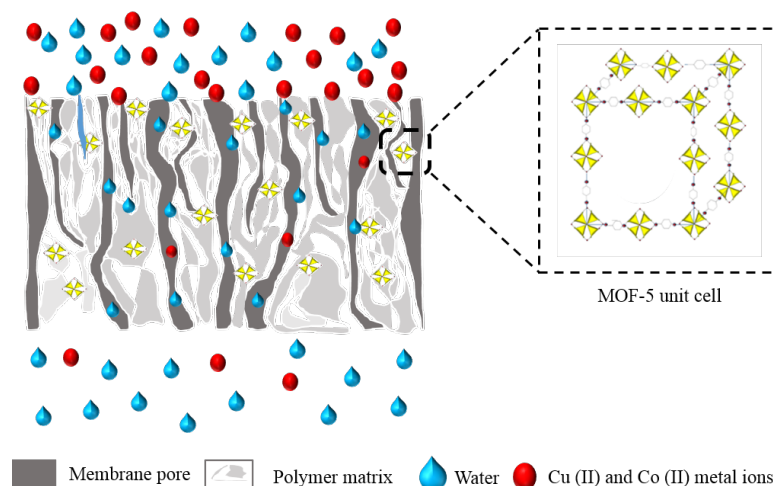
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546 Scheme. 1. Schematic representation of removal of heavy metal ions from aqueous solution

547 by MOF-5 incorporated membranes Nanofiltration.

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FIGURES

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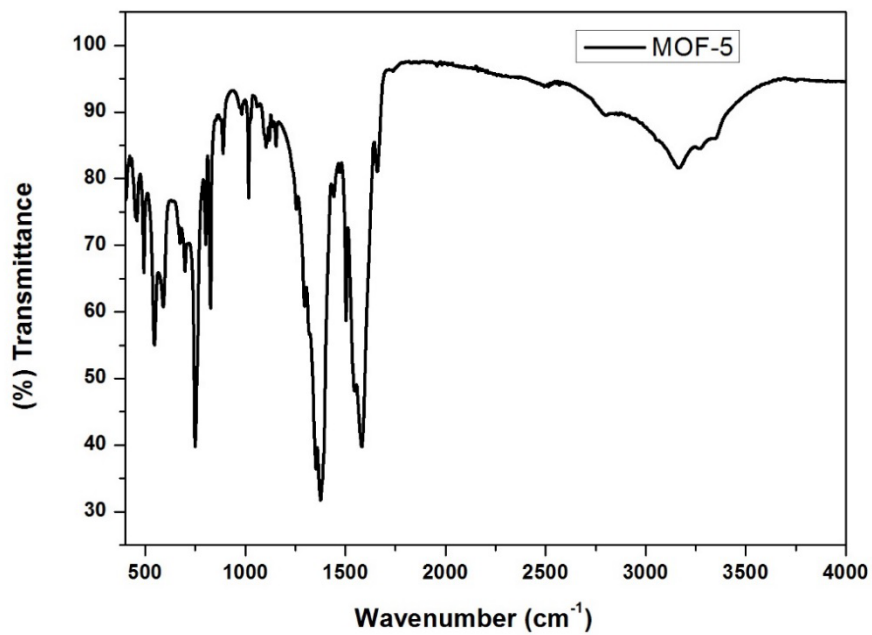
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Figure 1. FTIR spectra of MOF-5

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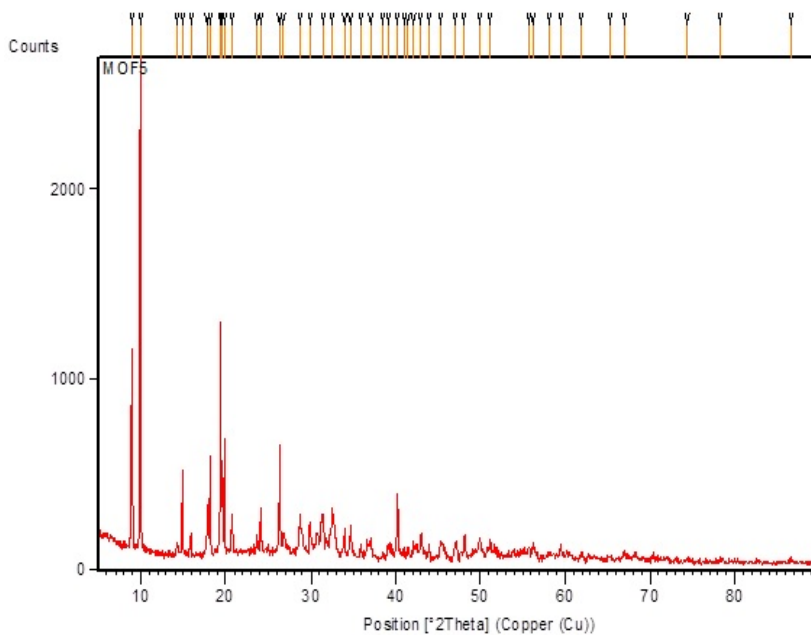
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Figure 2. XRD image of MOF-5

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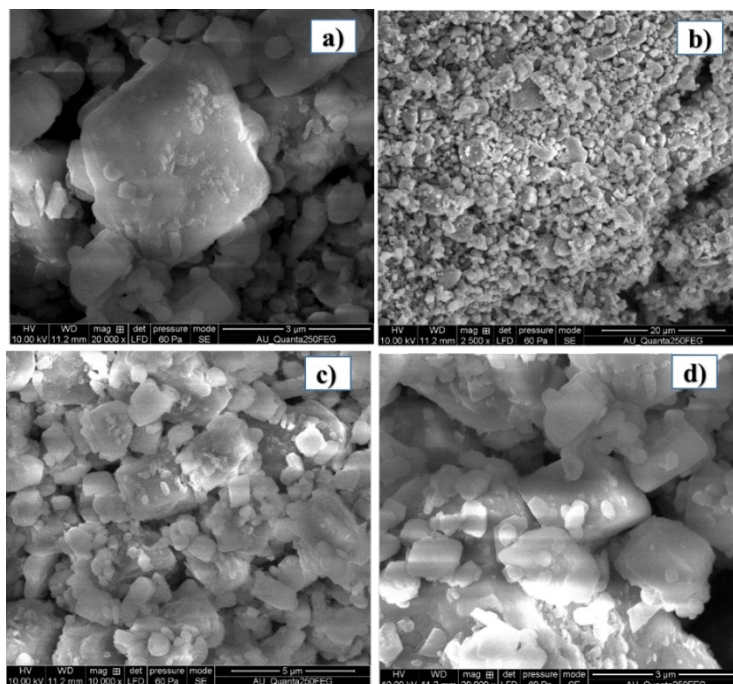
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Figure 3. SEM image of MOF-5

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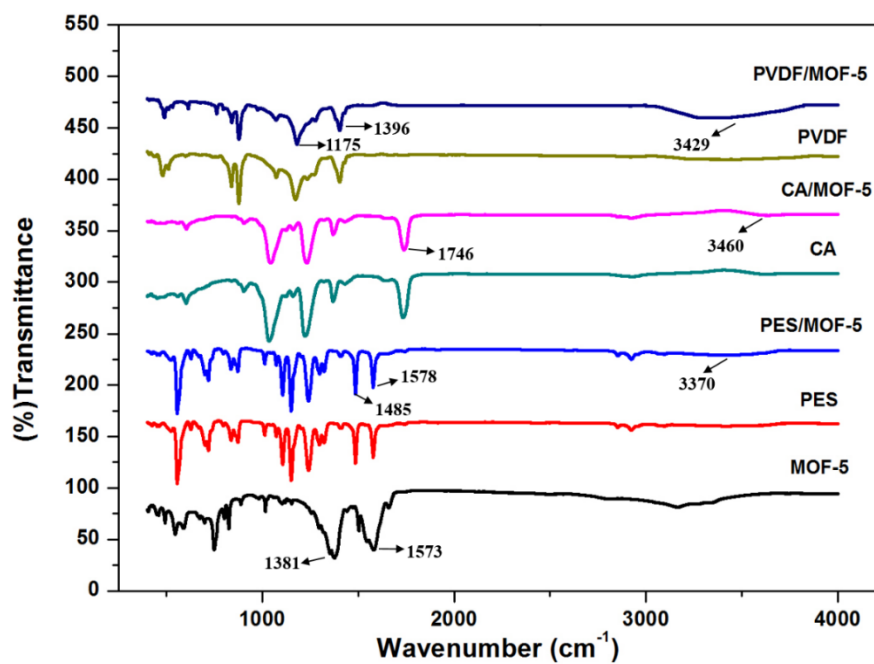
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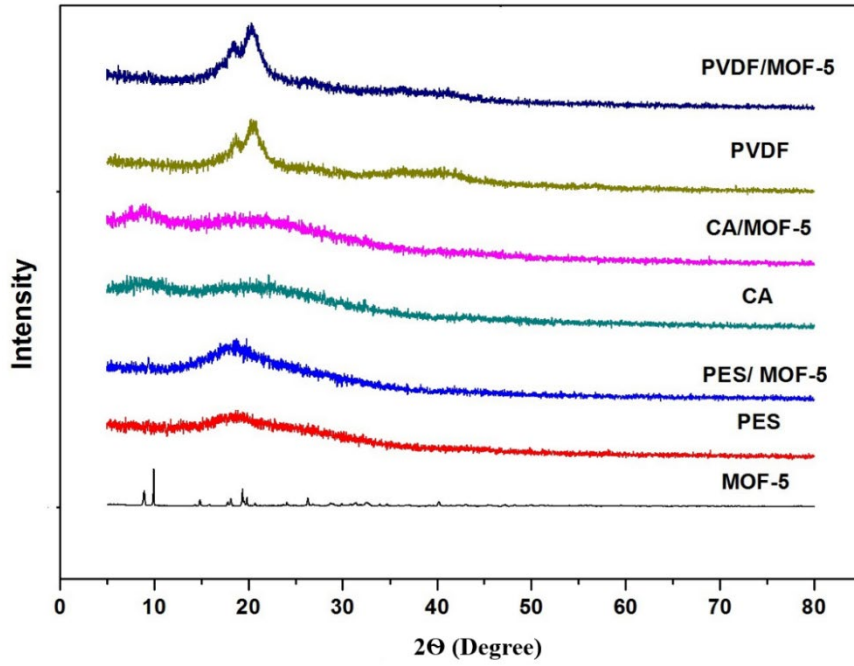
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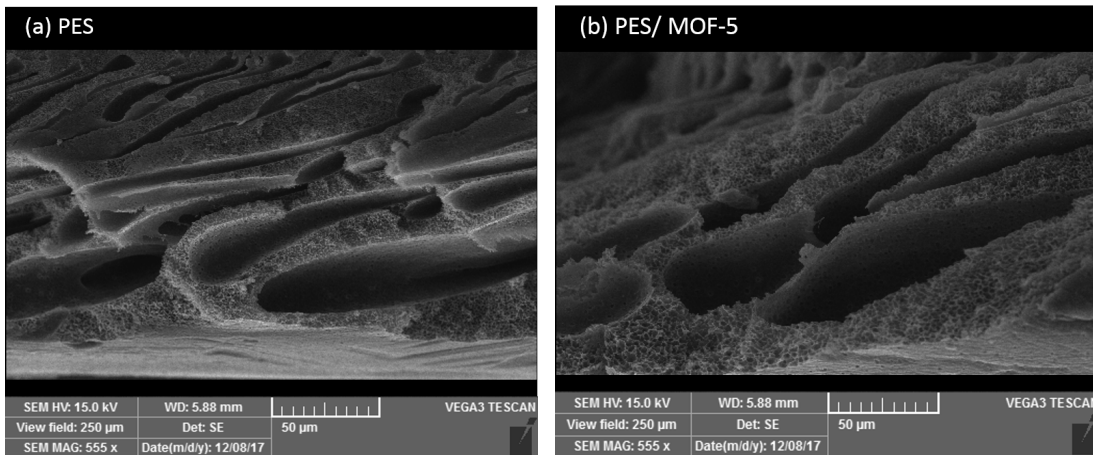
Figure 4. FT-IR spectra of MOF-5 and membranes



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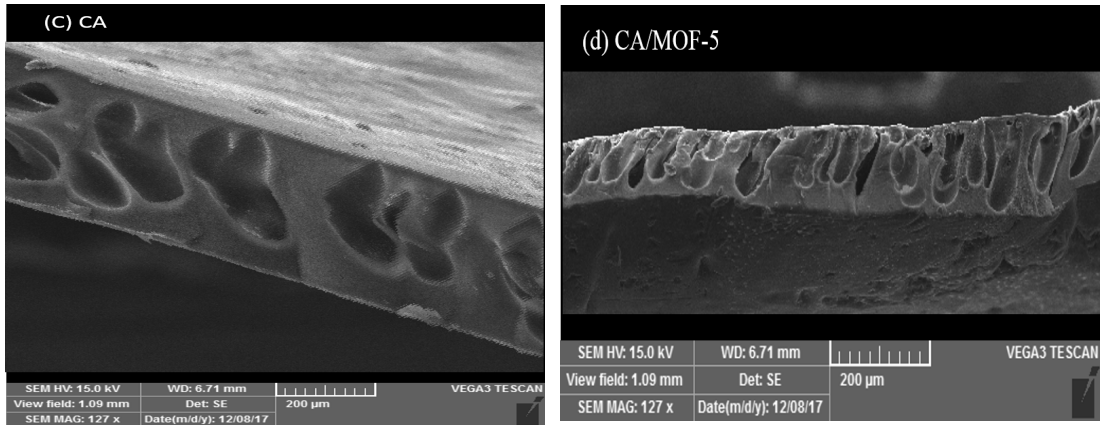
Figure 5. XRD analysis of MOF-5 and membranes



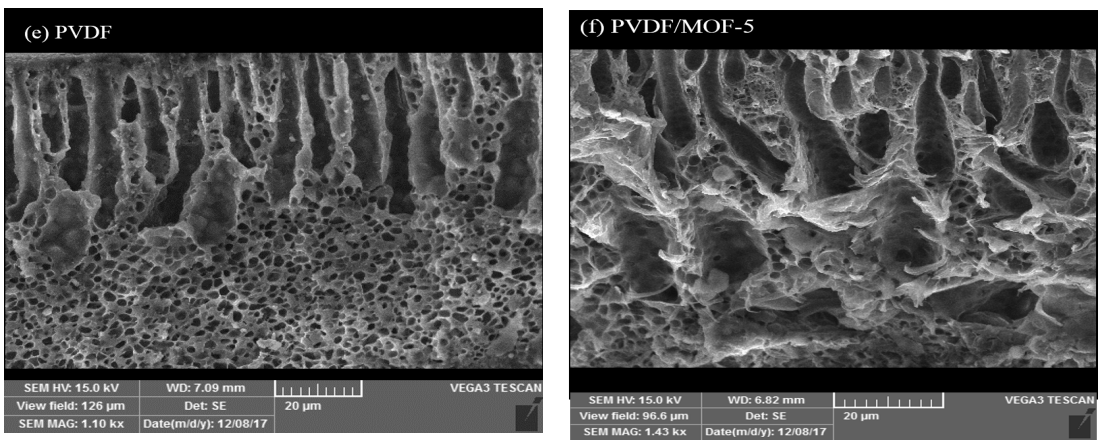
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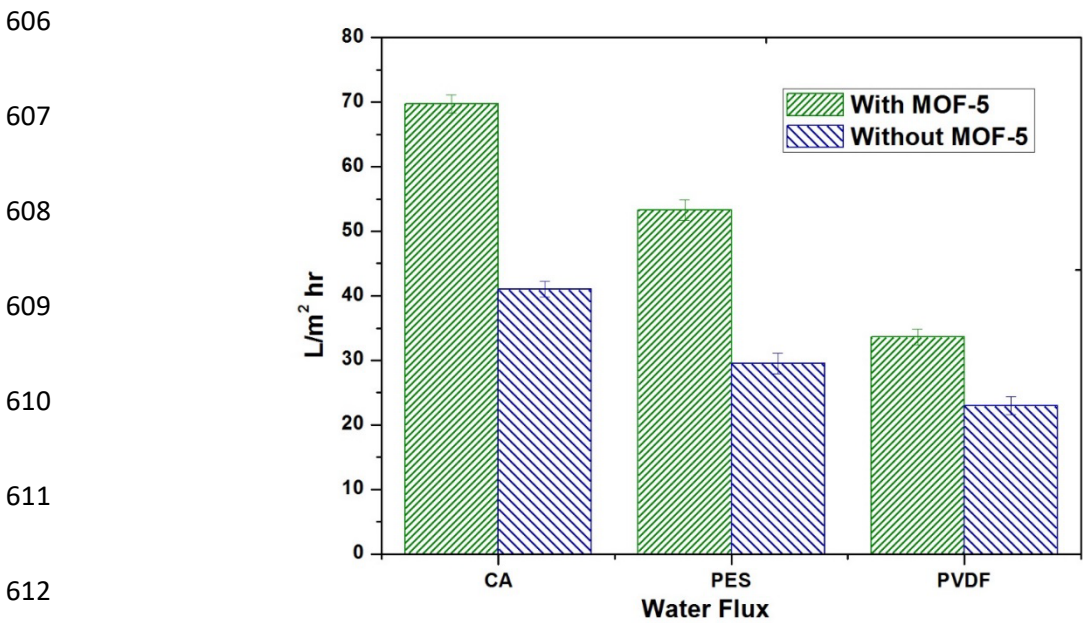
Figure 6. Cross-sectional view of (a) neat PES and (b) PES/MOF-5



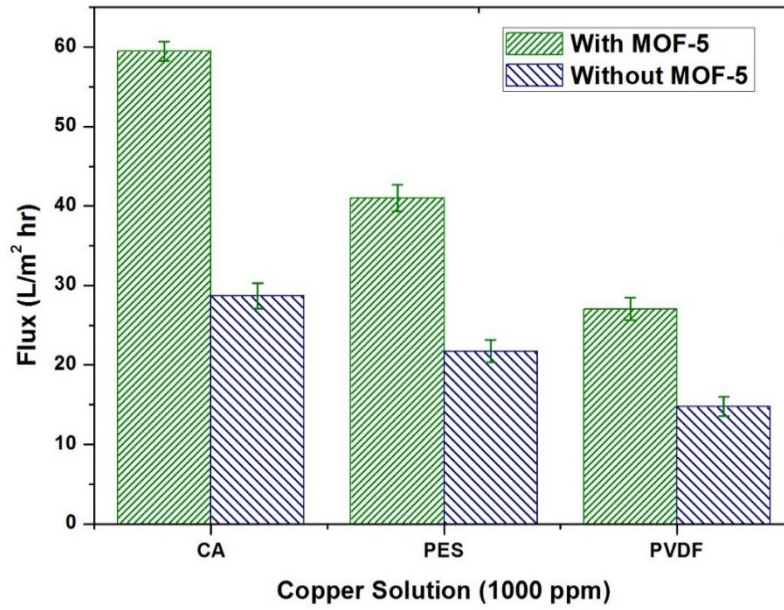
600 Figure 7. Cross-sectional view of (c) neat CA and (d) CA/MOF-5



605 Figure 8. Cross-sectional Image of (e) neat PVDF and (f) PVDF/MOF-5



613 Figure 9. Pure water flux of membranes



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Figure 10. Flux of copper feed solution for membranes

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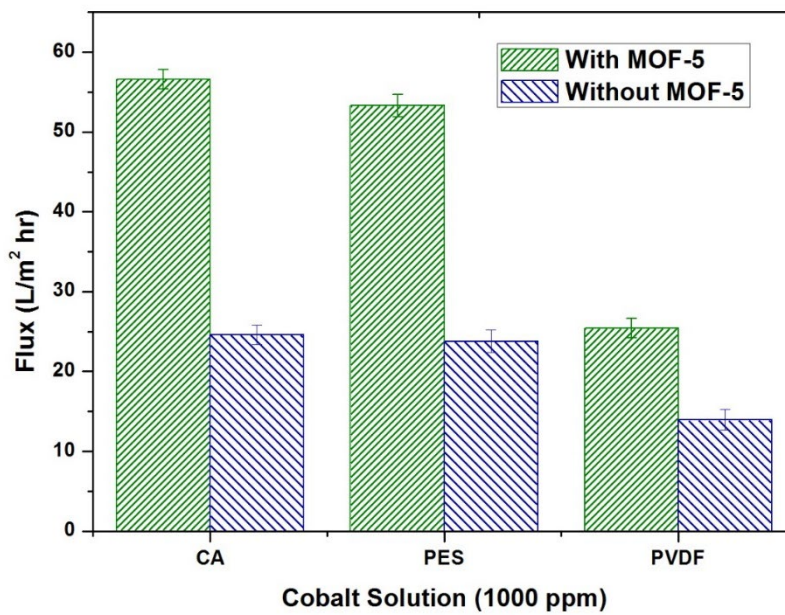
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Figure 11. Flux of cobalt feed solution for membranes

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