Tuning the surface charge and pore size in IPN arrested 'covalent organic nanostructures' through *in situ* exchangeable bonds for removal of persistent contaminants

*Ria Sen Gupta[a], Sk. Safikul Islam[a], Amit Malakar[a], Tridip Das[b] and Suryasarathi Bose[a]**

[a] Department of Materials Engineering, Indian Institute of Science, Bengaluru –560012, India

[b]Materials and Process Simulation Centre, California Institute of Technology, Pasadena, California – 91125, United States

* sbose@iisc.ac.in , *Fax: +91-(0)80-2360 0472*

SUPPORTING INFORMATION

EXPERIMENTAL SECTION

Materials and Methods

PVDF of Kynar 761 grade, having a molecular weight of 440,000 g/mol, was provided by Arkema. Sodium meta per-iodate ($NaIO_4$) at a purity of at least 99.8%, Dopamine hydrochloride monomer (DA) with a purity of 99%, and 11-Mercaptoundecanoic acid (purity >95%) were acquired from Sigma Aldrich. 2,4,6-triformylphloroglucinol (TP,>98.0%) and 3-3'-Dihydroxybenzidine (DHB, purity >99%) were provided by TCI chemicals. Buffer Tris(hydroxymethyl)aminomethane (Tris) with a purity of 99.8–100% was sourced from Sisco Research Laboratories Pvt Ltd. Sodium hydroxide pellets (NaOH) at a concentration of 97.0%, Hydrochloric acid (HCl) with a concentration of 35-38%, N, N-dimethylformamide (DMF, >99%)), N,N-Dimethylacetamide (DMAc, >99%), Acetone (>98%), Tetrahydrofuran (THF, >99.9%), Mesitylene (purity 98%), 1,4-Dioxane (purity 99.5%), N,N′-

Dicyclohexylcarbodiimide (DCC, purity >99%),4-Dimethylaminopyridine (DMAP, purity >98%) and Dichloromethane (DCM, purity >99%) were purchased from SD Fine Chemicals Ltd. All the dyes, namely Methyl Orange (MO) with a molecular weight of 327.33 Da, Rhodamine B (RB) with a molecular weight of 479.02 Da, Methylene Blue (MB, 319 Da), Methyl Red (MR, 269.30 Da), Congo Red (CR, 696.66 Da), Amido Black (AB, 616.49 Da), and Acrydine Orange (AO, 301.81 Da), were obtained from a local vendor. Tetracycline with a molecular weight of 444.43 Da, Amoxicillin with 365.40 Da molecular weight and Azithromycin with a molecular weight of 785 Da were obtained from a local medicine store.

Fabrication of Thiol-modified Covalent Organic Framework (SH-COF)

The preparation of this novel thiol-containing covalent organic framework (SH-COF) consists of two steps. In the first step, the hydroxyl-modified COF [OH-COF] was prepared and then the thiol group was introduced to make the thiol-modified COF [SH-COF] in the second step.

Step I:

In a beaker, TP (4.1 mmol) and DHB (5.9 mmol) were mixed followed by the addition of a prepared solution mixture containing mesitylene (0.03 mol) and 1,4-dioxane (0.4 mol). Next, acetic acid (3 mol) was added to the solution and allowed to stir for 15 minutes to mix properly. The orange-colored solution was then poured into a PTFE-lined stainless steel autoclave container (50 ml) and kept at 120 ° C for 72 hrs. The obtained deep orange residue was washed thoroughly with DMAc, acetone, and deionized water respectively, and kept in an oven (70 °C) for overnight drying. The resultant product was termed as OH-COF

Step II:

For the consequent thiol modification, 11-mercaptoundecanoic acid (0.71 mol), DCC (0.72 mol), DMAP (0.72 mol), and the prepared OH-COF were combined in a round-bottom flask, followed by the addition of 30-40 ml DCM. The resulting solution was bath sonicated for 10

minutes to achieve homogeneous dispersion. Subsequently, the solution was refluxed for 24 hours at 45 °C. The resulting brown-colored solution was washed with THF until a clear permeate was obtained. The resulting product was designated as SH-COF.

Synthesis of SH-COF tagged IPN membrane (SC-IPN)

To initiate the covalent tagging of the SH-COF moieties with the IPN membrane matrix, a 30 wt% dope solution was made using 2 gm of PVDF and 1 gm of dopamine monomer in DMF (7 ml), and the solution was mechanically agitated at 80 ° C to form a homogeneous solution. Next, SH-COF (6. wt%) was dispersed in DMF (3 ml) which upon complete dispersion was poured into the dope solution. The membranes were duly cast on a glass plate using a 300 µm doctor blade that was adjusted to a casting speed of 7-8 cm/s. The glass plate with the films were immersed in a coagulating bath containing a cold (4-5 ° C) Tris buffer solution (10 mM, pH=8.5) (buffer was intended to maintain the pH of the bath in order to aid in the auto-oxidative polymerization of the dopamine) and $NaIO_4$ (5 mM) (oxidizing agent for enhancing the auto oxidative polymerization process). Low temperature helps in faster solvent-non-solvent exchange. For optimized pore size reduction, the membranes were submerged in the buffer solution for seven days.[1] The membranes were thoroughly cleansed and cleaned with ultrapure water prior to any additional tests or evaluations. The fabricated membranes were denoted as SC-IPN membranes.

Characterization of synthesized SH-COF and SC-IPN membranes

In the beginning, the structures of the synthesized OH-COF and SH-COF were determined using Density functional theory using VASP 5.4.4. The details of the computational setup are mentioned in the supplementary section. The fabricated particle and membranes' characterization began with mid-IR FTIR- spectroscopy from the Parkin Elmer frontier. XPS data acquired with an Axis Ultra using Al as the monochromatic source (1.486 keV) were used

to support the FTIR results. For the synthesized SH-COF, ^{13}C-solid state-NMR was performed on a Bruker AV 500S-500 MHz having traditional CP-MAS probe with a 10 kHz MAS frequency where 2 ms remained contact time for CP. Using Micromeritics ASAP 2020, BET adsorption-desorption isotherms for pore-size measurement were achieved. The membrane's surface roughness was measured using a Park NX10 AFM (5N/m cantilever force constant, non-contact mode, tip radius curvature of 8nm). The morphological images and elemental composition were studied using an EDX detector on a Karl Zeiss Ultra55 FE-SEM scanning electron microscope. Thermogravimetric analysis was carried out using TA Q500. PANalytical X'pert PRO was used to investigate X-ray diffraction through the crystalline OH-COF, SH-COF, IPN membrane, and SC-IPN membranes. The membranes' hydrophilicity was investigated by measuring the contact angle keeping water as solvent choice. The dye, antibiotic and microplastic rejection efficiencies were calculated using UV-Vis spectrophotometer from Perkin Elmer and that for the mercury samples ICP-OES from Agilent was employed. Mechanical integrity was analysed using Micro UTM and DMA. TA Q800 was used in tension mode and a force of 0.01 N was applied in the temperature range of 30-140 °C with a 10 °C/min heating rate. A load cell of 25N was used in micro UTM and a loading rate of 10mm/min was applied for conducting the tensile tests. Using the Surpass 3 instrument and Anton Paar's adjustable cell with a gap height of 100 m and pH 7, the surface charge of the membranes was investigated from their Zeta Potential. The Zetasizer nano series (Malvern Instruments) was used to assess the zeta potential of the synthesised SH-COFs. Zeta pals from Malvern instruments were utilized for particle size measurements.

Membrane porosity, uptake and pore size distribution and pore size calculation

The nature of the fabricated membrane is determined through bulk hydrophilicity which in turn plays a significant role in its absorption capacity of water. A facile technique was adopted to calculate this. Briefly, after taking out from the vacuum oven, approximately ten membrane coupons of comparable size and surface area (0.63 cm^2) were weighed. After being completely submerged in distilled water, the identical membranes were weighed again. The uptake percentage was duly calculated utilizing Hebbar's formula[2]

$$\%\ Uptake = \frac{(W_w - W_d)}{W_w} \times 100 \qquad \text{equation (1)}$$

Where W_w = weight of immersed membranes after 24 hr. W_d = weight of dry membranes respectively.

The Zhang et al. method was optimised for measuring membrane porosity.[3] After being pad-dried using filter paper, the wet membrane's weight (Ww) was noted down. The membranes were then put in an air-circulating oven at 75 °C for 24 hours and dry weight (Wd) was calculated subsequently. The percentage of porosity ($\varepsilon\%$) can be mathematically calculated using the following equation:

$$\varepsilon\ (\%) = \frac{W_w - W_d}{A \times l \times \rho} \times 100 \qquad \text{equation (2)}$$

where, area of membrane = A, membrane thickness= 1 and density of distilled water = ρ (0.9975 g/cc at ambient temperature).

For pore size distribution, SEM micrographs were taken from sections of the membrane and around 100 pore diameters (measured 500 times) were analyzed using ImageJ software. Average pore diameters (d_p) were calculated by using the equation,

$$d_p = \left[\frac{\sum_{j=1}^{n} n_j d_j^2}{\sum_{j=1}^{n} n_j}\right]^{0.5} \quad \text{equation (3)}$$

where, n is the number of values of pore diameters considered, d_j is the j^{th} pore diameter value (nm), and n_j is the number of pores with the j^{th} diameter value.

The mean pore radius of the membrane was calculated using the Gerout-Elford-Ferry equation,

$$r_m = \left[\frac{(2.9 - 1.75\varepsilon)8 \times Q \times l \times \rho}{\varepsilon \times A \times \Delta P}\right]^{0.5} \quad \text{equation (4)}$$

Where, r_m is the mean pore radius (m), ε is the porosity of the membrane, representing the fraction of the membrane volume that is occupied by voids or pores, Q being the flow rate (m^3/s), l is the membrane thickness (m), ρ denotes the viscosity of water (Pa.s at 25°C), A is the effective membrane area (m^2) and ΔP is the operational pressure (Pa) respectively.

Molecular performance: Rejection studies, pure water flux, antifouling and chlorine tolerance.

Pure water Flux stability and Antifouling studies

A significant need of filtration modules is water flux which is commonly attained from the membranes. For typical commercial membranes, the common trade-off between membrane

permeability and selectivity frequently presents a gridlock. A filtration set up having an in-house cross-flow mechanism has been utilized to evaluate the pure water flux. Before beginning the experiment, 45 mm-diameter token membrane coupons were carefully installed into the test cell and compressed at 10 psi (about 0.7 bar) for about 30 minutes. Next, the transmembrane pressure was discretely changed from 10 to 150 psi (0.7 to 10.34 bar) and the resultant flux (Jw) was then calculated using the following formula:

$$J_w = \frac{V}{A \times t} LMH \qquad \text{equation (5)}$$

All tests were run in triplicate to ensure repeatability. These membranes should have long-term stable and continuous performance. In order to verify the membranes' stability, a transmembrane pressure of 125 psi (8.6 bar) was maintained continuously for 21 days.

For gauging the antifouling properties of the SC-IPN membrane, 1000 ppm BSA (Bovine Serum Albumin) solution was used as the model protein model. After evaluating pure water flux (Jw) generated by the membranes, again flux values with BSA solution recorded at 100 psi for 1 hr. To thoroughly backflush the membrane, 0.9 wt.% of NaCl solution was used. Subsequently pure water flux values were again recorded (Jw_1). Flux recovery ratio (FRR) evaluated to measure the antifouling performance of the membrane.

$$\% FRR = \frac{J_{w1}}{J_w} \times 100 \qquad \text{equation (6)}$$

Dye and antibiotic rejection studies

Some familiar dyes viz. Acridine Orange (AO), Amido Black (AB), Congo Red (CR), Methyl Red (MR), Methylene Blue (MB), Rhodamine B (RB), and Methyl Orange (MO) were considered as model dye foulants to study the dye rejection ability of the fabricated membrane. Similarly model antibiotic solutions of Amoxicillin, Azithromycin and Tetracycline were also prepared. First, 20 ppm solution of each dye and antibiotic was prepared using distilled water and a dead end setup was employed in which the coupon membranes (45 mm diameter) were carefully mounted. Each cycle consisted of 100 ml of the dye or antibiotic solution. The membranes were compacted and samples were collected for UV-Vis analysis. By determining the permeates' concentration through a UV-Vis spectrophotometer, the rejection efficiency of the SC-IPN membrane was calculated using the following equation:

$$\% \, Rejection = [1 - \frac{C_p}{C_f}] \qquad \text{equation (7)}$$

where C_p = permeate's concentration and C_f = feed's concentration.

Salt rejection studies

A 2000 ppm NaCl solution was prepared to assess the salt rejection performance of the fabricated SC-IPN membrane. The concentration of the permeates was surveyed through TDS (total dissolve solute) meter at regular intervals. The rejection analysis were carried out in an in-house FO set-up, owing to its low pressure requirements and FO being the most suited system for such membranes (nanofiltration/ultrafiltration). All the experiments were performed in triplicates/thrice. The experiment was conducted for a further 21 days to assess the membranes' durability. The following equation was employed for gauging the rejection performance,

$$\% \, Rejection \, = 1 - \frac{Cff - Cfi}{Cdi} * 100$$ equation (8)

Where C_{ff}, C_{fi}, and C_{di} represented the final feed concentration, initial feed concentration, and initial draw concentration in ppm, respectively.

Mercury removal experiments

1, 10, 20, and 100 ppm of $HgCl_2$ solutions were taken as model heavy metal contaminated samples. A dead-end set up was employed to carry out the process. Membrane coupons of 45mm diameter were mounted onto a dead-end set up and each cycle of removal consisted of 100 ml of the feed heavy metal solution. The heavy metal solutions were kept in contact with the membrane for a period of 2 hours after which permeates were collected with an application of a 1 bar vacuum. The Hg (II) ion concentration in the permeates were determined using an ICP-OES machine. The removal percentage of Hg (II) ions were calculated using the equation,

$$\% \, R = \left(\frac{C_o - C_e}{C_o} \right) \times 100$$ equation (9)

where Co and Ce are the initial and equilibrium concentrations of the Hg (II) solutions.

Microplastic Removal

The following stages make up the study on membranes' capacity to filter out microplastics. To begin, a tiny section of PVC pipe used for sanitary purposes was ground into powder using emery paper with a mesh size of 800. The powders were mixed with DI water and centrifuged for 10 minutes at 14000–15000 rpm to produce microplastics containing colloidal suspension. The supernatant was meticulously removed. Next, using a dead-end setup, the supernatant solution (feed) was passed over the SC-IPN membrane, and the permeate was properly collected. Particle size was measured by performing dynamic light scattering (DLS) in both

feed and permeate. The characteristic absorption peaks of PVC obtained through a UV-vis spectrophotometer were applied to confirm the microplastic filtering ability of the designed SC-IPN membrane.

Chlorine Tolerance evaluations

Chlorine tolerance evaluation in membranes commonly involves a comparison of the efficiency variation in salt rejection before and after exposure to concentrated sodium hypochlorite solution. The level of chlorine tolerance of the fabricated membrane increases with decreasing deviation. The membrane was initially immersed in a 2000 ppm (pH = 10) solution of sodium hypochlorite for more than 4 hours. After a thorough DI water wash, the membranes were tested to see if they could reject 2000 ppm of NaCl solutions in a manner like the salt rejection studies that were stated previously.

Invitro cytotoxicity measurements and recyclability studies

When determining the cytocompatibility of substances, MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide] cytotoxicity assays are frequently carried out. In these tests, metabolic activity serves as a proxy for cell viability. The yellow-colored water-soluble MTT metabolically turned into blue-violet insoluble Formazan when comes in contact with a living cell. The photometric evaluation of color intensity after Formazan was dissolved in DMSO gives a direct correlation between the color intensity and the number of living cells. For this experiment, the cell line L929 (NCCS/1469) was employed. Prior to the test, the cells were correctly maintained and cultured in Minimum Essential Media (MEM) containing Foetal Bovine Serum (FBS) (10%). To create the sample extract, 1 g of the sample (IPN membrane) was sterilized at 121°C for 15 minutes. The extract received 10 ml of fully prepared MEM

medium, which was then incubated for 24 hours at 37 °C (with 5% CO2 atmosphere). For the assay, a concentration range of 10 to 100% was maintained, with 100% corresponding to the neat extract.

10,000 cells per 100 ml of MEM culture per well were carefully seeded into a 96-well plate and kept there for 24 hours to successfully create a semi-confluent layer. The layer was exposed for 24 hours in the concentration range (10–100%) indicated above. By using an optical density (O.D.) measurement at 570 nm, the formazan formation in the growth control and concentration-treated sample was completely compiled at the end of the allotted period. For each treated concentration, the percentage of the proliferation of inhibition was computed through viability of cells using the following formula:

$$\%\, Viability = \frac{O.D\ for\ extract}{O.D\ for\ blank} \times 100 \qquad \text{equation (4)}$$

All the membranes used for dye and salt rejection were placed in a 100 ml round bottom flask filled with DMF and heated at 140 0C for 10-15 minutes to test the membranes' sustainability and recyclability. For a successful workup using the liquid extraction method, DCM and water were added to the blackish solution mixture. The extraction of DMF, salt, and dyes was done based on their various solubilities. The polymeric components could be obtained by evaporating the solvents, and as previously noted, the membrane was rebuilt using the NIPS method.

1. Predicting structure using Density Functional Theory: DFT calculation setup

For all density functional theory (DFT) computations in the ground state (0 K), VASP (Vienna Ab initio Simulation Package, v5.4.4) was used. Projector-augmented-wave

(PAW) potentials with valence configurations of $2s^2 2p^2$ for C, $2s^2 2p^4$ for O, $2s^2 2p^3$ for N, $3s^2 3p^4$ for S, and $1s^1$ for H were used to describe the valence electrons. Subsequently, Perdew, Burke, and Ernzerhof's (PBE) flavor of the generalized gradient approximation (GGA) functional was employed to describe the exchange-correlation potentials of the constituting elements. In addition, vdW correction (PBE-D3) with the Becke-Johnson parameters was included for the Grimme formulation. The accuracy of the electronic calculations was found to be within 1 μeV/atom. A gamma point energy calculation was performed to test the initial convergence of the input lattice. From the k-mesh calculations, it was concluded that a k-spacing of 0.2 Å-1 was sufficient for the required accuracy of 1 meV/atom when the cutoff energy was set to 500 eV. Ionic relaxations were performed until the Hellmann-Feynman force on each atom reached in the order of 10 meV/ Å.

Table 1: <u>Unit cell parameters</u>

The unit cell of OH-COF

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Unit cell of OH-COF generated by Tridip Das using Ovito and Avogadro
1.0
       28.2315686268        -0.0452006019        -4.9004818819
      -14.1242492415        25.4906152749         2.8518572881
       -0.7647970460         0.0713278858         4.5199893401
    C    H    O    N
   54   36   12    6
Cartesian
     2.591902867        15.578656114         0.578823685
     2.807489140        14.632037813         1.595202423
     4.043582397        14.009528086         1.749006658
     5.099040040        14.292114040         0.880027393
     4.888501247        15.202743430        -0.153793090
     6.936960530        12.672972175         0.292347147
     3.656223078        15.876981685        -0.297564154
     6.422011460        13.650960997         1.144449975
     7.095015082        13.934257500         2.334361641
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8.268326986	13.263981049	2.680233048
8.765838302	12.235788487	1.867042484
8.079407007	11.935373685	0.659814588
-0.773681276	18.653669392	1.994944840
0.840153971	17.218581665	0.885936195
10.307028779	10.397038085	2.056601937
-1.260794851	16.199443769	1.711212467
-0.383895891	17.343127935	1.506983723
11.471105349	9.847980589	1.527550238
11.557199562	8.388494781	1.516951350
12.269820686	10.674550158	0.664511445
-2.336993008	16.361111846	2.678521049
-2.553078884	17.590765381	3.425657689
-1.754546064	18.753254782	3.037890267
13.226815925	10.030001318	-0.203452212
13.368714974	8.573087944	-0.248683821
12.461805140	7.785838423	0.565205806
-2.127031426	20.006245260	3.557155598
-3.257974414	15.324260785	2.737327049
12.404608530	6.426562818	0.281185411
14.070060391	10.844918275	-0.937570138
16.794440635	12.012538361	-2.563935422
16.369932224	11.159391989	-1.534143194
-1.291818592	24.770462014	2.602674709
-1.177980520	23.398475267	2.474730334
-1.902212742	22.498261564	3.273781491
18.102768864	12.521581845	-2.587528449
-2.804947336	23.064527349	4.195423970
-2.886560103	24.462496269	4.347897793
-2.145901917	25.350210064	3.552900887
-6.259797841	14.415547138	2.243864531
-7.469747212	13.728714716	2.240761992
20.355948554	12.901511417	-1.571838222
-6.951617936	12.762831955	4.376096703

-5.698962503	13.394321426	4.336571866
-5.399629743	14.330188835	3.336295640
19.016739053	12.265504730	-1.553934161
12.499174653	3.515958180	-0.092976158
12.589290525	2.134229875	-0.099569617
11.834009879	1.331215664	0.772705596
10.946768150	1.991235675	1.633909506
10.807673326	3.392880336	1.621905727
11.621992756	4.183005355	0.770506816
18.565526301	11.476738532	-0.490713113
17.274445961	10.938195960	-0.479268201
4.923581418	15.525091311	3.670756775
1.982183323	14.385947403	2.268857817
4.188750780	13.327289601	2.585358245
6.420323303	12.399123005	-0.627180155
6.686532158	14.659689149	3.035358039
9.596651160	13.470236240	-0.946178099
3.172603625	16.670231269	2.445628112
8.469937162	11.173997426	-1.081846949
0.505426751	15.339615992	0.450327863
10.907489017	12.167771698	1.500101078
1.530297753	18.065211503	0.876587361
9.534545279	9.725243844	2.439516179
16.976663557	10.271341523	0.333866353
-2.932024490	19.981649336	4.291664828
-4.377085716	16.023766419	4.211119914
17.572556535	13.282257304	1.126570800
13.018814032	6.053458053	-0.540939544
-0.897436415	20.895441776	2.340168768
13.893928997	11.917842354	-0.900881999
-3.149121802	14.513173867	2.026359678
15.663030039	12.628387110	0.159185586
-0.759845421	25.374415587	1.872278931
-0.509837540	22.989743945	1.713932841

-3.620772703	24.809061771	5.072070200
-3.940302866	13.520527458	5.044755129
-5.999746409	15.064168734	1.404777162
19.400961148	13.801574055	0.951616833
-3.542050772	21.399442299	4.847145468
-7.123666674	12.061469209	5.187550966
13.127470604	4.082287775	-0.781591519
13.272760673	1.695864998	-0.818103035
10.581289111	3.629718848	-1.237901370
10.313305707	1.447220375	2.333878550
11.041871433	6.041882543	1.676811571
19.185595083	11.318880270	0.390103009
15.201869013	9.365358921	-1.569575740
2.676295950	16.895305610	3.277875210
8.579247177	10.949994910	-0.115614625
-1.085009552	15.119851194	1.062807675
-0.228834803	19.695027266	1.477777060
-3.515649958	17.680838875	4.250010149
10.782755275	7.684613109	2.240713654
12.110229984	11.951560416	0.647054418
14.242412225	8.023669718	-0.983591390
15.159437532	12.391293598	0.975777451
-3.637400493	22.352928919	5.011376419
-4.793400873	13.105712004	5.304167179
9.892804256	4.074014530	2.368135945
1.264982382	16.054647070	0.352866459
10.069448883	11.709440424	2.031433638
-4.308966232	15.223257912	3.544760427
-1.620480827	21.137256382	3.075215364
11.628066936	5.570659407	0.943201767
15.147184367	10.408896747	-1.612979675

Table 2: The unit cell for SH-COF

Unit cell of SH-COF generated by Tridip Das using Ovito and Avogadro

1.0

29.4342918977	-0.6319547146	0.5881321543
-15.2666722700	26.0751291458	0.0674356290
0.3327650860	0.2357442893	14.9653050613

C	H	N	S	O
120	156	6	6	18

Cartesian

4.433263166	14.461677155	7.879156170
4.579186869	13.093878536	8.174075212
5.777562791	12.431757438	7.969154851
6.907045075	13.114123880	7.474891535
6.741788379	14.462958991	7.124471179
9.257663878	12.918301453	6.554608725
5.532260618	15.120261173	7.298335575
8.218570356	12.451383369	7.381162934
8.485767081	11.344287059	8.201737241
9.726813191	10.726551983	8.201462134
10.762449049	11.179857233	7.357009640
10.497888710	12.295849509	6.548553494
1.384331924	18.206789854	8.652410023
2.909374157	16.345031209	8.306227576
12.348286409	9.351947104	7.670104193
0.516208362	15.831861100	8.651719510
1.609007828	16.775964505	8.553333205
13.626638654	8.827553419	7.652546581
13.746944459	7.447155319	8.134030987
14.762546064	9.606847524	7.202032136
-0.842704946	16.362228279	8.726634710
-1.120369041	17.789416000	8.815943562
0.023685706	18.698798702	8.803526352
16.075544473	8.950791795	7.227011735
16.222052732	7.530634017	7.524162238
15.056471162	6.806850416	7.979319379
-0.223137230	20.067629293	8.907814250

-1.844309373	15.415810039	8.601255670
15.109101866	5.461258091	8.304692610
17.176986461	9.768030137	7.079263697
20.809092037	9.841528189	6.824902067
19.537534474	10.172879279	7.325116567
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2. Deconvoluted XPS spectra

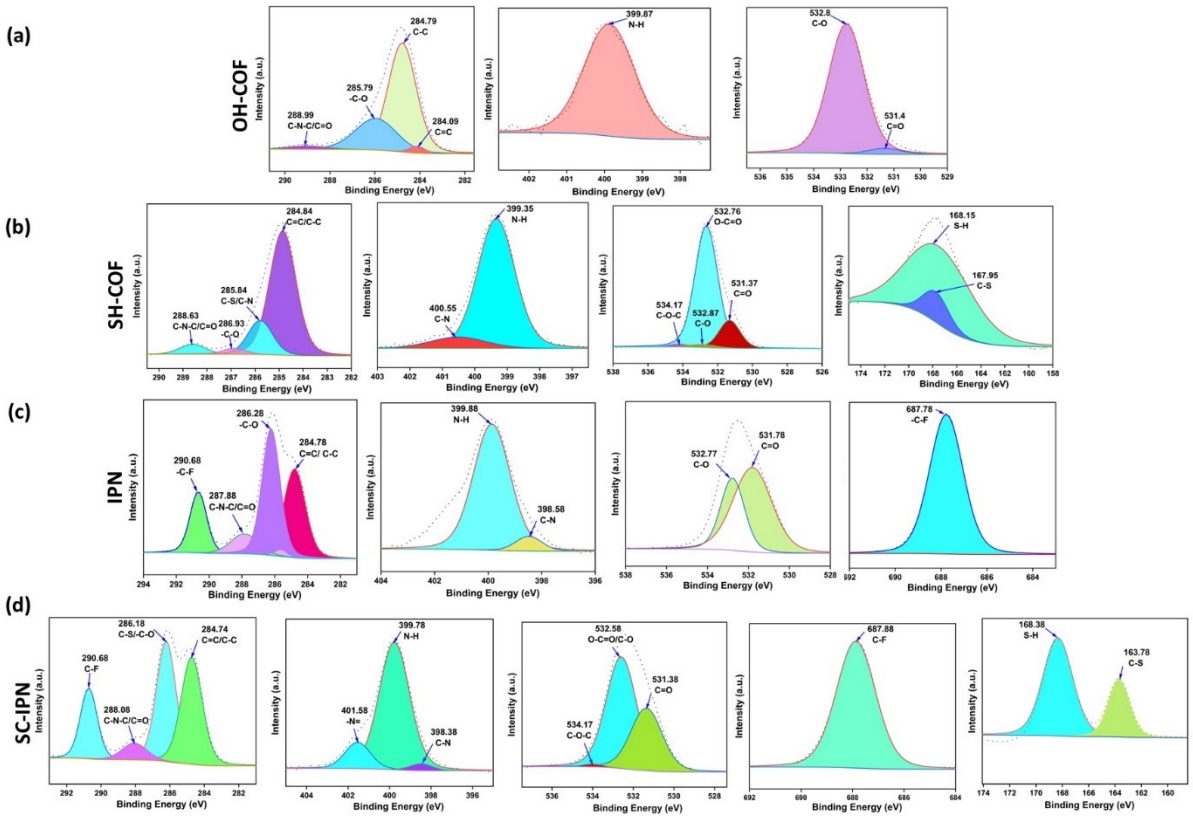

Figure S1. Deconvoluted C1s, N1s, O1s, F1s, and S1s spectra for (a) OH-COF, (b) SH-COF, (c) IPN and (d) SC-IPN membranes.

3. ^{13}C-NMR and BET of OH-COF

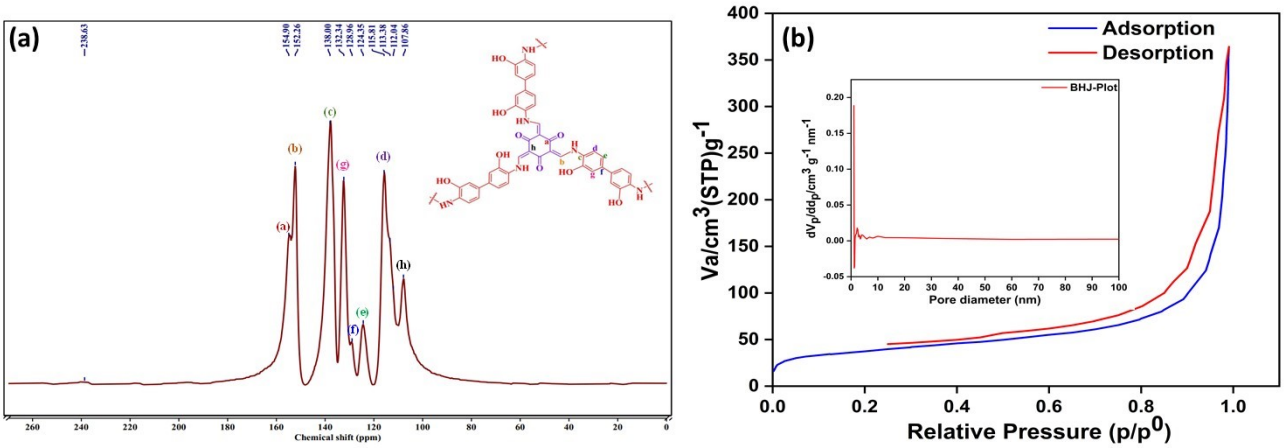

Figure S2. (a) ^{13}C-NMR and (b) N_2 adsorption-desorption isotherm for OH-COF.

4. Thermal profile of OH-COF and SH-COF

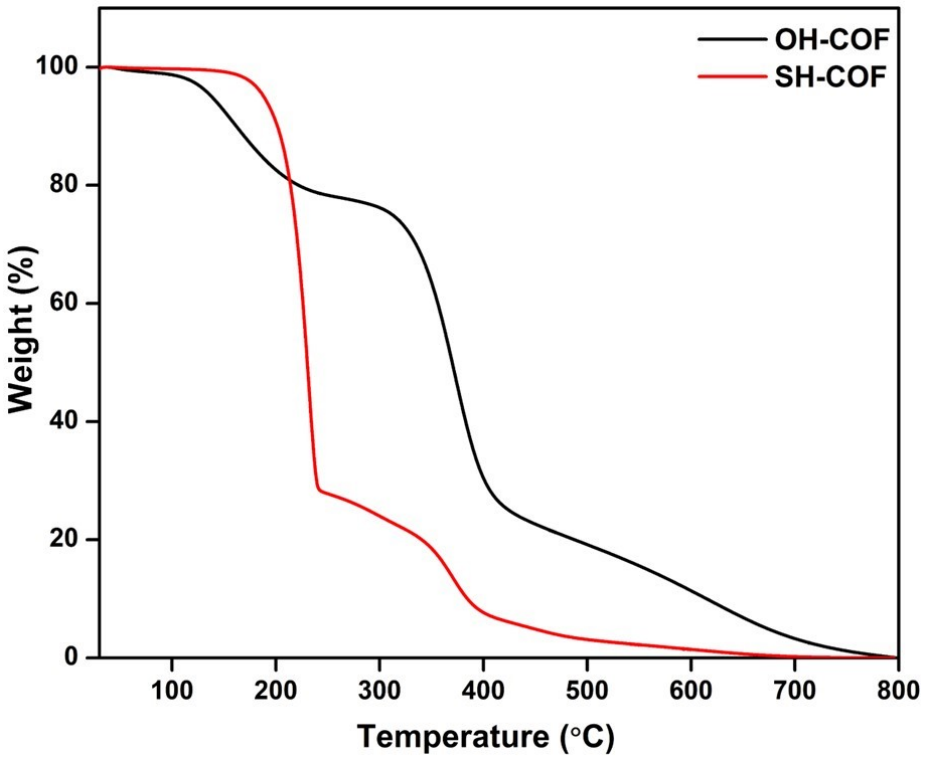

Figure S3. Thermogravimetric profile of the COF particles.

5. AFM line profile

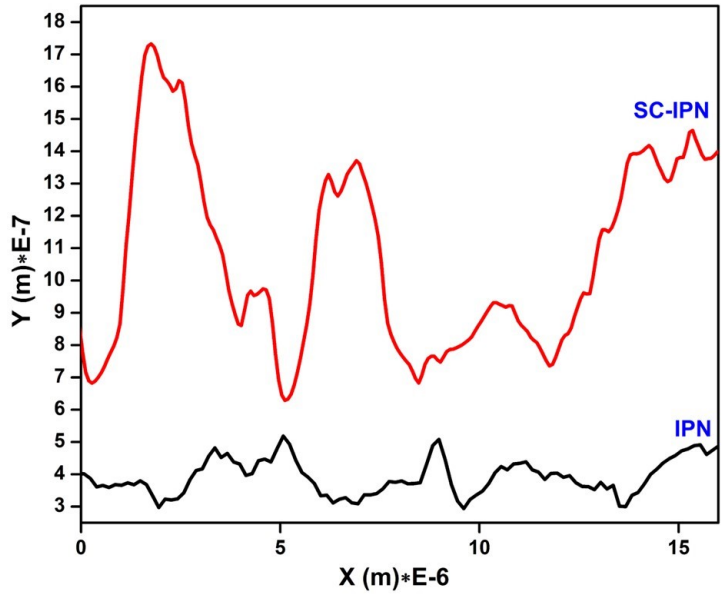

Figure S4. AFM line profile of the neat IPN and SC-IPN membranes.

6. Pore size distribution of neat IPN membranes

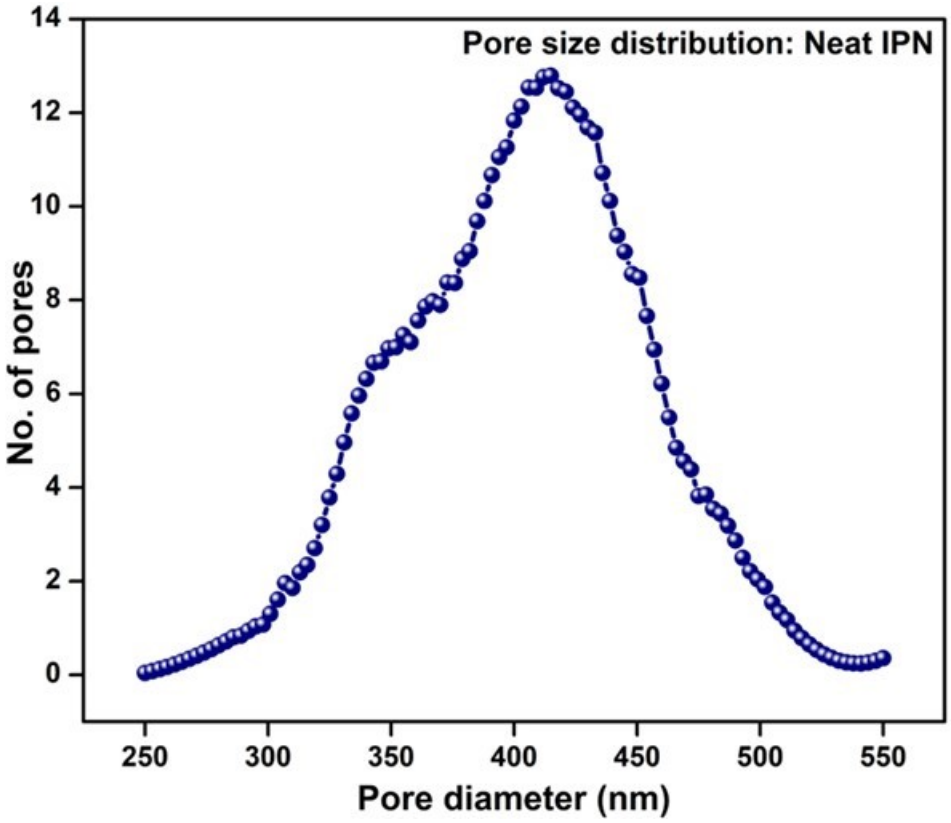

Figure S5. Pore size distribution of the neat IPN membranes via imaging 100 pore diameters from SEM

SEM micrographs were taken from various sections of the membrane to calculate the pore size distribution, and around 100 pore diameters were measured using ImageJ software. A histogram employing equation (3) mentioned in supplementary information was plotted, deliberating on the collected pore size data. The pore sizes were seen to range between 300-500 nm.

7. SEM and EDAX of OH-COF

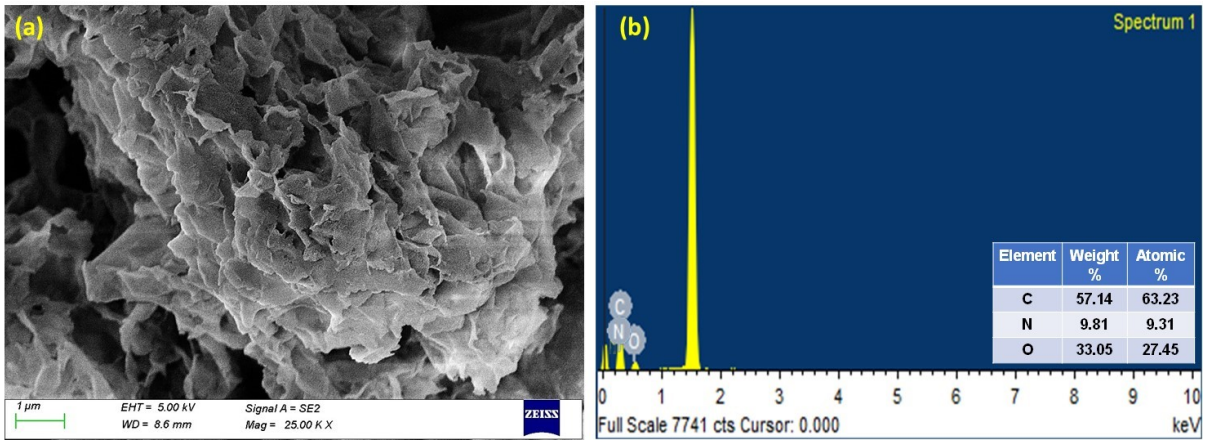

Figure S6. Surface morphological features of OH-COF and its EDAX spectra.

8. Pure water stability studies

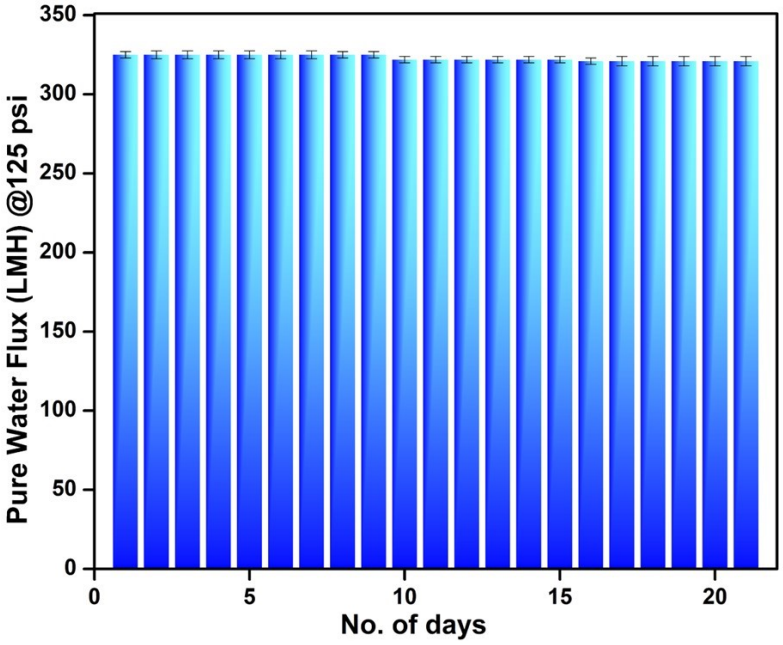

Figure S7. Pure water flux stability of the SC-IPN membranes.

9. UV-Vis spectra for the dye solutions

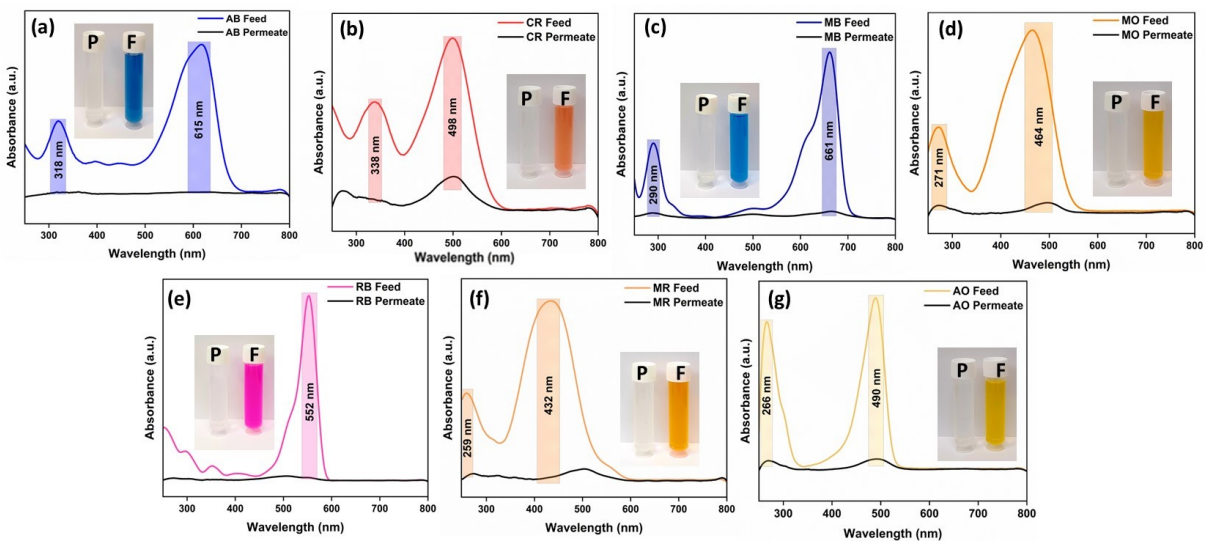

Figure S8. UV-Vis spectra of the feed and permeate dye solutions.

10. Dye rejection longevity

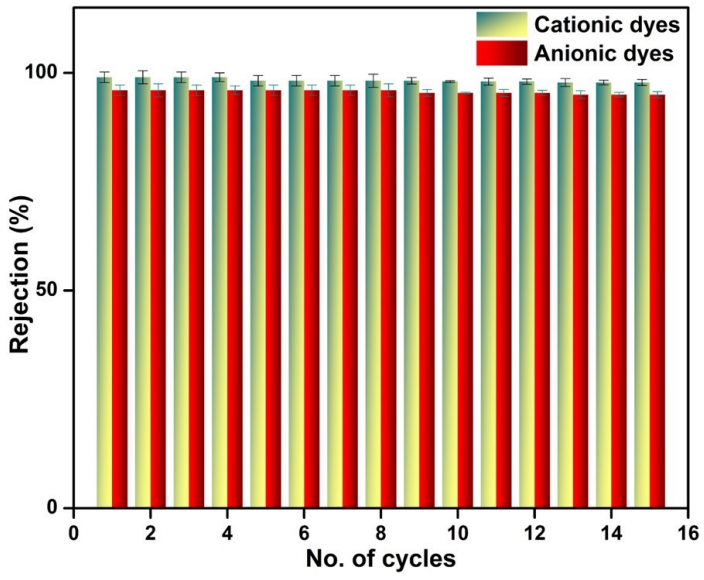

Figure S9. Dye rejection cycles for cationic and anionic dyes

11. UV-Vis spectra for the antibiotic solutions

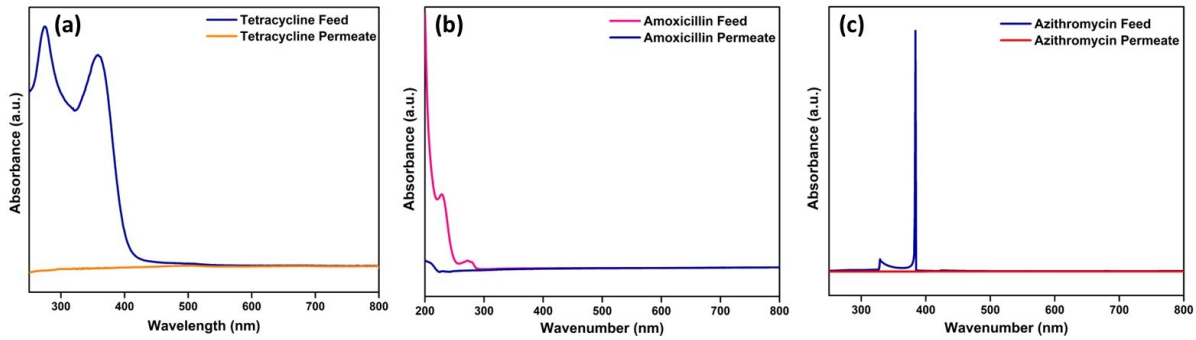

Figure S10. UV-Vis spectra for the feed and permeate antibiotic solutions.

12. FTIR spectra of PVC pipe powder

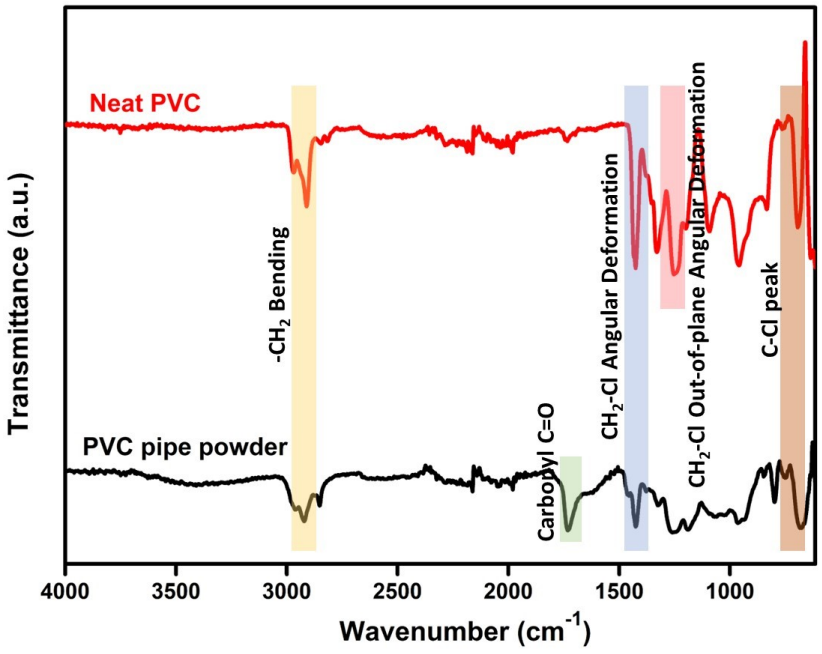

Figure S11. FTIR spectra of neat PVC powder versus the PVC powder obtained from sanitary pipes.

To have an idea regarding functional groups present in neat PVC and PVC pipe powder FTIR spectra for both were recorded in the wavenumber range 4000 to 615 cm-1. From Fig. S5, strong absorption peaks at 2912 cm-1 and 2920 cm-1 in both spectra were attributed to CH2 bending. The carbonyl stretching frequency in 1738 cm-1 in the case of pipe powder indicated the presence of carbonyl-based additives. The characteristic peak at 1426 cm-1 and 1252 cm^{-1} is associated with the angular deformation and out-of-plane angular deformation for the CH-Cl bond. Some additional peaks in the range of 900 cm-1 to 1230 cm-1 in PVC pipe powder could be ascribed to the addition of plasticizers or other associated additives. The C-Cl stretching resulted in an absorption peak near 690 cm-1 in both systems, indicating the presence of PVC.

13. SEM micrograph after microplastic removal

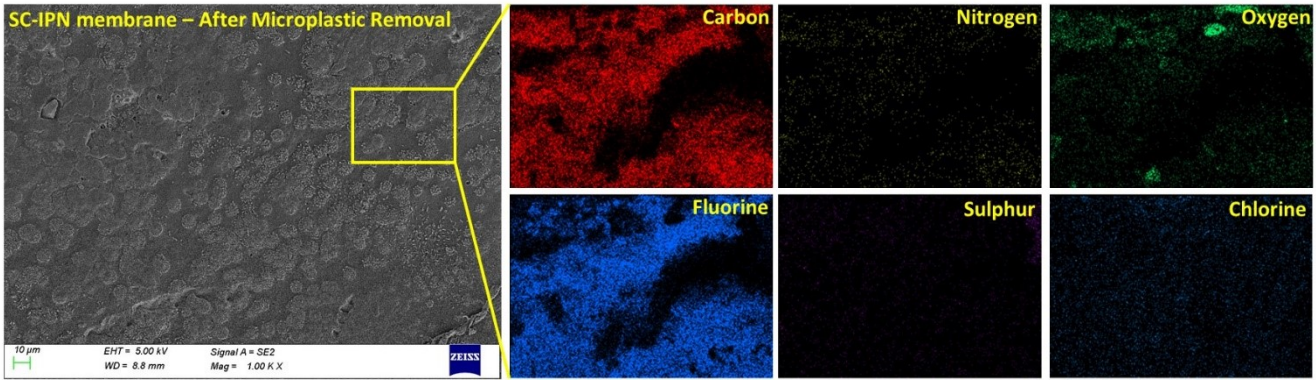

Figure S12. Surface morphology and EDAX elemental mapping after microplastic removal.

14. DLS of feed and permeate microplastic solution when passed through SC-IPN membranes

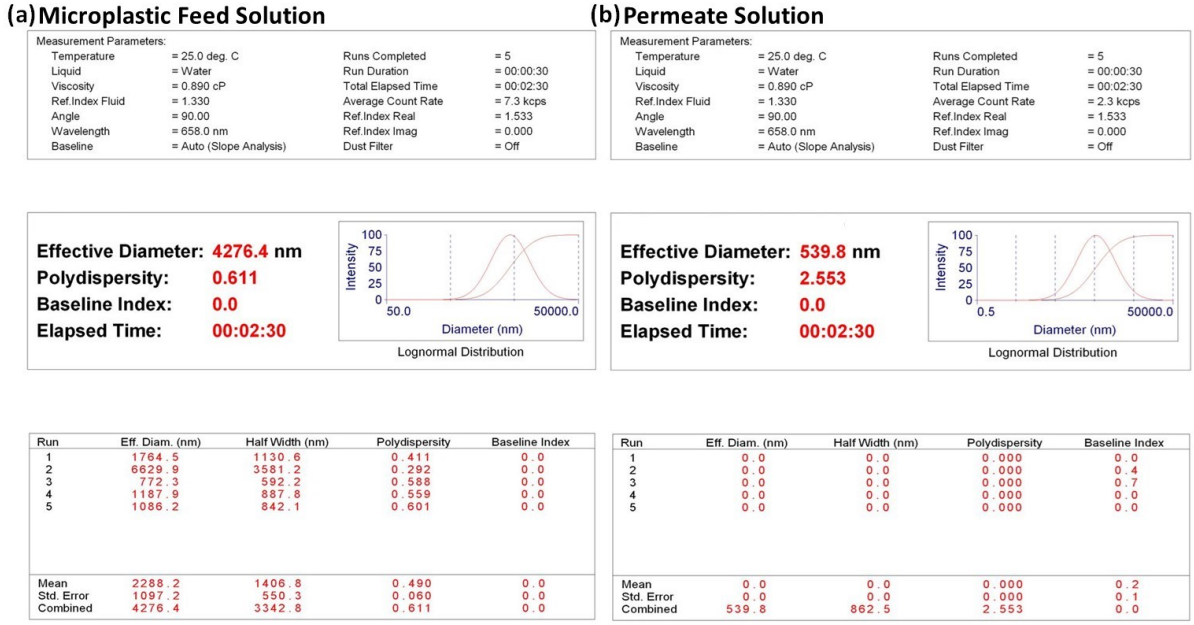

Figure S13. Dynamic Light scattering of feed microplastic solution and the permeate obtained thereafter.

The DLS studies were performed to get an idea of the size of the microplastics present in the spiked sample. It was observed that the colloidal suspension consisted of particles in the size range of 1000-7000 nm, whereas the permeate solutions had a size range of merely 500 nm, which further corroborated the efficient removal of microplastics via the fabricated SC-IPN membranes.

15. Microplastic removal efficiency

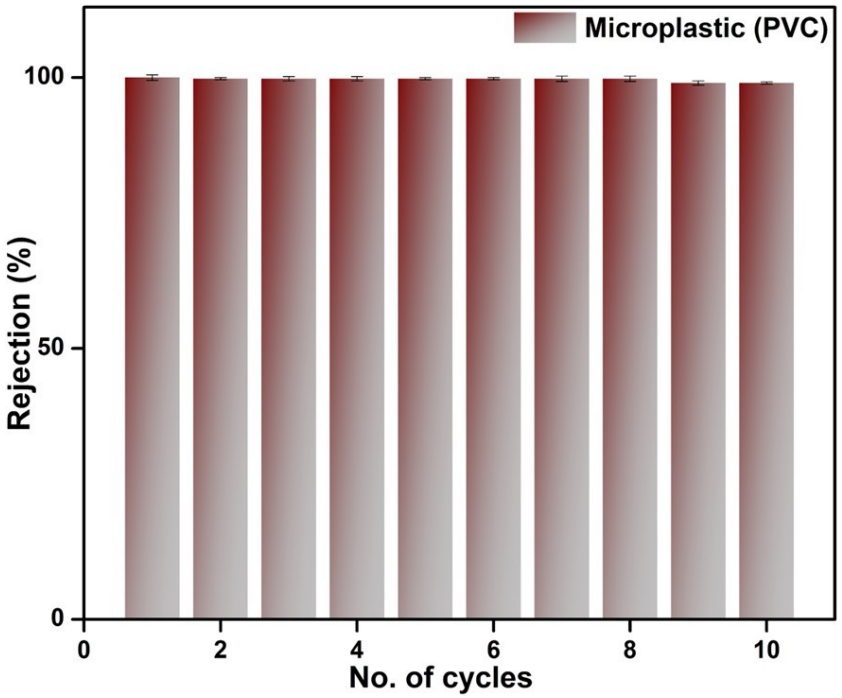

Figure S14. Microplastic removal efficacy of SC-IPN membranes

The SC-IPN membranes, having smaller pore sizes than the conventional microplastics, were potential candidates for removing microplastics from feed streams. From the UV-Vis spectra of the feed and permeate solutions coupled with the DLS analysis, the membranes were found to completely remove the microplastic, with their efficacy reaching up to 100%. Similar performance was observed in the next 10 operational cycles as well.

16. EDAX elemental mapping of the SC-IPN membranes after Hg(II) removal

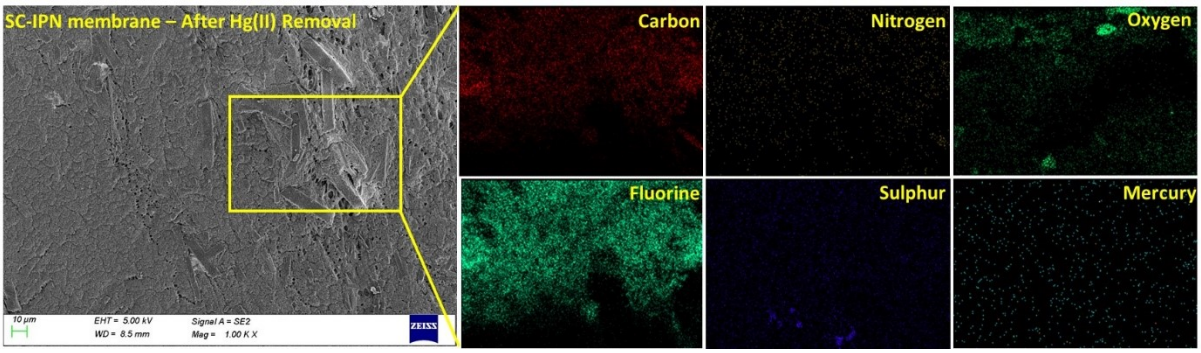

Figure S15. SEM micrograph of the SC-IPN membranes after Hg(II) removal and the elemental mapping showing the presence of mercury on the membrane surface.

17. Concentration of Hg(II) in the permeate solutions determined by ICP-OES

Figure S16. Hg (II) ion concentration in the permeate solution obtained after passing the solutions through SC-IPN membranes. The measurements were done using ICP-OES.

18. FTIR spectra before and after Hg (II) removal

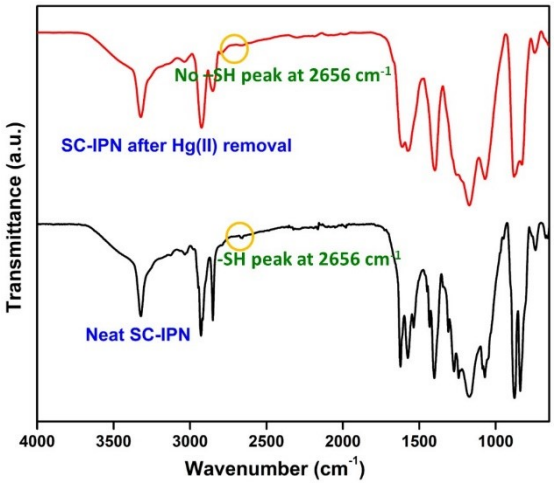

Figure S17. FTIR spectra of the SC-IPN membranes before and after Hg(II) removal.

From the FTIR spectra of the membranes after Hg (II) removal studies, it was seen that the thiol -SH peak was strategically absent from the spectra. Such observation further validates the formation of complexes between the thiol groups present and the incoming Hg (II) ions from the feed side.

19. Cytotoxicity assessment of SC-IPN membranes

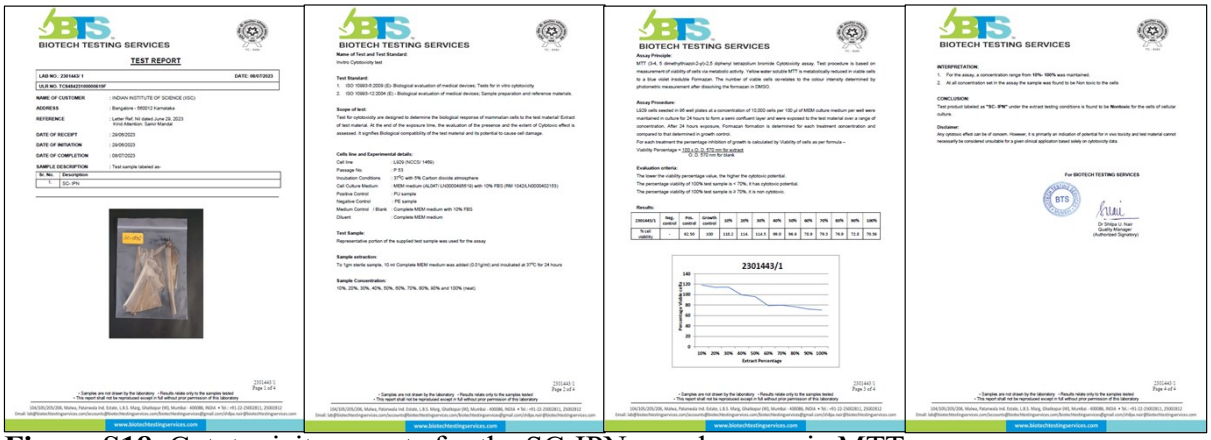

Figure S18. Cytotoxicity reports for the SC-IPN membranes via MTT assay.

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