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Rapid Communication

Highly efficient ultrafiltration membrane performance of PES@microcrystalline cellulose extracted from waste fruits for the removal of BrO$_3^-$ from drinking water samples

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1. Introduction

Water is a vital natural source of life, an essential component of all habitats. However, due to a rising human population needing clean water, freshwater availability is under increasing strain [1]. Thus, managing decontamination side products in drinkable water has become a major concern for water utilities in recent years [1,2]. The interactions between DBPs and original substances in water result in several by-products that could pose health hazards to people [3]. Ozone is the most capable reagent for water purification since it does not develop large levels of halogenated compounds, which are frequent in chlorination [4]. BrO$_3$ is an effective oxidant various compounds in potable water [5]. Ozone is considered a reactive ingredient in water for cleanup and taste control, as well as for destroying pathogens such as Giardia and cryptosporidium oocytes [5–7]. Thus, reducing of these pollutants is critical to ensure adequate water quality for human consumption [7].

The generation of bromate ions through bromide ion (Br$^-$) naturally occurring in water sources is a significant concern in water purification for drinking water using O$_3$ [8,9]. Bromate ion formation may be accomplished using the following processes [8,9]:

\[
O_3 + Br^- \rightarrow O_2 + BrO
\]

\[
2O_3 + BrO^- \rightarrow 2O_2 + BrO_3^-
\]

Ozone pollution is typically associated with the development of DBPs during the ozonation process of bromide-having drinkable water [8,9]. Therefore, BrO$_3$ ion is a critical DBP that has a detrimental role in essential biological functioning [3,10,11]. The most popular methods for regulating the generation of bromate are to modify the solution’s pH using ammonia and reduce ozone exposure [5,6]. Decreased ozone content also negatively influences pathogen inactivation [5] or DBP development regulation during chlorination [6]. As a result, in recent years, much emphasis has been placed on trace detection [2,4,12] and complete reduction [3,13] of bromate in potable water. Bromate removal from portable water remains challenging due to the considerable health concern among governing organizations [3,7,9,13]. Thus, in recent years, there has been a surge in interest in developing environmentally and highly effective processes for the total removal of bromate in drinkable water [13–18]. The primary of the cited approaches in the previous work focused on using various solid adsorbents [3,7,14–19]. However, each of these solid adsorbents has certain disadvantages.
Ultrafiltration (UF) process as a low-pressure-driven membrane can be effectively eliminated most of the contaminants from an aqueous solution. The usage of nanoparticles in a polymer matrix, specifically a mixed-matrix ultrafiltration membranes (MMMs), was found to increase performance metrics such as mechanical characteristics, fouling resistance, hydrophilicity, and removal performance [20–24]. Microcrystalline cellulose (MCC) is a partly hydrolyzed and depolymerized cellulose with disorganized amorphous parts [25]. The source and circumstance of cellulose hydrolysis influence the characteristics and structure of MCC [25]. Various investigations have shown that microcrystalline cellulose is highly porous with multifunctional polar moieties such as hydroxyl [26,27]. The quantitative value of the solid microcrystalline cellulose in decontaminating halogenated DBPs such as BrO\textsubscript{3}− from the aquatic environments is restricted [15,16]. In this regard, El-Shahawi et al. [28] used microcrystalline cellulose (MCC) as a new solid adsorbent for reduction of BrO\textsubscript{3}− ions as one of DBPs in portable water. The findings indicated that the MCC was utilized effectively to remove all bromate ions from ambient water samples. In comparison to commonly available adsorbents equivalents, the sorbent demonstrated exceptional sorption ability towards bromate ions.

The primary goal of this work was to fabricate a novel mixed-matrix ultrafiltration membrane (UF MMM) by incorporating microcrystalline cellulose (MCC) into a PES-based membrane. The study utilized UF tests to assess the impact of MCC in the dope solution on the membrane characteristics and the efficiency of the resulting membranes in the elimination of bromate. The novelty of using microcrystalline cellulose (MCC) and polyethersulfone (PES) for the development of ultrafiltration (UF) membranes lies in the significant improvements observed in the membrane properties. MCC is also advantageous due to its low cost and ecological acceptability, making it an attractive option for water treatment applications. Overall, the use of MCC and PES in UF membrane development excellent great potential for improving water treatment efficiency and sustainability.

2. Experimental

2.1. Materials

NaOH (≥98%), N-methyl-2-pyrrolidinone (≥99%, NMP), ethanol (99%), potassium nitrate (KBrO\textsubscript{3} ≥99.8%), HCl (37%), Na\textsubscript{2}SO\textsubscript{4} (≥99%), glacial acetic acid (CH\textsubscript{3}COOH, ≥99%), sodium chloride (NaClO\textsubscript{3}, 80%), Polyvinylpyrrolidone (PVP), and N,N-dimethylformamide (DMF, ≥99.5%), were provided from Sigma-Aldrich Co., USA. Dried powdered fruits were used to extract microcrystalline cellulose (MCC). Polyethersulfone (PES, Mr 58,000 g/mol) was purchased from Goodfellow, USA. All materials were utilized exactly as they were purchased. Ultra-pure water from a Millipore Milli-Q Direct 8 (Millipore, France) was used for all experiments.

2.2. Preparation of MCC

To remove color components and wax, an estimated weight (20 g) of the dried solid waste fruits was forcefully agitated with the blended solvent (2:1) ethanol-toluene (500 mL). The residue was collected by filtration, dried at 120 °C for 24 h, and thoroughly agitated with a solution of 1.4% w/v NaClO\textsubscript{3} (150 mL). The blend has adjusted at pH 4 using CH\textsubscript{3}COOH (5% m/v) and heated at 80 °C for 5 h. After adding iced water to the blend to partly remove the lignin, the bleached material was separated and rinsed with water till a neutral filtrate was attained. The obtained solid product was heated with a 40 mL solution of 5% w/v Na\textsubscript{2}SO\textsubscript{4} for 5 h, the remaining obtained was decanted and rinsed with deionized water to remove all hemicellulose and lignin and components. The obtained product was handled with 17% w/v NaOH (500 mL) at ambient temperature, and the blend was agitated for 24 h before being heated at 90 °C for 5 h to get rid of hemicellulose. The obtained cellulosic compound was hydrolyzed at 80 °C with 2 M HCl for 3 h before being rinsed many times with deionized water at ambient temperature till a neutral pH. The final powder was at 100 °C for 12 h, ground, and lastly kept in polyethylene bottles for usage, termed as MCC [28].

2.3. Fabrication of MPES@MCC membranes

The UF MMMs were fabricated using the non-solvent induced phase separation approach (NIPS). Typically, MCC nanoparticles were distributed in NMP for 20 min by sonication, resulting in a homogenous dispersion. Then, 18 wt% PES and 2 wt% PVP were gently added to the MCC dispersion while continuously stirring for 3 h at 350 rpm at 40 °C. As a hydrophilic addition, PVP was introduced to the casting solutions. The blend was stirred for 24 h at a comparable temperature to obtain a proper composite homogeneity. The polymeric solution was sonicated for 20 min before casting the membrane to eliminate air bubbles. A clean glass substrate was used to cast the mixture, utilizing a casting knife to achieve a film thickness of 250 µm. After drying in the air for 30 s, the membrane film was settled by immersing the plate in a non-solvent bath. The plate was maintained in the non-solvent bath for couple of minutes to enable the solvent and non-solvent exchange, which resulted in the membrane film separating from the substrate. To remove any remaining solvent, the membrane was washed with water. The membrane composition with 1, 3, and 5 wt% MCC donate as MPES-1%MCC, MPES-3%MCC, and MPES-5%MCC respectively (Table 1). A bare membrane (MPES) without MCC was also developed for comparison [29–31].

2.4. Characterisation

The chemical bonding and functional moieties on the MCC and the synthesized membranes were determined via FT-IR, Shimadzu IR Tracer-100 over the wavenumber from 400 to 4000 cm\textsuperscript{-1}. The structural properties were examined utilizing a powder X-ray diffractometer (Optima7000, Shimadzu, Japan). A Cu Kα radiation (λ = 0.15406 nm) was used in conjunction with the XRD across 2θ (10-80°) range. Thermal gravimetric assessment (TGA, STA−449F3, Shimadzu) was carried out in an N\textsubscript{2} atmosphere at a heating rate of 10 °C min\textsuperscript{-1} from 25 to 600 °C. The membrane morphology, including the cross-section and topsurface, was investigated using FESEM, Thermo Scientific Quattro ESEM, Thermo Fisher, Waltham, MA, USA. Tensile testing was performed using a Shimadzu EZ-S tensile tester. The hydrophilicity of the membrane was ascertained by measuring the contact angles using a Data Physics SCA20 Goniometer fitted with a digital camera. The prepared membrane’s porosity (ε) was estimated as follows: the membrane sheets (2 cm\textsuperscript{2}) were weighted and immersed in deionized water at room temperature for overnight. The wet sheets were dried under vacuum for 12 h at 60 °C before being weighed. The membrane’s porosity (ε) of the membrane was determined by applying Eq. (3) [29–31]:

\[ \varepsilon = \frac{W_1 - W_2}{A \rho} \]

where (W\textsubscript{1} and W\textsubscript{2}) are the dry mass and wet membrane mass, respectively, \( \rho \) is the water density, \( A \) is the area and \( \varepsilon \) is the thickness.

The average radius (r\textsubscript{m}) of the pores was measured using the Guerout-Ellford-Ferry employing Eq. (4) [29–31]:

\[ r_m = \frac{% \sqrt{2} \pi \sigma \varepsilon^2 M (1-\varepsilon)^3}{\lambda^2 \rho \varepsilon} \]

\[ \lambda = \frac{A \rho}{W_1} \]

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The casting solutions composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Casting composition</td>
</tr>
<tr>
<td></td>
<td>PES (wt%)</td>
</tr>
<tr>
<td>MPE</td>
<td>18</td>
</tr>
<tr>
<td>MPES-1%MCC</td>
<td>18</td>
</tr>
<tr>
<td>MPES-3%MCC</td>
<td>18</td>
</tr>
<tr>
<td>MPES-5%MCC</td>
<td>18</td>
</tr>
</tbody>
</table>

* Based on the total PES polymer fraction in the casting solution, the MCC percentage is calculated.
\[ r_m = \sqrt{\frac{(2.9 - 1.75e) \times 8 \mu Q}{\varepsilon \times A \times \Delta P}} \] (4)

where \( t \) is the thickness, \( \mu \) is the viscosity of water \( (8.9 \times 10^{-4} \text{ Pa s}) \), \( \Delta P \) is the applied pressure, and \( Q \) is the permeate pure water volume \( (\text{m}^3 \text{s}^{-1}) \).

The water uptake \( \varphi \) \( (\%) \) could be measured employing Eq. (5):

\[ \varphi \% = \frac{W_w - W_d}{W_d} \] (5)

where \( W_w \) and \( W_d \) are the wet and dry membrane weights (kg).

2.5. UF experiments of BrO\(_3\)-polluted drinking water

All the measurements were performed with the stock solution of 25 ppm. All the fabricated membranes were pre-compressed at 2 bar with deionized water for 30 min to ensure no leaks before all tests. Water permeation tests were operated at 1.0 bar pressure and the pure flux of water \( (J_w) \) was evaluated by measuring the permeate weight in 30 min according to Eq. (6):

\[ J_w = \frac{m}{\rho \times A \times t} \] (6)

where \( m \) is the permeate’s weight of the, \( t \) is the time, and \( A \) is the effective area of the membranes. The pure water flux obtained from a virgin membrane is stated as \( J_{w1} \). For the rejection trials, BrO\(_3\) was used as a model. After the water permeation tests, the feed solution was substituted by 25 ppm of bromate solution. The rejection experiment of BrO\(_3\) was performed at 1 bar for 30 min. The concentration of BrO\(_3\) in both the feed solution and permeate was determined using a UV–Vis spectrometer (Cary 60, Agilent) at a wavelength of 540 nm. The rejection \( (R) \) was estimated as follows:

\[ R(\%) = \left( \frac{C_f}{C_p} \right) \times 100 \] (7)

where \( C_f \) and \( C_p \) are the BrO\(_3\) content in the feed and permeate solution (ppm), respectively. After the BrO\(_3\) filtration, the membrane has rinsed with DI water to eliminate the accumulated foulant. The pure water flux of the cleaned membrane, \( J_{w2} \), was calculated for an additional 30 min. Flux recovery ratio \( (\text{FRR}) \), total fouling ratio \( (\text{Rt}) \), irreversible fouling ratio \( (\text{Rir}) \), and reversible fouling ratio \( (\text{Rr}) \), were derived to highlight antifoulid efficiency (Eqs. (8–11)):

\[ \text{FRR}(\%) = \frac{J_{w2} \times 100}{J_{w1}} \] (8)

\[ R_t = \frac{(J_{w1} - J_{w2})}{J_{w1}} \times 100 \] (9)

\[ R_{ir} = \frac{(J_{w1} - J_{w2})}{J_{w1}} \times 100 \] (10)

\[ R_r = \frac{(J_{w1} - J_{w2})}{J_{w1}} \times 100 \] (11)

3. Results and discussion

3.1. Membranes characterization

FTIR spectrum of the manufactured MCC powder is depicted in Fig. 1a. The infrared pattern of the synthesized MCC powder was identical to that of pristine cellulose, as described in the literature [32]. The broad characteristics band at 3322 cm\(^{-1}\) assigns to the stretching mode of OH moieties, while the characteristics band at 2892 cm\(^{-1}\) is associated with -CH\(_2\) moieties [33]. Water molecules cause the band at 1646 cm\(^{-1}\) adsorbed as a consequence of a great interaction between water and MCC. Asymmetric -CH\(_2\) bending mode is also attributed to the characteristic band at 1430 cm\(^{-1}\). This band, often referred to as the band of crystallinity, depicts cellulose’s degree of crystallinity. C=H rock and C-O-C stretching modes of MCC are ascribed to the bands at 1160 cm\(^{-1}\) and 890 cm\(^{-1}\), respectively. The spectra of the mixed-matrix ultrafiltration membranes (MPES/MCC) (Fig. 1b) matched those of the pristine membrane (MPES), particularly from 1600 cm\(^{-1}\) to 500 cm\(^{-1}\). This result suggests that the mixed-matrix ultrafiltration membranes might maintain their PES properties even after the incorporation of MCC. However, little changes were found at the peaks 31,646 cm\(^{-1}\), 2892 cm\(^{-1}\), and 3322 cm\(^{-1}\), representing water adsorbed, CH\(_2\) moieties, and the OH moieties, respectively. These bands are comparable to those seen for MCC powder, as depicted in Fig. 1a, demonstrating that MCC integration into the PES framework was feasible. The OH moieties of the MCC were then responsible for creating novel H-bonds connections with PES. The H-bonds are electrostatically linked to the MCC molecules with PES, resulting in membranes with MCC characteristics while retaining the PES properties. As a consequence, the membrane’s hydrophilicity.
was improved.

The successful incorporation of MCC in the framework of the polymer was also explored using XRD as displayed in Fig. 2. The MPES displayed a broad diffraction band at 22°, a feature of PES [29–31]. In the case of the XRD patterns of the mixed-matrix ultrafiltration membranes (MPES/MCC), there were well-defined diffraction peaks at 2θ = 15.2° (110) and 2θ = 22.1° (200), as well as a weak diffraction peak at 2θ = 34.9° assigning to (040) reflection of the synthesized MCC (JCPDS file, No. 50–2241). These results confirmed the integration of the MCC into PES polymer framework. Furthermore, the intensity was raised by raising the concentration of MCC. The XRD patterns of all mixed-matrix ultrafiltration membranes reveal a similar diffraction peak of the PES membrane, suggesting that the mixing of MCC does not seem to alter the polymeric matrix of PES.

TGA was employed to examine the thermal stability of the membrane, as illustrated in Fig. 3. The pristine MPES membrane decomposed at 245 °C, while all MCC-integrated PES membranes with 5% MCC disintegrated at greater temperatures at (428 °C). The integration of MCC into PES resulted in an improvement in thermal stability. Furthermore, for each membrane, two distinct weight-loss phases were found. The physisorbed water loss is related to the 1st weight-loss peak of <200 °C. The 2nd peak in the 200–600 °C was ascribed to carbon framework breakdown, followed by residual polymer chain structure deterioration at higher temperatures. The integration of microcrystalline cellulose (MCC) into the polyethersulfone (PES) membrane has been found to positively impact the thermal stability of the resulting membrane. MCC has high thermal stability due to its crystalline structure, which can reinforce the PES matrix. When MCC is added to the PES membrane, it forms a network structure with PES, which enhances the thermal stability of the resulting composite membrane. The interaction between MCC and PES can also create more crosslinking points in the membrane framework, which can increase the thermal stability of the composite membrane. Moreover, MCC has a higher decomposition temperature than PES, which means that MCC can act as a thermal stabilizer for the PES matrix.

3.2. Membrane morphology

The morphological investigation of the mixed-matrix ultrafiltration membranes (MPES/MCC) in this work was illustrated in Fig. 4. All developed membranes possessed an asymmetric architecture, with a narrow packed thick-top layer sustained by finger-like voids in the center and macro-void pores at the bottom. MCC is visible on the membrane surface, as illustrated in Fig. 4. This shows that the crystalline cellulose was effectively integrated into the PES frameworks. The influence of different MCC concentrations on the sizes and pore architecture is feasible. The surface of the mixed-matrix ultrafiltration membranes (MPES/MCC) shows an augmentation of porosity concerning MCC content, as illustrated in Fig. 4. Likewise, analysis of the membrane’s cross-section morphology indicates that the pores were enlarged in the macro-void, while the finger-like pores in the resultant membrane increased in length as they extended downward. This phenomenon may be explained by the presence of MCC in the doping solution, which facilitated the diffusion of water into the casting solution due to its hydrophilic properties. [34]. When 5 wt% MCC was added, distinct pore configurations were observed, characterized by thicker and more spongy pores. The thickness of these pores increased as the amount of MCC used was raised. The observed phenomenon was ascribed to the predominance of casting solution viscosity over MCC’s hydrophilicity in controlling the rate of phase inversion, leading to the formation of thicker top-layer membranes through a minor phase inversion process. As a result, there was a decrease in the macro-voids, an increase in spongy pores, and a decline in finger-like pores. The presence of MCC resulted in an increase in both mean pore radius and total porosity of the fabricated membranes, as compared to virgin PES membrane, as demonstrated in the following illustration. Table 2. This affirms that the created membrane can expedite the phase separation process, which in turn leads to the creation of larger pores within the SPES. This results in an anticipated increase in permeability and greater water absorption capacity (as seen in Table 2).

3.3. Membrane hydrophilicity

The interaction between microcrystalline cellulose (MCC) and polyethersulfone (PES) in a composite material is primarily governed by mechanical interlocking and hydrogen bonding. Mechanical interlocking occurs when the MCC particles are dispersed within the PES matrix and physically entangled with the polymer chains. Hydrogen bonding occurs because of the existence of hydroxyl moieties on the surface of the MCC particles, which can form hydrogen bonds with the carbonyl and ether moieties in the PES polymer chains. This bonding effect can enhance the compatibility between the MCC and PES, leading to improved interfacial adhesion and a more homogeneous distribution of the MCC particles within the PES framework. The static contact angle

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Fig. 2. XRD patterns of bare MPES and MCC-integrated PES membranes (1, 3, and 5 wt% MCC).

Fig. 3. TGA profiles of bare MPES and MCC-integrated PES membranes (1, and 5 wt% MCC) in the temperature range from 25 to 800 °C.
of the mixed-matrix ultrafiltration membranes (MPES/MCC) is illustrated in Fig. 5. The contact angle of the pristine MCC and pristine PES were 40.1° and 60.1°, respectively. The water contact angle of the mixed-matrix ultrafiltration membranes containing various content of MCC (1, 3, and 5 wt%) are (56.8°, 50.1°, and 43.1°), respectively. The behavior reveals that increasing the MCC content enhances the hydrophilicity of the mixed-matrix ultrafiltration membranes PES/MCC. Microcrystalline cellulose in the doping solution boosted the membrane hydrophilicity by chemically introducing the OH moieties on the surface of the membrane. The OH moieties have a great potential to attract water, which makes any air voids on the surface of the membrane more likely to fill with water and promote membrane wetting. The quantity of OH moieties rise as the quantity of MCC boosts. As a consequence, the wetness of the membrane increases. As a result, introducing hydrophilic MCC with a significant concentration of OH moieties considerably increased the hydrophilic character of the membrane containing PES.
3.4. Mechanical properties

Microcrystalline cellulose (MCC) is a relatively stiff and brittle material that can contribute to the increased rigidity of a composite material when combined with a polymer such as polyethersulfone (PES). The MCC particles act as a reinforcement in the PES matrix, which can enhance the mechanical features of the composite nanofibers, such as stiffness and strength. The stress-strain profiles of pure PES and MCC-integrated PES membranes were compared in Fig. 6. It was observed that the mixed-matrix ultrafiltration membrane (PES/MCC) exhibited a significant drop in elongation-at-break while the tensile strength remained relatively unchanged compared to a PES membrane made entirely of PES. This is because MCC is a relatively rigid and inelastic material, which can limit the ability of the composite material to deform and stretch under stress. Moreover, the existence of MCC in the PES matrix can also affect the stress distribution within the composite material. The MCC particles can act as stress concentrators, which can lead to the formation of stress concentrations and the initiation of cracks or fractures in the composite material. This can further contribute to the reduced elongation at break and increased rigidity of the composite material.

3.5. Permeability

The synthesized membranes were subjected to ultrafiltration operations to evaluate their water permeability and ability to reject BrO₃⁻ solution. The findings for the water flux are depicted in Fig. 7a. At 1 bar working pressure, a pristine PES membrane observed a water flux of 153 L m⁻² h⁻¹. This is owing to the membrane’s tiny porosity and poor hydrophilicity, which often prevents water molecules from passing through the pores of the membrane. The low permeation rate of water is attributable to the absence of a pore-forming agent, which led to the formation of minuscule membrane pores. The MCC contents of 1, 3, and 5 wt% boosted the water flux to 169, 178, and 180 L m⁻² h⁻¹, respectively. The combined effect of the OH functional group and pore size led to a significant increase in the synthesized membranes’ water flux compared to the original PES membrane. The pore size and hydrophilic nature of the developed membranes are primarily responsible for the significant alterations in flux. The hydrophilic character of MCCs might boost the rate of movement of water molecules due to the excellent OH moieties. The OH moieties on the surface attracted H₂O molecules due to the enhanced hydrophilic characteristics of the produced membranes. These membranes’ expanding surface pores allowed much H₂O molecules to transfer within them. The BrO₃⁻ solution flux for all synthesized membranes examined is displayed in Fig. 7b. Feed solutions with a content of 25 ppb BrO₃⁻ were utilized in the filtration process. The findings revealed that the flux of BrO₃⁻ solution was less than that of water flux, as displayed in Fig. 7b. This might be owing to BrO₃⁻ deposition on the membrane’s surface and inside the pores. Meanwhile, the BrO₃⁻ solution flow increased substantially with the addition of MCC. The strong layer of hydration of the linked water may inhibit the accumulation of BrO₃⁻ solution on the membrane’s surface. Membrane fouling occurs when suspended or dissolved particles, such as organic matter or

<table>
<thead>
<tr>
<th>Membrane</th>
<th>ϵ (%)</th>
<th>φ (%)</th>
<th>r_m (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPES</td>
<td>24.3±0.2</td>
<td>29.3±0.2</td>
<td>5.3±0.1</td>
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<tr>
<td>MPES-1%MCC</td>
<td>33.4±0.3</td>
<td>35.2±0.1</td>
<td>6.9±0.2</td>
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<tr>
<td>MPES-3%MCC</td>
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<td>39.5±0.3</td>
<td>8.3±0.2</td>
</tr>
<tr>
<td>MPES-5%MCC</td>
<td>44.5±0.3</td>
<td>44.2±0.3</td>
<td>10.4±0.2</td>
</tr>
</tbody>
</table>

Table 2
The porosity, ϵ (%); water uptake, φ (%); and mean pore radius, r_m (nm) of the synthesized membranes.

Fig. 5. Static water contact angle of pure MPES and MCC-integrated PES membranes (1, 3 and 5 wt% MCC).

Fig. 6. Stress-strain curves of pure MPES and MCC-integrated PES membranes (1, and 5 wt% MCC).
salts, accumulate in the pores or membrane surface, reducing its performance over time. The strong layer of hydration surrounding the membrane surface can help prevent or reduce the adhesion of foulants by creating a repulsive force that prevents them from approaching the surface. Additionally, the hydration layer can create a barrier that prevents foulants from penetrating the membrane surface [35,36].

By integrating MCC, the adsorptions of BrO$_3^-$ solution was boosted as illustrated in Fig. 8a. For the MPES+5% MCC membrane, the largest collected BrO$_3^-$ amount was observed (BrO$_3^-$: 840 μg cm$^{-1}$). This could be attributed to the highest hydrophilicity degree, which enabled hydration layers to form and decreased BrO$_3^-$ adsorption. The flux recovery ratio (FRR) was measured and presented in Fig. 8b to emphasize the antifouling characteristics of the developed membranes. As shown in Fig. 8b, the FRR of the MCC-containing membrane is obviously greater than that of the pristine PES membrane. MPES+5%MCC has the maximum FRR (99%), suggesting that raising hydrophilicity might boost the antifouling character.

The low rejection of 7.2% BrO$_3^-$ solution was captured for the virgin PES membrane owing to the membrane’s tiny pores. All MCC-integrated PES membranes displayed a much greater BrO$_3^-$ rejection than the bare PES membrane with 60.8%, 80.2, and 92% BrO$_3^-$ rejection for 1%, 3%, and 5% MCC, respectively. The robust BrO$_3^-$ rejection is due to the MCC-integrated PES membranes’ physicochemical characteristics (hydrophilicity and pore size). All MCC-integrated PES membranes displayed the development of a thicker-top layer, due to the small phase rate of inversion caused by excellent viscosity. Moreover, the membranes had a high extent of hydrophilicity, resulting in a thick and durable layer of hydration above them throughout the filtering process [37]. The combination of these features facilitated in the removal of BrO$_3^-$ while allowing water molecules to flow through. As a result, hydrophilicity and pore diameters seem to have played an important role in BrO$_3^-$ removal (Fig. 9). Table 3 has been included to facilitate a more comprehensive comparison. The table outlines the efficiency values for the various membranes, highlighting significant variations. Notably, the results presented in the table demonstrate that the membranes created in this study showed considerably higher efficiency levels than previously reported membranes [38–43].

### 3.6. Rejection mechanism

The rejection mechanism of bromate species by MCC/PES membranes is mainly attributed to size exclusion and charge repulsion effects. Size exclusion is based on the membrane’s molecular weight cut-off (MWCO), which determines the maximum size of the solutes that can pass through the membrane. Bromate ions have a relatively large molecular size (96.9 g/mol), thus, they are expected to be effectively rejected by ultrafiltration membranes with a small MWCO. MCC/PES composite membranes typically have a small MWCO, which can prevent...
bromate species from the flow within the membrane and, thus, increase their rejection rate. Furthermore, the charge repulsion effect is based on the electrostatic interaction between bromate ions and the negatively charged surface of the MCC/PES composite membrane. Bromate ions are negatively charged and, thus, can be repelled by the negatively charged surface of the composite membrane, resulting in their rejection. MCC contains carboxylic and hydroxyl functional groups that can create negative charges on the membrane surface, further enhancing the electrostatic repulsion between the bromate ions and the membrane. In addition to size exclusion and charge repulsion effects, the adsorption of bromate ions onto the MCC surface can also contribute to their rejection. MCC has a high surface area and porosity, which can facilitate the adsorption of bromate ions onto the surface of the composite membrane. The adsorption process can reduce the concentration of bromate ions in the feed solution, leading to higher rejection rates. Overall, the rejection mechanism of bromate ions by MCC/PES composite membranes can be related to the integration of charge repulsion, size exclusion, and adsorption effects, which work together to prevent bromate species from the flow within the membrane and, thus, increase their rejection rate.

4. Conclusion

In conclusion, this study demonstrated the successful development of mixed-matrix ultrafiltration membranes (MMs) composed of polyethersulfone (PES) and microcrystalline cellulose (MCC) for the elimination of bromate (BrO₃⁻) from an aquatic environment. The findings displayed that the incorporation of MCC up to 5 wt% in PES membranes led to a significant improvement in membrane properties, including increased hydrophilicity as indicated by a remarkable decrease in the contact angle from 60° of meat PES to 43.1°, improved membrane permeability as shown from the enhancement in the water flux to 180 L m⁻² h⁻¹, and enhanced antifouling properties. The MCC-integrated PES membranes also exhibited superior performance in removing of bromate ions, with rejection rates of up to 92%, which was much greater than that of the bare PES membrane. Overall, using MCC as a low-cost and ecologically acceptable chemical makes its incorporation into PES membranes an attractive option for water treatment applications. Further studies could focus on optimizing the concentration of MCC and exploring the potential of mixed-matrix membranes in eliminating other contaminants from water.

CRediT authorship contribution statement

Ibrahim Hotan Alsohaimi: Conceptualization, Methodology, Investigation, Resources, Formal analysis, Writing – original draft, Software, Validation. Abdulelah Nashmi Alarashidi: Investigation, Formal analysis, Validation. Hassan M.A. Hassan: Conceptualization, Methodology, Investigation, Resources, Formal analysis, Supervision, Writing – review & editing. Qiao Chen: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Software, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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