1 Introduction

Dwindling water resources due to environmental pollution and the increasing demand for potable water for the growing population worldwide urge the search for efficient water purification technologies.\textsuperscript{1,2} Pressure-driven membrane separation processes for water treatment offer multiple advantages, including energy efficiency, easy-integration and scalability compared to traditional separation methods.\textsuperscript{3,4} Nanofiltration (NF) particularly has gained much attention due to its unique advantages in wastewater purification and separation of organic molecules, multivalent ions, and industrial residues.\textsuperscript{5,6} NF membranes have properties in between those of ultrafiltration (UF) and reverse osmosis (RO), and can reject solutes ranging from 1–10 nm diameter via size exclusion.\textsuperscript{5,7,8} Nanoporous membranes are currently the core component of NF technologies.\textsuperscript{5,6} A vast number of polymer composites with various inorganic nanomaterials have been explored to date for the development of nanoporous membranes.\textsuperscript{9–12} However, these membranes are highly susceptible to chemical instability,\textsuperscript{13} low water flux, and high surface fouling (organic fouling, colloidal fouling, and biofouling),\textsuperscript{14} and therefore require high-cost and frequent replacement. Biofouling is an inevitable hindrance that reduces the overall performance of nanoporous membranes, including rejection, flux, and durability.\textsuperscript{15} Thus, engineering a bacterial resistant membrane that is chemically stable and maintains a high water flux is crucial for water purification and desalination industries.

MXenes have emerged as one of the most important and widely studied classes of 2D metal carbides.\textsuperscript{16,17} The ability to produce MXenes in large and stable quantities allowed for their exploration in a variety of applications such as adsorption of organic molecules,\textsuperscript{18} capacitive deionization,\textsuperscript{19} water treatment,\textsuperscript{20–22} environmental remediation,\textsuperscript{23} photocatalysis,\textsuperscript{24} and disinfection.

Low flux and fouling are critical issues in membrane based separation processes. Here we report a two-dimensional (2D) MXene (Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}) modified with Ag nanoparticles (Ag@MXene) as a promising alternative for ultrafast water purification membrane applications. The novel Ag@MXene composite membrane with variable AgNP loadings (between 0–35%) was produced by self-reduction of silver nitrate on the surface of MXene sheets in solution, where the MXene acted simultaneously as a membrane forming material and a reducing agent. The most suitable membrane, 21% Ag@MXene with 470 nm thickness and 2.1 nm average pore size, exhibited an outstanding water flux (~420 L m\textsuperscript{-2} h\textsuperscript{-1} bar\textsuperscript{-1}) compared to the pristine MXene membrane (~118 L m\textsuperscript{-2} h\textsuperscript{-1} bar\textsuperscript{-1}) under the same experimental conditions. The 21% Ag@MXene membrane demonstrated high rejection efficiency for organic molecules with excellent flux recovery. Moreover, the 21% Ag@MXene composite membrane demonstrated more than 99% E. coli growth inhibition, while the MXene membrane exhibited only ~60% bacteria growth inhibition compared to the control hydrophilic polyvinylidene difluoride (PVDF) based membrane. Furthermore, the 21% Ag@MXene membrane achieved favorable rejection to organic foulants like bovine serum albumin (BSA) and methyl green (MG) in comparison to other reported membranes. This combination of controlled permeability and bactericidal properties makes Ag@MXene layered nanosheets attractive candidates towards the development of nanofiltration membranes for water purification and biomedical applications.
purification of alcohol-based mixtures,25 electrochemical energy storage,26,27 and substrates for surface-enhanced Raman spectroscopy (SERS).28 MXenes are both hydrophilic due to the presence of surface terminations (T_x = –O, –OH and/or –F) as well as electrically conductive in nature.16,20 Recently, MXenes have been investigated as membrane materials for water treatment applications, owing to their antifouling properties, mechanical flexibility, chemical and thermal stability, metallic electronic conductivity, hydrophilicity, excellent film forming ability, etc. The combination of these properties is rarely present simultaneously in a material.29,30

Our group previously reported on both the potential of MXenes as selective ion and charge sieving membranes as well as their antibacterial activity.21,31,32 Although these membranes demonstrated a higher bacterial resistance toward both Gram-negative and Gram-positive bacteria compared with graphene oxide (GO), the moderate water flux (37.4 L bar^{-1} h^{-1} m^{-2}) limited the membrane use in practical applications. Wang et al. also reported a 2D lamellar MXene membrane with increased interlayer spacing and improved flux for water purification.29 Grafting silver nanoparticles (AgNPs) onto MXenes is expected to further improve the antifouling properties of MXene membranes and increase the water flux, as observed for other 2D materials.33–35 Single-step solution processing of AgNP/MXene (denoted here as Ag@MXene) based hybrid materials has been used recently for Li-ion storage and SERS applications.36,37 However, the antibacterial activity, fouling rejection, and water flux of Ag@MXene composite membranes for water purification applications have never been investigated.

In this study, we fabricated 2D layered Ag@MXene nanostructures as novel membranes with excellent water flux and high rejection performance in water purification applications. Ag@MXene composite membranes were prepared by a facile two-step method. First, Ag nanoparticles were deposited onto the surface of MXene nanosheets by efficient self-reduction of silver nitrate (AgNO_3) in aqueous media, where the MXene (Ti_3C_2T_x) acts both as a membrane material and a reducing agent. Second, the Ag@MXene composite solution was coated onto a PVDF substrate via a vacuum-assisted assembly method to create a favorable nanoporous framework. The newly developed composite membrane showed high mechanical stability, excellent water flux, and improved antifouling properties suitable for practical water treatment applications.

2 Experimental
2.1 Materials
Sodium chloride (NaCl), magnesium chloride (MgCl_2), aluminium chloride (AlCl_3), lithium fluoride (LiF), Rhodamine B (RhB), bovine serum albumin (BSA), and methyl green (MG) were purchased from Sigma-Aldrich. A hydrophilic PVDF membrane (47 mm diameter) was purchased from EMD Millipore. Ti_3AlC_2 was purchased from Y-Carbon, Ltd., Ukraine. All other solvents and reagents were of analytical grade and used as received.

2.2 Preparation of delaminated MXene (Ti_3C_2T_x) nanosheets
The delaminated MXene was achieved by acid etching of the aluminum layers in MAX (Ti_3AlC_2), followed by ultrasonication.38 The MAX (90 mg) powder was added to 1.8 mL of LiF (90 mg) acid solution (concentrated HCl and water in 1:1 volume ratio) and magnetically stirred for 30 h at 40 °C. The residue containing the etched multi-layered MXene was collected using centrifugation, followed by decantation and freeze drying. Delamination was carried out by probe sonication of the etched multi-layered MXene in degassed water, under a flow of argon (Ar) gas for two hours. The resulting solution was centrifuged at 5000 rpm for 30 min and decanted, after which the supernatant was freeze dried to obtain the delaminated MXene nanosheets.

2.3 Preparation of Ag@MXene composite nanoporous membranes
Ag@MXene composite nanoporous membranes were prepared by self-reduction of AgNO_3 to AgNPs on the surface of MXene nanosheets, where the MXene acted as a reducing agent. Typically, the MXene (3 mg) was dispersed in water (400 mL) by bath sonication. An aqueous solution of AgNO_3 was added dropwise into the uniformly dispersed MXene solution under continuous stirring to achieve different silver (Ag) loadings (between 0–35 wt% Ag in the MXene). The resulting mixture was then bath sonicated at 25 ºC for 1 h. Subsequently, Ag@MXene composite membranes (~470 nm thick) were prepared by vacuum-assisted filtration of the mixture on a hydrophilic PVDF membrane (47 mm diameter, Millipore) with a pore size of 0.22 µm. The membrane effective area was about 9.60 cm^2. The prepared composite membranes were denoted as X% Ag@MXene, where X is the weight percentage of the Ag loading, namely 0, 7, 14, 21, 28 or 35 wt% to the MXene. The PVDF support membrane was used as a control in this study.

2.4 Characterization
The ultraviolet-visible (UV-vis) absorbance spectra were collected using a Jasco V-670 absorption spectrophotometer (medium response, UV/vis bandwidth 2 nm, scan speed 100 nm min^{-1}). Wide angle X-ray diffractograms (WXRDs) were recorded using a Bruker D8 Advance (Bruker AXS, Germany) X-ray diffractometer with Cu-Kα radiation (λ = 1.54056 Å) at a voltage of 40 kV and a current of 15 mA with a step scan and scanning speed of 0.02° per step and 1° min^{-1}, respectively. X-ray photoelectron spectroscopy (XPS) analysis of the given samples was performed with an ESCALAB 250Xi (Thermo Fisher Scientific) using AlKα excitation radiation (25 W, hv = 1486.5 eV) and 1 eV energy resolution. For the XRD and XPS analyses, the samples were prepared by depositing freeze dried nanocomposite films onto a silicon substrate. Transmission electronic microscopy (TEM) images of the MXene and Ag@MXene composite samples were recorded using a FEI Talos F200X TEM. The powder samples were dispersed in ethanol and mounted on a lacey Formvar carbon coated Cu grid. The study of the morphology of the MXene and composite membranes
was performed by scanning electron microscopy (SEM) using a FEI Quanta 650 FEG SEM, after gold sputter coatings on samples. Energy-dispersive X-ray spectroscopy (EDS) was performed using a QUANTAX EDS, Bruker. Optical images of different membranes were taken using a Nikon digital camera (DS100 AF-S DX NIKKOR 18–55 mm f/3.5–5.6G VR). The thermal stability of Ag@MXene membranes was studied using a thermogravimetric analyzer (TGA) (TA Instruments SDT-Q600) under a N₂ atmosphere with 20 °C min⁻¹ heating rate from 20 to 500 °C. Water contact angles for the prepared Ag@MXene membranes were measured using Rame-hart contact angle goniometers equipped with a video camera and an image analysis system.

2.5 Membrane flux, rejection and pore radius measurements

Membrane flux and rejection performance were measured using a dead-end filtration set-up (HP4750 Stirred cell, STERLITECH) with an effective filtration area of about 9.60 cm². To determine the pure water flux, deionized (DI) water was filtered through the composite membranes with varying pressure at 25 °C. The DI water flux (J₀) was calculated using the following equation:

\[ J_0 = V/AtP \]  

where \( V \) is the permeate volume, \( A \) is the effective area of the membrane, \( t \) is the operation time, and \( P \) is the applied pressure.

The feed aqueous stream containing 2000 mg L⁻¹ salts (NaCl, MgCl₂ and AlCl₃), and 50 and 100 mg L⁻¹ of rhodamine B (RhB), methyl green (MG), and bovine serum albumin (BSA) were used to evaluate the rejection performance of the prepared membranes. The rejection was calculated using the following equation:

\[ \text{Rejection} \% = \frac{C_F - C_P}{C_F} \times 100 \]  

where \( C_F \) and \( C_P \) are the feed and permeate concentrations of NaCl, MgCl₂ and AlCl₃, and RhB, MG and BSA.

The Ferry equation (eqn (3)) was used to calculate the effective pore size of the prepared membranes:

\[ R = 100 \left[ 1 - \left( 1 - \frac{r}{a} \right)^2 \right] \]  

where \( R \) is the solute rejection (%), \( r \) is the solute diameter, and \( a \) is the effective pore size (diameter) of the prepared membranes.

UV-vis spectroscopy was used to calculate the concentration of RhB, MG and BSA solutes in the feed and permeate. The experimental rejection rate and water flux values were obtained from the average of the three measurements.

2.6 Fouling test and flux recovery

The organic fouling behavior of the Ag@MXene composite membranes was assessed by the adsorption (fouling) characteristics of BSA protein and MG dye. Initially, 2000 mL of DI water was filtered through the composite membranes with constant pressure at 25 °C, using a dead-end filtration device. After stabilizing the water flux, an aqueous 2000 mL feed solution of organic foulants (BSA and MG) was prepared with different concentrations (50 and 300) mg L⁻¹, which fall within the typical fouling concentration range, and filtered with the same composite membranes. All membranes were removed after being soaked in DI water, and kept in a shaker for 24 h. The tests were conducted in triplicate. After extensive washing, additional DI water was filtered through the device. The fouling behavior of the composite membranes was observed in the form of flux recovery and calculated using the following equation:

\[ \text{Flux recovery} \% = \frac{J_s}{J_0} \times 100 \]  

where \( J_s \) is the DI water flux after the fouling with solutes. In addition, the flux decline during organic molecule filtration for the prepared composite nanoporous membranes was evaluated using the following equation:

\[ \text{Flux decline} \% = \frac{J_s - J_a}{J_s} \times 100 \]  

where \( J_a \) is the water flux of the foulant solution (BSA or MG dissolved in DI water).

2.7 Cell preparation and antibacterial activity evaluation

The model waterborne bacteria E. coli was cultured in Luria-Bertani (LB) medium at 36 °C. 1 mL of overnight cell suspension was further sub-cultured and harvested after 4 h at the exponential growth phase. E. coli cell culture was centrifuged at 4500 rpm for 5 min and the obtained pellets were washed three times with phosphate buffered saline (PBS). The cell pellets collected by centrifugation were re-suspended in PBS and diluted to an approximate cell concentration of \( 2 \times 10^9 \) CFU mL⁻¹.

The antibacterial activity of control PVDF support, MXene, and Ag@MXene membranes was tested by filtering the E. coli bacterial suspension through membranes. The filtration assembly and all utilized glassware were sterilized in an autoclave prior to each experiment. The membrane samples, including the control, were sterilized in a 75% v/v ethanol solution, air-dried and UV irradiated for 30 min prior to the filtration assays. A 50 µL bacterial suspension (\( 2 \times 10^3 \) CFU mL⁻¹) was further diluted in PBS to 10 mL solution and suction-filtered through the control PVDF, MXene and Ag@MXene modified membranes. Bacteria treated membranes were placed on LB agar plates and incubated overnight at 36 °C. Finally, the growth of the colonies on the membrane surface was observed. After incubation for 24 h at 36 °C, the number of colonies grown on the membrane surface was counted to quantify the bactericidal efficiency of Ag@MXene membranes. The viability of bacterial cells on membranes was determined by the colony counting method against E. coli and reported as percent (%) inhibition relative to the control PVDF support. Each experiment was repeated three times and average values were reported.

The bacterial cell morphology on the membrane surfaces was analyzed by SEM. The membrane samples for SEM analysis were fixed in glutaraldehyde (2.5%) dehydrated in a series of ethanol solutions (20, 40, 60, 80 and 100%) as described earlier.
3 Results and discussion

3.1 Optical and surface properties of the MXene (Ti₃C₂Tₓ), and Ag@MXene composites

The UV-visible spectra of the delaminated MXene, AgNO₃ precursor, and Ag@MXene composites are depicted in Fig. 1.

Both the MXene and Ag@MXene composites showed a uniform dispersion in water. It was observed that after self-reduction of AgNO₃ to AgNPs, the color of the Ag@MXene composite solution turned from dark grey to dark golden color (inset of Fig. 1). The UV spectrum of the delaminated MXene displayed characteristic high absorption bands at ~260 nm, which may correspond to the band-gap energy of the delaminated MXene. Additionally, Ag@MXene composites exhibited a surface plasmon resonance absorption band in the visible region at ~443 nm, corresponding to the successful in situ formation of AgNPs within the delaminated MXene nanosheets (Fig. 1). The intensity of the AgNP peak also increased with respect to the Ag loading.

The Ag self-reduction and surface chemical bonding with different functional groups (including ~O, ~OH and ~F) of the MXene and Ag@MXene composites were investigated by XPS. The survey spectra of the MXene and Ag@MXene composites indicate the presence of Ti, C, O and F components in Ag@MXene composites (Fig. 2a). The presence of C 1s and O 1s peaks in the MXene and Ag@MXene composites confirmed the surface functionalization with OH groups.

The 3d Ag core level spectra of the Ag@MXene composites showed doublet peaks of the Ag 3d₃/₂ and 3d₅/₂ located at ~366.9 eV and ~372.9 eV, respectively, confirming the self-reduction of silver (Fig. 2b). Additionally, the difference in the binding energy between the two doublets was observed to be about 6 eV, indicating the presence of AgNPs in the Ag@MXene composites. The intensity of the 3d Ag peak also increased as a function of the integrated AgNPs. It was also observed that contributions from C–C (or −CH₂ and −CH₃) were dominant while the contributions from Ti–C and C–O were reduced with respect to the Ag concentration in the composite matrix. The delaminated MXene featured two distinct deconvoluted peaks for the low-valence Ti species, located at ~456.2 eV for the Ti(iii) peak and ~455.21 eV for the Ti(iv) peak, in addition to a minor Ti(iv) 2p peak located at ~457.76 eV (Fig. 2c). However, the intensities of the Ti(iv) 2pₓ/₂ and Ti(iv) 2pᵧ/₂ peaks increased with respect to the AgNP concentration. These peaks indicate the increased formation of TiO₂, thereby providing additional confirmation of the formation of AgNPs via a redox reaction on the surface of the MXene (Fig. 2d and S1†).

The TEM image of the delaminated MXene revealed single or a few layers of flat sheets that were exfoliated with a wrinkled structure (Fig. 3a). Fig. 3b displays the low magnification TEM image of the 21% Ag@MXene composite where different shapes and various size distributions of AgNPs were clearly observed on the surface of the MXene nanosheet. Typically, AgNPs exhibit both large and small spherical, pseudo-spherical and rectangular shapes. The diameter distribution varies from 20 to 70 nm with an average size of 44 nm (Fig. 3c). High-resolution TEM images of the MXene and 21% Ag@MXene composite showed a constant interplanar distance of about 12 Å, consequently confirming the fact that the AgNPs are mainly located on the surfaces of MXene layers (Fig. 3a (inset) and d (inset)).

3.2 Ag@MXene composite membranes

Fig. 4 shows the XRD patterns of the MXene, and Ag@MXene composite membranes at different Ag loadings. The membranes were prepared by vacuum-assisted filtration from diluted Ag@MXene composite solutions. Acid etching of the aluminum layer from MAX (Ti₃AlC₂) was confirmed by the total extinction of the most intense peak at 2θ = ~39° in the delaminated MXene. Furthermore, the broadening and shift of the (002) peak to the lower angle (2θ = ~6.40°) also confirmed the successful conversion of Ti₃AlC₂ into the delaminated MXene.29 XRD spectra of the Ag@MXene composite membranes exhibited three major diffraction peaks, namely (2θ = ~38.1) (111), (200), and (220), corresponding to the silver single crystal, and confirmed the formation of AgNPs.27,28 It was found that the intensity of the Ag peaks increased with respect to Ag loading concentration, while the intensity of the (002) peak, characteristic of the MXene phase decreased due to the presence of AgNPs (Fig. 4 and S2†). Moreover, the (002) peak position of the MXene membrane remains unchanged in the composite membranes, indicating the formation of AgNPs on the surface of the MXene.
Membranes prepared with higher than 21 wt% of AgNPs were weak and brittle because of the aggregation of AgNPs and the oxidation of the MXene nanosheets. Thus, the 21% Ag@MXene composite membrane was used for further experiments.

Fig. 5a–e show the top-view and cross-sectional SEM micrographs, representing the morphology of the PVDF substrate, MXene and 21% Ag@MXene composite membranes. The surface morphology of the PVDF substrate exhibited a highly rough surface with large pores (pore size ~0.22 μm). On the other hand, the SEM of the 21% Ag@MXene composite membrane showed a rather smooth and tightly packed surface with a defect free structure (Fig. 5a and b). Cross-sectional SEM images of the MXene and the 21% Ag@MXene composite membranes revealed their lamellar structure (Fig. 5c and d). The optical micrograph of a bent 21% Ag@MXene composite membrane shows its mechanical flexibility and stable formation of the membrane film on the PVDF substrate (Fig. 5e). The presence of AgNPs as well as OH, and F functional groups on the MXene surface was further confirmed by the energy-dispersive spectroscopy (EDS) spectrum as observed in Fig. S3.†

The thermal stability of Ag@MXene composite membranes was identified by a three-step weight loss recorded by TGA (Fig. S4†). Below 150 °C, weight loss was observed, due to the evaporation of absorbed and bound water present in the membrane matrix. In the second step (150–250 °C), the weight loss was observed from the decomposition of oxygen-containing functional groups (–O–, –OH, CO2, etc.). Beyond 250 °C, weight loss was most likely due to the thermal desorption of surface moieties from MXene nanosheets. Finally, no more than 10 wt% loss was observed for all the composite membranes, suggesting the thermal stability of the Ag@MXene composite membrane up to 250 °C. Furthermore, TGA was used to evaluate the water retention capability. Two types of water are present in the membrane matrix, namely bound water and bulk water. The bound water content was measured by the evaluation of weight loss (%) during sample heating from 100 to 150 °C in TGA (Fig. S4b†). The bound water content of the Ag@MXene composite membranes increased with increasing Ag content. A bound water content of ~1.162 wt% was found in the 21% Ag@MXene membrane, while the pristine MXene membrane exhibited ~0.906 wt%. The high content of bound water in the 21% Ag@MXene membrane improved its water-retaining capacity and water permeability.
3.3 Membrane flux, rejection and organic fouling

To evaluate the pure water flux of the as-prepared membranes, DI water was filtered at differential pressures from 0.5 to 3 bar in increments of 0.5 bar (Fig. 6). The flux demonstrates a linear dependence on pressure ranging from 0.5 to 3 bar for all membranes, suggesting the high structural stability of pore channels.

More importantly, the pure water flux for the 21% Ag@MXene composite membrane was ~3.55 times higher than that of the pristine MXene membrane at 1 bar pressure. The incorporation of AgNPs into the MXene considerably improves the pure water flux properties, attributed to the short transport pathway, formation of additional nanopores in the composite membranes through the AgNPs attached on the surface of MXene nanosheets and their hydrophilic nature. Compared to membranes with similar rejections, the Ag@MXene hybrid has an improved water flux (Table 1). The pore diameters of MXene and 21% Ag@MXene composite membranes were found to be 2 nm and 2.1 nm, respectively, which are in the typical range of nanofiltration membranes.

One of the most challenging obstacles in membrane separation technology is the organic fouling of membranes due to the adsorption of organic molecules onto their surface. The resistance of the prepared membranes towards organic fouling was evaluated by BSA protein, RhB, and MG dye adsorption experiments at 25 °C. Fig. 7a and b show the water flux and...
rejection results of RhB, MG and BSA aqueous solutions for the MXene and 21% Ag@MXene composite membranes. The UV-vis absorption spectra for the rejection results are summarized in Fig. S5a and b.† The 21% Ag@MXene membrane with a thickness of ~470 nm shows a water flux of 387, 354, and 345 L m⁻² h⁻¹ bar⁻¹ for RhB, MG, and BSA aqueous solutions, respectively. Flux was shown to increase as a function of the AgNP concentration in the Ag@MXene composite membranes, during the filtration of organic foulants. The 21% Ag@MXene composite membrane exhibited more than 4 times of the water flux, during RhB, MG, and BSA rejection, compared to the pristine MXene membrane flux. The improved water flux of the 21% Ag@MXene can be attributed to the formation of additional nanochannels or interlayer voids created by the presence of AgNPs which can facilitate water circulation through a shorter transport pathway.‡ However, rejection was found to decrease with increasing amounts of AgNPs.

The 21% Ag@MXene membrane demonstrated 92.32% and 79.93% rejection for MG, and RhB, respectively, which are slightly less than those of the pristine MXene membrane (Fig. 7b). In the meantime, the 21% Ag@MXene membrane exhibited an insignificant flux decline with increasing molecular weight of rejected molecules, as compared with the pristine MXene membrane (Fig. S6†). The total concentration of the molecules from both the permeate and retentate sides was close to the original feed concentration, implying a typical molecular sieving effect based on size exclusion. Both MXene and 21% Ag@MXene composite membranes showed ~100% rejection for BSA, most likely due to their high molecular weight and
Additionally, the 21% Ag@MXene membrane was able to demonstrate the moderate rejection of salts with sizes less than 1 nm at 25.8%, 41.3% and 49.5% for NaCl, MgCl₂, and AlCl₃, respectively. Evidently, 21% Ag@MXene membranes showed decreased rejection performance due to their more open structure. The membrane thickness also showed a prominent effect on the separation performance of 21% Ag@MXene composite membranes. Rejection of RhB dye increased to 81.61% and 85 ± 2% for 969 and 1420 nm thick membranes, respectively. This decrease can result from the obstruction of bigger pores with increased stacking of Ag@MXene nanosheets. Based on these results, the membrane thickness of 470 nm was optimum, yielding ultrahigh water flux while retaining good rejection (Fig. S7†).

The extent of fouling due to organic molecule adsorption on the membrane is a key parameter to estimate the flux recovery of the membrane. Fig. 8 shows the flux recovery percentage of the prepared composite membranes after exposure to MG and BSA at 2000 mL of 50 mg L⁻¹ MG and BSA. The 21% Ag@MXene composite membrane exhibited about ~97% and ~91% flux recovery as compared to ~86% and ~81% for the pristine MXene membrane, respectively. Interestingly, at a higher concentration of feed solution (2000 mL of 300 mg L⁻¹ MG and BSA), the 21% Ag@MXene composite membrane exhibited ~98% and ~92% flux recovery as compared to ~87% and ~83% for the pristine MXene membrane, respectively (Fig. S8†). This slight increase in flux recovery may be ascribed to the faster formation of a thick fouling film at higher solute concentration, which could be easily washed during the flux recovery.

Furthermore, the high percentage flux recovery, in the case of 21% Ag@MXene, could be attributed to the incorporation of AgNPs, which increased the resistance of the membrane surface towards organic fouling. The latter mainly occurs because of the hydrophobic–hydrophilic interaction between the membrane surface and organic molecules. Therefore, to reduce organic

**Table 1** Comparison of the separation performance of the prepared Ag@MXene composite membranes with reported nanoporous membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Molecule</th>
<th>Water permeance (L m⁻² h⁻¹ bar⁻¹)</th>
<th>Rejection (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-PVDF</td>
<td>RhB</td>
<td>61.90</td>
<td>67.80</td>
<td>40</td>
</tr>
<tr>
<td>NF hollow fiber membrane</td>
<td>RhB</td>
<td>7.425</td>
<td>97.5</td>
<td>41</td>
</tr>
<tr>
<td>[PEI/SCF]ₓ/PAN</td>
<td>RhB</td>
<td>2.43</td>
<td>93.7</td>
<td>42</td>
</tr>
<tr>
<td>GO-IPDI</td>
<td>RhB</td>
<td>100 ± 10</td>
<td>96.2</td>
<td>43</td>
</tr>
<tr>
<td>ZCA</td>
<td>BSA</td>
<td>137.96</td>
<td>98.7</td>
<td>44</td>
</tr>
<tr>
<td>PVDF/nylon-6,6/chitosan</td>
<td>BSA</td>
<td>393</td>
<td>93</td>
<td>45</td>
</tr>
<tr>
<td>UiO-66-PSBMA/PSf</td>
<td>BSA</td>
<td>301</td>
<td>98.5</td>
<td>46</td>
</tr>
<tr>
<td>M-Fe₃O₄/GO</td>
<td>BSA</td>
<td>595.4</td>
<td>92</td>
<td>47</td>
</tr>
<tr>
<td>PVDF-GO</td>
<td>BSA</td>
<td>401.4</td>
<td>55</td>
<td>48</td>
</tr>
<tr>
<td>PVDF-GO/OMWNTs</td>
<td>BSA</td>
<td>203</td>
<td>81.6</td>
<td>49</td>
</tr>
<tr>
<td>MXene composite membrane</td>
<td>RhB</td>
<td>806 ± 38</td>
<td>85 ± 2</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>BSA</td>
<td>790 ± 35</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>MXene (TiₓC₂Tx)</td>
<td>RhB</td>
<td>90.28</td>
<td>81.04</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>MG</td>
<td>84.53</td>
<td>94.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BSA</td>
<td>66.46</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>21% Ag@MXene</td>
<td>RhB</td>
<td>387.05</td>
<td>79.93</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>MG</td>
<td>354.29</td>
<td>92.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BSA</td>
<td>345.81</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 7** Comparison of the performance of the MXene (TiₓC₂Tx) and 21% Ag@MXene membranes for the separation of RhB, MG and BSA molecules at 25 °C: (a) flux, and (b) rejection.
Fouling of the membrane, the surface should be hydrophilic. The AgNPs not only improved the water flux, but also enhanced the membrane surface hydrophilicity through the formation of hydrated silver and thereby enhanced the antifouling properties of the membrane.\textsuperscript{34,35}

Water permeance and rejection of organic molecules of similar nanostructured membranes are compared with those of our composite Ag@MXene membranes under similar experimental conditions as summarized in Table 1.\textsuperscript{20,40–49} Our 21% Ag@MXene composite membrane shows excellent separation efficiency, revealing the high suitability of the 21% Ag@MXene membrane for water treatment applications.

### 3.4 Antibacterial activity of the Ag@MXene nanoporous membrane

As mentioned earlier, biofouling is a serious challenge in membrane based wastewater treatment processes. Generally, filtration membranes are fouled with microbes that deteriorate the efficiency. A comparative analysis was performed to assess the bactericidal properties of 21% Ag@MXene and pristine MXene membranes. \textit{E. coli} (Gram-negative bacteria) was used as common model bacteria to evaluate the anti-biofouling activity of the as-prepared Ag@MXene composite membranes. Fig. 9a shows the photographs of \textit{E. coli} cells grown on PVDF (control), MXene and 21% Ag@MXene composite membranes incubated at 35 °C for 24 h. As depicted in Fig. 9, the 21% Ag@MXene composite membrane exhibited more than 99% \textit{E. coli} growth inhibition, while the MXene membrane exhibited ~60% cell growth inhibition relative to the PVDF membrane.

The growth inhibition of the 21% Ag@MXene composite membrane toward the tested \textit{E. coli} strain was more efficient compared with the growth inhibition values of the pristine MXene and control PVDF membranes. Moreover, increasing the concentration of AgNPs in the MXene had a positive effect on bacterial growth inhibition. This could be attributed to the formation of AgNPs and TiO\textsubscript{2} compounds on the composite 21% Ag@MXene surface. TiO\textsubscript{2} formation on the surface of the MXene was found to enhance the antibacterial properties, especially under UV radiation.\textsuperscript{31} As a matter of fact, AgNPs have been widely used as an anti-microbial agent owing to their strong capability to inhibit the growth of microbes.\textsuperscript{34,35,50} TiO\textsubscript{2} was formed on the surface of 21% Ag@MXene composites, most likely during the self-reduction of silver nitrate to AgNPs, thereby inhibiting the bacterial growth rate. No previous studies have been performed to investigate the antibacterial activity of the membranes based on the AgNP modified MXene.

The mechanism of bacterial growth inhibition can be understood from the nano-bio interaction at the interface.\textsuperscript{31} SEM images show the morphology of the \textit{E. coli} cells grown on control PVDF and 21% Ag@MXene membranes (Fig. 10). The \textit{E. coli} bacterial cells grown on the PVDF membrane were viable with no observed membrane damage or cell death (Fig. 10a). On the other hand, the majority of \textit{E. coli} cells on the 21% Ag@MXene membrane became ruptured, flattened, and lose their cellular integrity (Fig. 10b). The higher magnification (lower panel of Fig. 10) showed a single bacterium on the PVDF control protected by an intact cytoplasmic membrane, while the single bacterium in contact with 21% Ag@MXene was clearly suffering from outer membrane damage, leading to cell growth inhibition. This bactericidal effect due to the induced stress on the cell membrane was observed in other nanomaterials such as carbon nanotubes (CNTs), graphene and other MXenes.\textsuperscript{31,52}

### 3.5 Transport mechanism of the Ag@MXene membrane

Generally, 2D nanosheets such as graphene and MXene based membranes are often prepared by filtration-based deposition
on highly porous substrates. This method produces compact films with reduced porosity, thereby reducing the water flux. In our Ag@MXene membrane, AgNPs created a slit interspacing of 1–4 nm between the MXene nanosheets providing additional nanopores in the Ag@MXene membranes and thereby enhancing the water flux as illustrated in Fig. 11. Similarly, other reports showed significant improvement in the water flux of 2D nanostructures through nanochannels with a little impact on the rejection rate.\textsuperscript{53} The water contact angle decreased from 39.5° to 35.0° with increasing AgNP content from 0 to 21% in the MXene matrix and confirmed that the membrane surface hydrophilicity has increased due to the presence of AgNPs (Fig. S9†).\textsuperscript{54} Furthermore, the nanopores effectively reject the large molecules (diameter > 1 nm) such as RhB, MG, and BSA and bacteria. In addition, silver acts as the anti-microbial agent in the membrane matrix, thus increasing the resistance of the composite membranes towards biofouling.

4 Conclusions

In summary, we report on the fabrication of an anti-fouling 2D nanostructured Ag@MXene composite-based membrane with excellent separation performance for water purification applications. The Ag@MXene composite membranes were prepared by vacuum-assisted filtration after direct reduction of AgNO\textsubscript{3} on the surface of the MXene, where the MXene acted as the membrane matrix and reducing agent. The TEM and SEM images showed that the AgNPs were homogeneously dispersed in the membrane matrix with low exclusion and agglomeration. The 470 nm thick 21% Ag@MXene membrane with 2.1 nm average pore size demonstrates excellent water flux (\( \approx 420 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1} \)) and favorable rejection to organic foulants such as BSA and MG. The membrane also showed rejection capability to multi-valent ions up to 50%. These are important characteristics for nanofiltration membranes.
Furthermore, the 21% Ag@MXene composite membrane showed improved bactericidal properties as demonstrated by over 99% E. coli growth inhibition, compared with ~60% for the pristine MXene membrane. The outstanding properties of the Ag@MXene composite can support the development of efficient nanofiltration membranes for water purification and biomedical applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge the financial support of the Qatar National Research Fund (A member of Qatar Foundation) through the NPRP grants # 9-254-2-120. The statements made herein are solely the responsibility of the authors. The authors are thankful to Mohamed Helal, Sergey Suslov, and R. Essehli at the Core lab of QEERI/HKBU, Doha, Qatar for SEM, TEM and XRD analysis, and S. Buczek, Drexel University, for valuable input.

References

33 S. S. Liu, F. Fang, J. J. Wu and K. S. Zhang, Desalination, 2015, 375, 121–128.