Comprehensive Analysis of Spinel-Type Mixed Metal Oxide-Functionalized Polysulfone Membranes toward Fouling Resistance and Dye and Natural Organic Matter Removal

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ABSTRACT: Nanostructured polymeric membranes are of great importance in enhancing the antifouling properties during water filtration. Nanomaterials with tunable size, morphology and composition, surface modification, and increased functionality provide considerable opportunities for effective wastewater treatment. Thus, in this work, an attempt has been made to use spinel-structured MnCo$_2$O$_4$ as a nano-filler in the fabrication of nanostructured polysulfone (PSF) mixed matrix membranes and is investigated in terms of morphology, hydrophilicity, permeability, protein and natural organic matter separation, dye removal, and, finally, antifouling properties. The MnCo$_2$O$_4$ nanomaterials are synthesized and characterized via X-ray diffraction and field emission scanning electron microscopy and are loaded into a membrane matrix with varied concentrations (0 to 1.5 wt %). PSF nanocomposite membranes are prepared via a nonsolvent-induced phase-separation process. The results show an enhancement in hydrophilicity, porosity, and permeability with respect to the modified nanocomposite membranes because of oxygen-rich species in the membrane matrix, which increases affinity toward water. It was also found that the modified membranes display remarkably greater pure water flux (PWF) (220 L/m$^2$ h), higher Congo red rejection coefficient (99.86%), higher humic acid removal (99.81%), higher fouling resistance, and a significant flux recovery ratio (FRR) (88%) when tested with bovine serum albumin protein when compared to a bare PSF membrane (30 L/m$^2$ h PWF and 35% FRR). This is because the addition of MnCo$_2$O$_4$ nanoparticles into the polymeric casting solution yielded tighter PSF membranes with a denser skin layer and greater selectivity. Thus, the enhanced permeability, greater rejection coefficient, and antifouling properties show the promising potential of the fabricated PSF-spinel nanostructured membrane to be utilized in membrane technology for wastewater treatment.

1. INTRODUCTION

Membrane technology has received notable attention amidst other separation and purification technologies in order to purify the fluid in various applications such as the pharmaceutical and food industries, industrial and municipal wastewater treatment, and brackish and sea water desalination. Polymeric membranes have been greatly used in membrane technology because of their greater stability and easy film-forming ability. Nonetheless, the polymeric membrane’s widespread application is restricted because of its major fouling problem (due to its hydrophobic nature), poor chemical stability, and low chemical tolerance in harsh environments. During the last decade, the popular approach exercised in membrane science to overcome these limitations was to modify and redesign the membrane materials either by bulk modification (such as blending the functional additives or fillers with a polymeric solution) or via surface modification (by grafting, coating, and chemical post-treatment). The very common and easy method is blending with nanofiller additives to develop strong polymeric membranes with greater water permeability and effective separation ability, lower fouling tendency, and higher chemical and thermal stability.

With the greater developments in nanotechnology, enormous efforts have been put forth in the fabrication of novel polymeric nanocomposite membranes with the incorporation/embodiment of multifunctional and versatile nanomaterials within the polymeric matrix. The fabricated nanocomposite polymeric membranes benefit from the intrinsic properties of organic polymers and from the remarkable and tunable

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functionality of the dispersed nanofillers. A vast variety of nanomaterials consisting of (i) organic fillers namely biopolymers, carbon nanotubes, graphene-based materials such as graphene oxide, and metal–organic frameworks and (ii) inorganic nanomaterials with various metals and metal oxides including TiO₂, ZnO, SiO₂, Fe₂O₃, Al₂O₃, zeolite, and so forth were thoroughly explored in the literature. It is greatly illustrated that several key features of the prepared polymeric nanocomposite membranes such as fouling resistance, separation performance, and chemical and thermal tolerance can be effectively tailored for specific treatment purposes with the incorporation of functional organic and inorganic nanoaditives. However, the use of such nanomaterials in polymeric membranes has encountered various challenges along with the agglomeration of these nanomaterials in the polymeric membrane matrix, which reduces the membrane’s mechanical strength and decreases the water flux. Besides, the leaching out of nanomaterials from the membrane matrix brings down the overall membrane performance.

Thus, in order to overcome agglomeration, Pendergast and Hoek utilized a combination of nanocomposites to mitigate fouling and to improve the membrane’s selectivity, strength, and permeability. Also, various nanoparticles with mixed metal oxide nanocomposites such as pyrochlores and spinels have been used earlier to attain the required physiochemical properties of a polymeric membrane while diminishing the fouling phenomenon. Spins with the general formula AB₂O₄ could be considered to be the strategic materials because of their magnetic, optical, catalytic, and electronic properties, among others. These spinel mixed oxides contain only 3d transition metals or both rare earth elements and 3d transition metals. AB₂O₄ (where A and B are the 3d transition metals) can be designed using various methods including sol–gel processing, traditional ceramic powder technology, nitrate decomposition, and coprecipitation. Interestingly, the spinel oxides containing cobalt, such as MnCo₂O₄, NiCo₂O₄, ZnCo₂O₄, MgCo₂O₄, and CuCo₂O₄ have been explored as potential catalytic materials for water decomposition, and coprecipitation. MnCo₂O₄ mixed oxide spinel has not been explored for the demonstration of antifouling polymeric membranes. In this research, we aim to improve the fouling and to improve the membrane selectivity, strength, and permeability.

2. MATERIALS AND METHODS

2.1. Materials. Manganese(II) chloride tetrahydrate (MnCl₂·4H₂O), cobalt (II) chloride hexahydrate (CoCl₂·6H₂O), sodium hydroxide (NaOH), and ascorbic acid supplied by Merck were used for the synthesis of MnCo₂O₄ nanoparticles. PSF (P3500LCD) was from Udel, polyvinylpyrrolidone (PVP, average Mn = 40,000) was supplied by SRL, and N-methyl-2-pyrrolidone (NMP) supplied by Merck was used as a solvent for the preparation of the polymeric membrane. BSA from SD Fine Chem Ltd. was used as a foulant for antifouling studies. HA from Nice Chemicals and CR from SD Fine Chem Ltd. were used for rejection studies. All the other reagent-grade chemicals were used as such without further purification.

2.2. Synthesis of Spinell-Structured MnCo₂O₄ Nanoparticles. MnCo₂O₄ nanoparticles are synthesized via the coprecipitation method using the procedure reported in the literature. Briefly, 1:2 molar ratios of MnCl₂·4H₂O (0.015 M) and CoCl₂·6H₂O (0.03 M) were dissolved in 50 ml of deionized water and stirred for 30 min. Then 0.2 M NaOH was added dropwise until the pH reached 10–11. 0.1 M ascorbic acid was then slowly added to the abovementioned solution by maintaining a temperature of 60–70 °C for 1 h. The obtained precipitate was filtered, washed with ethanol and water multiple times, and dried at room temperature (RT). Dried samples were calcined at 450 °C for 2 h. The resulting compound was used for further studies.

2.3. Preparation of Spinell-Incorporated PSF Nanocomposite Membranes. The flat sheet PSF MMMs were prepared via a nonsolvent-induced phase separation technique. The precise amounts of MnCo₂O₄ nanoparticles (0–1.5 wt %) were dispersed thoroughly in the NMP solvent using an ultrasonicator. 0.5 wt % PVP and calculated amounts of PSF were added at regular intervals to the above-mentioned solution with continuous stirring. The stirring continued at a set rpm until a clear (homogenous) casting solution was obtained. The solution was kept aside for a few hours to remove air bubbles. It was then casted onto a clean glass plate using a casting blade to obtain a film of approximately 150 μm. The casted films were quickly placed in a nonsolvent chamber where the phase inversion takes place with the exchange between the solvent and nonsolvent. Once the phase inversion is complete, the membranes were washed thoroughly with distilled water and stored in water for further use.

2.4. Characterization of MnCo₂O₄ Nanoparticles and PSF Nanocomposite Membranes. The diffraction patterns were measured via an X-ray diffractometer supplied by Rigaku, Japan, with a scan range from 10 to 80°, and a scan rate of 3°/min and equipped with a K-beta filter at an accelerating voltage of 40 kV. The morphology synthesized nanoparticles and

Table 1. Different Compositions of PSF Membranes with Varied Concentrations of MnCo₂O₄ Nanoparticles

| membrane | PSF (wt %) | PVP (wt %) | MnCo₂O₄ (wt %) |
|----------|------------|------------|----------------|
| M0       | 18.0       | 0.5        | 0              |
| M1       | 17.5       | 0.5        | 0.5            |
| M2       | 17.0       | 0.5        | 1.0            |
| M3       | 16.5       | 0.5        | 1.5            |
membranes were characterized using a field emission scanning electron microscope supplied by JEOL (JSM 7100F) at an accelerating voltage of 10 kV (nanoparticles) and 5 kV (membranes). Before scanning, all the prepared membrane samples of suitable size were taken and dipped in liquid N₂ for some time, and then they were fractured cryogenically to get sharp and clear cross sections of the membranes. The obtained samples were then overlaid with an ultrathin platinum conductive layer and FESEM images were captured. The surface topography of the membranes was analyzed using an atomic force microscope supplied by APE Research, Italy, with an A100 AFM model. The surface roughness parameters were measured in terms of mean average roughness (Rₐ) and root mean square (Rₛ) with a sample scan area of 5 μm × 5 μm.

The PSF membrane’s contact angle measurements were studied with the help of a goniometer (KYOWA, Japan) using the sessile drop method. All the membrane samples were thoroughly dried before analysis. In brief, ~2 μL water droplets were dropped at four different places on the polymeric membrane surface; later, the droplet images were recorded to calculate the contact angle of prepared membranes. The obtained values are the averages of four trials.

The porosity, ε (%) of prepared polymeric membranes was measured via the gravimetric method and is interpreted with the help of the equation given below (eq 1)

\[
ε (%) = \left(\frac{W_w - W_d}{A \times l \times d_w}\right) \times 100
\]  

where \(W_w\) and \(W_d\) are the wet weight and dry weight of the polymeric membranes, respectively; \(l\) is the membrane thickness (m), \(d_w\) is the density of water (0.998 g cm⁻³), and \(A\) is the membrane’s effective area (m²). The mean pore diameter \(r_m\) of the membranes was estimated using the Guerout–Elford–Ferry equation as mentioned below (eq 2)

\[
r_m = \sqrt{(2.9 - 1.75ε) \times 8ηQ \over ε \times A \times ΔP}
\]

where \(η\) is the water viscosity (8.9 × 10⁻⁴ Pa·s), \(ΔP\) is the operating pressure, \(ε\) is the porosity, and \(Q\) is the pure water flow rate in m³/s.

Zeta potential analyses were performed using an electrokinetic analyser (Anton Paar Surpass 3) and the zeta potential at the membrane surface was determined at neutral pH from the measurement of the streaming potential using an adjustable gap cell. The conductivity of the dip-in-cell was calibrated before use. The membrane sheets were cut into the required size and mounted onto the measuring cell. Before measurement, the analyser was rinsed with the KCl buffer (0.01 M) solution and the results were analyzed.

**2.5. Membrane Performance.**

2.5.1. Water Uptake Measurements. The hydrophilicity of the polymeric membranes is evaluated using water uptake measurements. Briefly, the membranes of the fixed area were immersed in distilled water for 24 h, and later, the membrane’s wet weight was taken. The same wet membrane was then thoroughly dried for 24 h at RT to measure the dry weight. Based on the weight difference between the wet and dry membrane, the water uptake (%) was calculated via the equation (eq 3)

\[
\% \text{ of water uptake} = \left(\frac{W_w - W_d}{W_d}\right) \times 100
\]

where \(W_d\) is the dry membrane’s weight and \(W_w\) is the wet membrane’s weight. The water uptake capacity of each polymeric membrane was measured thrice, and the average of three trials has been reported in the paper.

2.5.2. Permeation Studies. The performance of the prepared nanocomposite membranes was assessed by measuring the pure water flux (PWF) via a customized dead-end filtration unit. The dead-end unit was equipped with a N₂ cylinder to provide the required pressure. Polymeric membranes with a 10.17 cm² effective area were fastened into the filtration cell and subsequently distilled water was filled into the cell. Later, the membranes were compacted with the help of N₂ at 4 bar pressure for nearly 30 min to reach the steady permeate state. The pressure was then decreased to 2 bar where the permeate flux of polymeric nanocomposite membranes was collected with a 10 min interval for nearly 2 h. The PWF of the nanocomposite membranes was quantified using the following equation (eq 4).

\[
J_w = \frac{Q}{A \cdot Δt}
\]

where \(J_w\) is the PWF measured in L/m² h; \(Q\) is the volume of water collected in liters (L); \(A\) is the effective area of the membrane in m², and \(Δt\) is the permeation time in hours (h).

2.5.3. Antifouling Performance Evaluation of Spinel-Functionalized PSF MMMs Using BSA as a Model Fouulant.

2.5.3.1. BSA Filtration. BSA was used as a model foulant in order to study the rejection coefficient of PSF-based membranes. Briefly, the filtration unit was filled with a feed solution of 200 mg L⁻¹ BSA protein, and it was then stirred at a speed of 300 rpm to minimize concentration polarization. BSA rejection studies were then performed for 2 h at 2 bar pressure and the BSA rejection (%) was later calculated with the help of the below equation (eq 5),

\[
\% \text{ rejection} = \left(1 - \frac{C_p}{C_f}\right) \times 100
\]

where \(C_p\) and \(C_f\) are the concentrations of BSA protein in permeate and feed solutions, respectively, which were determined using a UV−visible spectrophotometer (Shimadzu 1800 PC) at an absorption wavelength of 280 nm.

2.5.3.2. Membrane Fouling Analysis. 2.5.3.2.1. Flux Recovery Ratio. The antifouling properties of PSF-based nanocomposite membranes were assessed with the help of a dead-end filtration unit. A BSA with a 200 mg L⁻¹ concentration solution was used as a foulant. Initially, the PWF \(J_1\) of the polymeric membranes was measured at 2 bar pressure under RT. Later, the dead-end unit was filled with the 200 mg L⁻¹ BSA protein solution, where the permeate was collected within a 10 min interval for nearly 3 h. Once the BSA filtration was completed, the polymeric membranes were washed thoroughly with distilled water for some time, and the BSA rejection \(J_2\) of the same membranes was measured again. The fouling resistance of the membranes is usually assessed with flux recovery ratio (FRR) values, which can be estimated with the below equation (eq 6),
% FRR = \left( \frac{I - I_p}{I} \right) \times 100 \tag{6}

The BSA rejection (%) was calculated using eq 3.

2.5.3.2.2. Reversible and Irreversible Fouling Studies: To thoroughly understand the fouling behaviour of polymeric PSF-based membranes, the ratios of total fouling (R_t), reversible fouling (R_r), and irreversible fouling (R_ir) were estimated with the below equations (eqs 7–9)

\begin{align*}
R_t (\%) & = \left( \frac{I - I_p}{I} \right) \times 100 \\
R_r (\%) & = \left( \frac{I - I_p}{I} \right) \times 100 \\
R_ir (\%) & = \left( \frac{I - I_p}{I} \right) \times 100
\end{align*}

where, \( I_p \) is the permeate flux during BSA filtration.\textsuperscript{23}

2.5.4. Rejection Studies. CR of 30 ppm concentration and HA of 100 ppm concentration were used as feed solutions to evaluate the rejection properties of prepared MMMs. The rejection performance was carried out for M2 (because of its better permeability) and M0 (bare) membranes using a dead-end filtration unit (see Section 2.5.3.1. for procedure). The concentrations of feed and permeate of CR and HA solutions were measured using a UV–visible spectrophotometer at an absorption wavelength of 497 and 254 nm, respectively.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis. The diffraction patterns of PSF MMMs, the composition of synthesized particles, and their phase purity is examined via X-ray diffraction (XRD) and are given in Figure 1. As shown in the figure, the diffraction peaks of MnCo_2O_4 are indexed as face-centered cubic lattice, the space group of \( Fd3m \) with a spinel \((AB_2O_4)\) type of structure, which matches with the JCPDS no: 23-1237. No other diffraction peaks (such as MnO_2) were observed, indicating the pure phase of synthesized spinel as reported in the literature.\textsuperscript{24}

The intense peaks between 35 and 70° confirm the successful incorporation of spinel-type nanoparticles in the PSF membrane matrix (M1–M3). The intensity of the XRD peaks increased with an increase in MnCo_2O_4 nanoparticle loading (0 to 1.5 wt %) into the membrane matrix.

3.2. Morphological Studies of Nanoparticles and Membranes. Figure 2 reveals that the synthesized spinel-structured MnCo_2O_4 particles consist of varied geometries with a diameter ranging from 20 to 150 nm. The particles are well dispersed, and not much agglomeration is seen.

Figure 3 shows the cross-sectional morphologies of bare PSF and PSF MMMs. All the PSF membranes show an asymmetric nature, consisting of a dense selective top layer and a thick porous sublayer with finger-like projections. The prominent finger-like pores are extended throughout the membrane structure with long and narrow projections for PSF MMMs (especially for M1 and M2) compared to the bare PSF membrane because of the quick phase inversion process with rapid exchange between the solvent (NMP) and nonsolvent (water). This change in morphology is mainly because of the strong interaction between the oxygen moieties of MnCo_2O_4 and the PSF membrane.

However, at higher concentrations (1.5 wt % MnCo_2O_4, M3 membrane), the agglomeration of particles was observed and also the viscosity of the casting solution increased, which delayed de-mixing between the solvent and nonsolvent, resulting in a thicker skin layer with a relatively less number of macrovoids (Figure 4).

The surface morphology of the membranes is measured in terms of mean average roughness (R_a) and root mean square (R_q) using atomic force microscopy (AFM) and is shown in Figure 5. Evidently, the surface roughness of the membranes decreased upon the addition of spinel from 0 to 1 wt %; however, the roughness parameters slightly increased with 1.5 wt % spinel concentration, which may be because of the agglomeration of particles. The mean surface roughness of the membrane decreased from 73.5 nm (M0) to 42.7 nm (M1) to 23.6 nm (M2), and then slightly increased to 25.6 nm (M3). The roughness increase in the M3 membrane directly corresponds to the aggregation of spinel on the membrane surface. However, the decrease in surface roughness in MMMs leads to an increase in the antifouling performance of the membranes by avoiding the accumulation of foulants on the surface.

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Figure 2. FESEM image of spinel-structured MnCo_2O_4 nanoparticles.

Figure 1. XRD patterns of MnCo_2O_4 nanoparticles and PSF nanocomposite membranes.
3.3. Porosity, Contact Angle, Water Uptake, and Zeta Potential Studies of the Membranes. Physical parameters such as porosity, contact angle, water uptake capacity, and zeta potential studies of PSF MMMs are shown in Table 2. As shown in the table, the porosity and the mean pore size of MMMs are much higher compared to the bare PSF membrane, and the porosity (%) increased from 38.65 to 64.10% and the mean pore size from 3.21 to 5.09 nm with an increase in MnCo$_2$O$_4$ spinel-structured nanoparticles loading into the PSF membrane matrix. This is because the presence of abundant oxygen groups in MnCo$_2$O$_4$ spinel increases the affinity of membranes toward water, which eventually helps in forming more number of pores, in turn increasing the porosity of nanocomposite membranes.

The hydrophilicity of membranes is the most prominent parameter in understanding the performance and antifouling properties of membranes. The hydrophilicity of the membranes is usually studied in terms of contact angle and water

| membrane | porosity $\varepsilon$ (%) | mean pore size (nm) | contact angle (deg) | water uptake capacity (%) | zeta potential (mV) pH = 7 |
|----------|-----------------------------|---------------------|---------------------|---------------------------|-----------------------------|
| M0       | 38.65 ± 2.01                | 3.21 ± 0.9          | 72.13               | 110.19 ± 3.16             | −20.17                      |
| M1       | 49.82 ± 2.83                | 4.02 ± 1.3          | 65.19               | 160.38 ± 2.87             | −31.70                      |
| M2       | 58.31 ± 1.90                | 4.76 ± 1.1          | 58.85               | 183.90 ± 3.44             | −42.36                      |
| M3       | 64.10 ± 2.28                | 5.09 ± 0.9          | 52.09               | 201.27 ± 2.99             | −37.01                      |
uptake measurements. As shown in Table 2, the contact angle of the PSF membranes decreased from 72.13 to 52.09° upon an increase in the loading of MnCo₂O₄ nanoparticles (0 to 1.5 wt %) to the PSF membrane, which in turn shows that the modified membranes are more hydrophilic compared to bare PSF membranes. The presence of oxygen-rich species in membranes makes them more hydrophilic by forming strong hydrogen bonds with the water molecules, which in turn decreases the contact angle of membranes. The water uptake capacity of the PSF membranes increased from 110.19 to 201.27% with an increase in the MnCo₂O₄ loading concentration (0 to 1.5 wt %) into the membrane matrix because of the increased porosity and hydrophilicity (as determined from contact angle values). The zeta potential values suggest that the MMMs are highly negatively charged compared to the bare PSF (M0) membrane and the negative charge increases from −20.17 to −42.36 mV with an increase in the addition of MnCo₂O₄ nanoparticles from 0 to 1 wt % because of the presence of oxygen-rich moieties in the membrane matrix; however, a further increase in the loading of MnCo₂O₄ (1.5 wt %) decreased the zeta potential value to −37.01 mV. This decrease is mainly because of severe agglomeration, as shown in Figure 4.

3.4. Permeability Studies. Permeability studies of PSF membranes are usually carried out in terms of PWF measurements. The PWF of bare PSF and PSF MMMs is shown in Figure 6. From the figure, it is clear that the water flux of the modified PSF membranes is higher because of increased porosity and hydrophilicity compared to the bare PSF membrane. Also, the oxygen-rich spinel species in the membrane matrix increase affinity to water molecules forming a large water layer on the membrane surface that helps in passing the water through channels with ease. The PWF increased upon an increase in the loading of MnCo₂O₄ nanoparticles up to 1 wt %, whereas a decrease in the water flux was observed for the M3 membrane with 1.5 wt % spinel because of the thicker skin layer, lesser finger-like projections, and the agglomeration of nanoparticles, as shown in Figure 4.

3.5. Antifouling Study of PSF Membranes: BSA Rejection, FRR, and Reversible and Irreversible Fouling. Fouling is one of the major challenges to overcome in all the membrane-based separation processes as it badly affects the performance and lifespan of membranes. In this study, the antifouling properties of the prepared membranes were evaluated using BSA as a foulant, and the obtained results are shown in Figure 7. The prepared nanocomposite membranes showed lesser flux decline and enhanced antifouling properties compared to the bare PSF membrane because of the presence of hydrophilic spinel moieties in the membrane matrix which hinders the adsorption of BSA molecules on the membrane surface thus enhancing fouling resistance.

Figure 7a shows the flux of PSF membranes during protein separation. The permeate flux of all the nanocomposite membranes is higher compared to the bare PSF membrane because of the incorporation of MnCo₂O₄ nanoparticles, which could favourably decrease the fouling. However, the permeate flux of all the PSF membranes is less when compared to the PWF of the same membranes because of cake formation and pore blockage by BSA molecules, but the flux of nanocomposite membranes could be successfully restored to a large extent because of increased hydrophilicity. Figure 7b shows the percentage of BSA rejection and FRR of PSF membranes. It can be seen from the figure that the BSA rejection of the bare PSF membrane is 90%, whereas it increased to ~95% for all the nanocomposite membranes because of the higher hydrophilic surface of the membranes (resulting from the incorporation of spinel), which weakens the interaction of protein molecules with the membrane surface, leading to higher BSA rejection. Also, the FRR of modified PSF membranes was much higher compared to bare PSF membranes and the percentage of FRR increased upon an increase in the loading of MnCo₂O₄ nanoparticles to the membrane matrix. The highest FRR of 88% was observed for the M3 membrane with 1.5 wt % of nanoparticles, whereas the bare PSF membrane showed only 35% FRR because of its hydrophobic nature. Figure 7c shows the fouling parameters of PSF membranes and it can be seen that the fouling ratios such as total fouling, reversible fouling, and irreversible fouling of all the nanocomposite membranes decreased upon an increase in the loading concentration of spinel nanoparticles due to the enhanced hydrophilicity of the membranes, which confirms that the modified PSF membranes are less prone to fouling compared to bare PSF membranes. However, the irreversible fouling of all the membranes is higher compared to reversible fouling because of increased porosity, wherein some of the BSA molecules would have gotten blocked inside the pores as shown in Figure 4. Nevertheless, the percentage of fouling is significantly less in the case of nanocomposite membranes compared to bare PSF membranes.

3.6. CR and HA Removal Studies. The rejection capability of the membranes was evaluated using CR and HA foulants for M2 (better permeability) and M0 (bare PSF) membranes. Figure 8a shows the permeate flux and Figure 8b shows the rejection percentage during CR and HA removal, respectively. The permeate flux of the CR feed is slightly higher for both M0 and M2 membranes compared to the permeate flux of the HA feed (Figure 8a). This is because the HA molecules are larger in size compared to the CR moieties, and these heavier molecules would have hindered the easy flow of water during filtration. However, the flux of the M2 membrane was enhanced significantly compared to the M0 membrane during both CR and HA removal due to its better hydrophilicity and higher negative charge. Figure 8b shows that the rejection coefficient of both CR and HA is higher for the M2 membrane when compared to the M0 membrane. The enhanced rejection of M2 (99.86% CR and 98.11% HA) is
mainly because of its higher negative charge, as confirmed by the zeta potential values (Table 2). Because both CR and HA molecules are negatively charged, there will be an electrostatic repulsion between the foulants and the same charged membrane, hence higher rejection.

**CONCLUSIONS**

The PSF nanocomposite membranes are successfully prepared with the incorporation of spinel-structured MnCo2O4 nanoparticles. The porosity and hydrophilicity of the nanocomposite membranes increased upon an increase in the loading of MnCo2O4 nanoparticles as confirmed from water uptake and contact angle measurements. The increase in hydrophilicity is because of the presence of oxygen-rich species in the membrane matrix which increases affinity to water molecules. The permeability properties of modified membranes are also enhanced to a great extent because of increased porosity and surface wettability. Even though the water flux of the M3 membrane was slightly less (because of the thicker skin layer), the antifouling property of the same membrane did not get affected. The nanocomposite membranes showed greater flux, greater rejection (~98%) of dyes and natural organic matters, and better antifouling properties (~88% FRR) compared to bare PSF membranes. The FRR, BSA rejection, and antifouling parameters of PSF membranes increased upon an increase in MnCo2O4 loading. AFM analysis reveals that the modified membranes possess a smoother surface upon the incorporation of spinel into the membrane matrix. The smoother surface in turn enhanced the antifouling performance of the membranes. Thus, the present work shows great potential in the application of MnCo2O4 spinel to open up interesting paths in the fabrication of polymeric nanocomposite membranes with greater permeability and antifouling properties for water treatment.
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Notes
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REFERENCES

(1) (a) Chen, J. P.; Mou, H.; Wang, L. K.; Matsuura, T.; Wei, Y. Membrane Separation: Basics and Applications. Membrane and Desalination Technologies; Springer Science & Business Media, 2011; pp 271–332. (b) Singh, R. Water and Membrane Treatment. Membrane Technology and Engineering for Water Purification; Butterworth-Heinemann, 2015; pp 81–178.

(2) (a) Goosen, M. F. A.; Sablani, S. S.; Al-Hinai, H.; Al-Obeidani, S.; Al-Belushi, R.; Jackson, D. Fouling of Reverse Osmosis and Ultrafiltration Membranes: A Critical Review. Sep. Sci. Technol. 2005, 39, 2261–2297. (b) Hilal, N.; Ogubiyi, O. O.; Miles, N. J.; Nigmatullin, R. Methods Employed for Control of Fouling in MF and UF Membranes: A Comprehensive Review. Sep. Sci. Technol. 2005, 40, 1957–2005.

(3) (a) Ahmad, A. L.; Abdulkarim, A. A.; Ooi, B. S.; Ismail, S. Recent development in additives modifications of polyethersulfone membrane for flux enhancement. Chem. Eng. J. 2013, 223, 246–267. (b) Khorshide, B.; Thundat, T.; Fleck, B. A.; Sadrazadeh, M. Thin film composite polyamide membranes: parametric study on the influence of synthesis conditions. RSC Adv. 2015, 5, 54985–54997. (c) Zhao, C.; Xue, J.; Ran, F.; Sun, S. Modification of polyethersulfone membranes—A review of methods. Prog. Mater. Sci. 2013, 58, 76–150.

(4) (a) Khorshide, B.; Biswas, I.; Ghosh, T.; Thundat, T.; Sadrazadeh, M. Robust fabrication of thin film polyamide-TiO2 nanocomposite membranes with enhanced thermal stability and anti-biofouling propensity. Sci. Rep. 2018, 8, 784. (b) Khorshide, B.; Hajinasiri, J.; Ma, G.; Bhattacharjee, S.; Sadrazadeh, M. Thermally resistant and electrically conductive PES/ITO nanocomposite membrane. J. Membr. Sci. 2016, 500, 151–160.

(5) (a) Karkooti, A.; Yazdi, A. Z.; Chen, P.; McGregor, M.; Nazemifar, N.; Sadrazadeh, M. Development of advanced nanocomposite membranes using graphene nanoribbons and nanosheets for water treatment. J. Membr. Sci. 2018, 560, 97–107. (b) Li, R.; Zhang, L.; Wang, P. Rational design of nanomaterials for water treatment. Nanoscale 2015, 7, 17167–17194. (c) Al Aani, S.; Wright, C. J.; Atieh, M. A.; Halal, N. Engineering nanocomposite membranes: Addressing current challenges and future opportunities. Desalination 2017, 401, 1–15.

(6) (a) Ng, L. Y.; Mohammad, A. W.; Lee, C. P.; Hilal, N. Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review. Desalination 2013, 308, 15–33. (b) Richards, H. L.; Baker, P. G. L.; Iwuoha, E. Metal Nanoparticle Modified Polysulfone Membranes for Use in Wastewater Treatment: A Critical Review. J. Surf. Eng. Mater. Adv. Technol. 2012, 02, 183–193. (c) Jhaveri, J. H.; Murthy, Z. V. F. A comprehensive review on anti-fouling nanocomposite membranes for pressure driven membrane separation processes. Desalination 2016, 379, 137–154. (d) Goh, P. S.; Ng, B. C.; Lau, W. J.; Ismail, A. F. Inorganic Nanomaterials in Polymeric Ultrafiltration Membranes for Water Treatment. Sep. Purif. Rev. 2014, 44, 216–249. (e) Lau, W.-J.; Emadzadeh, D.; Shahrin, S.; Goh, P. S.; Ismail, A. F. Ultrafiltration Membranes Incorporated with Carbon-Based Nanomaterials for Antifouling Improvement and Heavy Metal Removal. In Carbon-Based Polymer Nanocomposites for Environmental and Energy Applications; Elsevier, 2018; pp 217–232.

(7) (a) Mollahosseini, A.; Rahimpour, A.; Jahamshahi, M.; Peyravi, M.; Khavarpour, M. The effect of silver nanoparticle size on performance and antibacteriality of polysulphone ultrafiltration membrane. Desalination 2012, 306, 41–50. (b) Safarpour, M.; Khataee, A.; Vatanpour, V. Preparation of a Novel Polyvinilidene Fluoride (PVDF) Ultrafiltration Membrane Modified with Reduced Graphene Oxide/Titanium Dioxide (TiO2) Nanocomposite with Enhanced Hydrophilicity and Antifouling Properties. Ind. Eng. Chem. Res. 2014, 53, 13370–13382. (c) Vatanpour, V.; Madaeni, S. S.; Moradian, R.; Zinadini, S.; Astinchap, B. Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polyethersulfone nanocomposite. J. Membr. Sci. 2011, 375, 284–294.

(8) Pendergast, M. M.; Hoek, E. M. V. A review of water treatment membrane nanotechnologies. Energy. Environ. Sci. 2011, 4, 1946.

(9) Ganjali, M. R.; Badiei, A.; Mouradzadegan, A.; Vatanpour, V.; Rezania, H.; Mousavi Khadem, S. S.; Shamiry, F.; Munir, M. T.; Habibzadeh, S.; Saeb, M. R. Nanostructured polyethersulfone membranes for dye and protein separation: Exploring antifouling role of holmium (III) molybdate nanosheets. Polym. Test. 2020, 91, 106796.

(10) Borges, F. M. M.; Melo, D. M. A.; Câmara, M. S. A.; Martinelli, A. E.; Soares, J. M.; de Araújo, J. H.; Cabral, F. A. O. Magnetic behavior of nanocrystalline MnCo2O4 spinels. J. Magn. Magn. Mater. 2006, 302, 273–277.

(11) Silambaram, M.; Padmanathan, N.; Ramesh, P. S.; Geetha, D. Spinel CuCo2O4 Nanoparticles: Facile One-Step Synthesis, Optical, and Electrochemical properties. Mater. Res. Express 2016, 3, 095021.

(12) Li, L.; Zhang, Y. Q.; Liu, X. Y.; Shi, S. J.; Zhao, X. Y.; Zhang, H.; Ge, X.; Cai, G. F.; Gu, C. D.; Wang, X. L.; et al. One-dimension MnCo2O4 nanowire arrays for electrochemical energy storage. Electrochem. Acta 2014, 116, 467–474.

(13) Padmanathan, N.; Selladurai, S. Solvothermal synthesis of mesoporous NiCo2O4 spinel oxide nanomaterials for high-performance electrochemical capacitor electrode. Ionics 2013, 19, 1535–1544.

(14) (a) Fu, W.; Li, X.; Zhao, C.; Liu, Y.; Zhang, P.; Zhou, J.; Pan, X.; Xie, E. Facile hydrothermal synthesis of flowerlike ZnCo2 O 4
microspheres as binder-free electrodes for supercapacitors. Mater. Lett. 2015, 149, 1–4. (b) Rashid, J.; Barakat, M. A.; Mohamed, R. M.; Ibrahim, I. A. Enhancement of photocatalytic activity of zinc/cobalt spinel oxides by doping with ZrO2 for visible light photocatalytic degradation of 2-chlorophenol in wastewater. J. Photochem. Photobiol., A 2014, 284, 1–7.

(15) Krishnan, S. G.; Reddy, M. V.; Harilal, M.; Vidyadharan, B.; Misnon, I. I.; Rahim, M. H. A.; Ismail, J.; Jose, R. Characterization of MgCo2O4 as an electrode for high performance supercapacitors. Electrochim. Acta 2015, 161, 312–321.

(16) Pendashteh, A.; Moosavifard, S. E.; Rahmanifar, M. S.; Wang, Y.; El-Kady, M. F.; Kaner, R. B.; Mousavi, M. F. Highly Ordered Mesoporous CuCo2O4 Nanowires, a Promising Solution for High-Performance Supercapacitors. Chem. Mater. 2015, 27, 3919–3926.

(17) (a) Zasada, F.; Stelmachowski, P.; Maniak, G.; Paul, J.-F.; Kotarba, A.; Sojka, Z. Potassium Promotion of Cobalt Spinel Catalyst for N2O Decomposition-Accounted by Work Function Measurements and DFT Modelling. Catal. Lett. 2008, 127, 126–131. (b) Manova, E.; Tsonecheva, T.; Estournès, C.; Paneva, D.; Tenchev, K.; Mitov, I.; Petrov, L. Nanosized iron and iron-cobalt spinel oxides as catalysts for methanol decomposition. Appl. Catal., A 2006, 300, 170–180. (c) Dou, J.; Yin, S.; Chong, J. Y.; Zhang, B.; Han, J.; Huang, Y.; Xu, R. Carbon spheres anchored Co3O4 nanoclusters as an efficient catalyst for dye degradation. Appl. Catal., A 2016, 513, 106–115.

(18) (a) Padmanathan, N.; Selladurai, S. Mesoporous MnCo2O4 spinel oxide nanostructure synthesized by solvothermal technique for supercapacitor. Ionics 2013, 20, 479–487. (b) Ge, X.; Liu, Y.; Goh, F. W. T.; Hor, T. S. A.; Zong, Y.; Xiao, P.; Zhang, Z.; Lim, S. H.; Li, B.; Wang, X.; et al. Dual-phase spinel MnCo2O4 and spinel MnCo2O4/nanocarbon hybrids for electrocatalytic oxygen reduction and evolution. ACS Appl. Mater. Interfaces 2014, 6, 12684–12691. (c) Lu, D.; Feng, Y.; Ding, Z.; Liao, J.; Zhang, X.; Liu, H.-R.; Li, H. MoO3-Doped MnCo2O4 Microspheres Consisting of Nanosheets: An Inexpensive Nanostructured Catalyst to Hydrolyze Ammonia Borane for Hydrogen Generation. Nanomaterials 2018, 9, 21. (d) Yang, W.; Hao, J.; Zhang, Z.; Lu, B.; Zhang, B.; Tang, J. Synthesis of hierarchical MnCo2O4.5 nanostructure modified MnOOH nanorods for catalytic degradation of methylene blue. Catal. Commun. 2014, 46, 174–178. (e) Lesani, P.; Babaei, A.; Aitae, A.; Mostafavi, E. Nanostructured MnCo2O4 synthesized via co-precipitation method for SOFC interconnect application. Int. J. Hydrogen Energy 2016, 41, 20640–20649.

(19) Lavanya, C.; Geetha Balakrishna, R. Naturally derived polysaccharides-modified PSF membranes: A potency in enriching the antifouling nature of membranes. Sep. Purif. Technol. 2020, 230, 115887.

(20) Lavanya, C.; Soontarapa, K.; Jyothi, M. S.; Geetha Balakrishna, R. Environmental friendly and cost effective caramel for congo red removal, high flux, and fouling resistance of polysulfone membranes. Sep. Purif. Technol. 2019, 211, 348–358.

(21) Lavanya, C.; Balakrishna, R. G.; Soontarapa, K.; Padaki, M. S. Fouling resistant functional blend membrane for removal of organic matter and heavy metal ions. J. Environ. Manage. 2019, 232, 372–381.

(22) Lavanya, C.; Balakrishna, R. G.; Soontarapa, K.; Padaki, M. S. Fouling resistant functional blend membrane for removal of organic matter and heavy metal ions. J. Environ. Manage. 2019, 232, 372–381.

(23) Lavanya, C.; Kusuma, J.; Geetha Balakrishna, R. Pyrochlores: oxygen-rich moieties as ceramic fillers in uplifting the antifouling property and dye removal capacity of polymeric membranes. Sep. Purif. Technol. 2021, 272, 118946.

(24) Kalawa, O.; Kidkhunthod, P.; Chanlek, N.; Khajonrit, J.; Maensiri, S. Synthesis and electrochemical properties of polymer solution prepared MnCo2O4 nanoparticles. Ionics 2019, 26, 457–469.