Silane-Grafted MXene (Ti$_3$C$_2$T$_X$) Membranes for Enhanced Water Purification Performance

Tayyaba Yousaf, Aneeqa Areeb, Maida Murtaza, Akhtar Munir, Yaqoob Khan, and Amir Waseem*

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ABSTRACT: The current communication describes the modifications of MXene (Ti$_3$C$_2$T$_x$) with silane grafting reaction for membrane preparation for enhanced water purification. The MXene was successfully grafted with *n*-octadecyltrichlorosilane (MODCS), *n*-octyltrichlorosilane (MNOCS), and triphenylchlorosilane (MTPCS) in order to make a hydrophobic MXene that could be able to bind with the organic matrix/polymers. The modified MXenes were transformed into thin membranes by forming an MXene/polyvinyl alcohol (PVA) composite over a filter paper support, that is, MCE (mixed cellulose ester filter paper). MXene membranes were also formed without the MCE support by using PVA and glutaraldehyde (PVA/GA) where GA was used as a cross-linker to stabilize PVA and make it water-resistant. The conditions of membrane formation were optimized to investigate optimum compatible conditions with the modified materials. The resulting membranes were tested for the removal of various organic pollutants that included mesitylene (or trimethylbenzene); polyaromatic hydrocarbons (chrysene, as a model); biphenyl; bisphenol A; benzene, toluene, ethylbenzene, and styrene; methylene blue; and Sudan II dyes. The MTPCS PVA/GA cross-linked membrane showed the best results for a pollutant removal efficiency up to 98%. Overall, all six types of membranes showed the removal efficiency in the range of 52−98%. It was observed that the membrane exhibits reusability up to five cycles.

INTRODUCTION

The adequate and potable water in the modern world of rapid urbanization is a requisite.[1] A global environmental challenge is posed by the pollutants like pharmaceuticals, heavy metals, aromatic compounds, dyes, and salts that are present in water and wastewater streams; a majority of them are toxic and threatening for living organisms.[2] Organic micropollutants (OMPs) are typically present (ng L^{-1} to μg L^{-1} orders) in relatively low concentrations. They are present in reservoirs of fresh water, natural bodies of water, effluents for water treatment, and soil sediments and have shown the potential for significant health threats to humans and marine life.[3] Membrane filtration is very versatile and has become increasingly popular for water treatment.[4] Especially, for the removal of micropollutants that pose a challenge in the traditional water treatment techniques and remain unaffected, membrane treatment offers a satisfactory alternative as in the case of membrane filtration, there is a mechanism of surface retention of contaminants.[5,6] Membrane filtration is considered a robust treatment technology because of the large range of selectivity or preservation of pollutants in water. There are few mechanisms for the removal of OMPs by membrane filtration, for example, (i) size exclusion[7] adsorption and interaction of hydrophobic OMP to hydrophobic membrane surfaces, (ii) electrostatic repulsion between the surface of the charged membrane and charged molecules of OMP,[8] and (iii) hydrophobic surface interactions and hydrogen bonding between OMPs and the membrane. Generally, the size

exclusion mechanism is followed in membrane filtration.[5] Size exclusion membrane filtration is a widely used simple technique. In size exclusion, pollutants are sieved out based on their sizes and OMPs with a larger size than the membrane pore are retained. The mechanism of size exclusion is well understood, especially in the application for the removal of particulate matters and suspended solids, which are large in size. However, the size of OMPs should not be exclusively based on the molecular weight; the length of the molecule or shape (width) should also be considered.[5]

In 2011, Drexel University scientists discovered a new family of two-dimensional (2D) materials, reporting the 2D layered materials resulting from the exfoliation of three-dimensional (3D) transition-metal carbides through the selective etching of "A" elements from the MAX phases. The members of the MXene family are transition-metal carbides, nitrides, and carbonitrides.[9] The suffix "ene" in MXene indicates the similarity to graphene.[10] The MAX phases are precursors of the MXenes. These are 3D carbides or nitrides of ternary metals, represented as M$_{n+1}$AX$_n$ (MAX), where M is a

transition metal (Mo, Cr, Zr, Ti, etc.); A represents elements in the periodic table from group 13 to 16 such as Al, Si, Ge, Ga, and so forth; X may be either nitrogen or carbon, or their combination; and n varies between 1 and 3.[11] MXenes have distinct properties from their MAX phase precursors and are generally described as $M_{n+1}X_nT_x$, while T_x represents the terminated functional groups ($-O$, $-F$, $-OH$) resulting from the acid interaction in the etching step. The first synthesized MXene was $Ti_3C_2T_x$,[12] and up to now, MXenes (especially $Ti_3C_2T_x$) have drawn much attention. Owing to unique characteristics, such as high electronic conductivity and hydrophilicity and adsorptive, reductive, and antibacterial characteristics, MXenes are an excellent fit for environmental applications.[13] By reason of element abundance and nontoxic decomposition, $Ti_3C_2T_x$ has found the most applications in water treatment.[14]

MXene membranes can alter interlayer distances and respond by intercalating ions (molecular/ion sieving mechanism). They are also used for desalination because of hydrophilic behavior.[15] The three most common fabrication techniques include[16] (i) preparation of lamellar-structure membranes by employing MXenes as skeleton materials, (ii) mixed-matrix membranes with MXenes prepared by using additives or other nanomaterials such as TiO_2 and graphene oxide and so forth, and (iii) coating materials on membrane supports including polyvinylidene fluoride, anodic aluminum oxide, and so forth. The increased efficiency of MXene composite membranes can be attributed to (i) more water transport pathways provided by MXene nanosheets/nanofragments/combination with other materials than pristine membranes, (ii) increased interlayer spacing and production of abundant nanochannels due to separation of pores resulting from intercalated nanoparticles, and (iii) functionalization of MXene-based membranes with different functional groups (e.g., $-COOH$, $-NH_2$, C_6H_6), which enhances transport of solvents like toluene, n-heptane, isopropanol, and so forth.[16] MXene polymeric and nanoparticle composites in the membrane form have also been used.[2]

Hydrophobic MXene membranes for solar steam generation have been prepared for seawater desalination, wastewater remediation, and sunlight harvesting. The author reported the use of Ti_3C_2 nanosheets layered with trimethoxy-($1H,1H,2H,2H$-perfluorodecyl)silane for solar desalination.[17] Similarly, $1H,1H,2H,2H$-perfluorooctyltriethoxysilane was used for the surface modification of MXenes[18] to develop a superhydrophobic matrix for solar desalination systems. In another study, MXene membranes (Ti_3C_2) were fabricated using an aqueous suspension of an MXene which was filtrated using a commercial PVDF membrane, causing a deposition of Ti_3C_2 thin layers stacked on the upper surface of the PVDF substrate.[19] Grafted sulfonated polyelectrolyte brushes on the surface of the MXene ($Ti_3C_2T_x$) earlier functionalized with [3-(methacryloxy)propyl]trimethoxysilane] using a surface-initiated precipitation polymerization technique has been reported[20] to fabricate proton-conducting membranes. 3-Aminopropyltriethoxysilane was used in another study to functionalize the surface of $Ti_3C_2T_x$ in a polyacrylonitrile or polydimethylsiloxane matrix to develop thin-film membranes that showed selectivity for alcohol-based solvents and strong enhancement in flux.[21] Functionalizing the MXene surface with silane coupling agents with various organofunctional groups will enable a wide variety of applications.[22]

In the current study, organo-MXene composite filtration membranes were synthesized using silane grafting to produce a hydrophobic MXene that could be able to bind with the organic matrix/polymers. The modified MXenes were transformed into thin membranes by forming a MXene/polyvinyl alcohol (PVA) composite over a filter paper support, that is, MCE (mixed cellulose ester filter paper). MXene membranes were also formed without the MCE support by using PVA/glutaraldehyde (GA),[23] where GA was used as a cross-linker to stabilize PVA and make it water-resistant. The conditions of membrane formation were optimized to investigate optimum compatible conditions with the modified materials. The resulting membranes were tested for the removal of various organic pollutants that included mesitylene (or trimethylbenzene); polyaromatic hydrocarbons (PAHs) (chrysene, as a model); biphenyl; bisphenol A; benzene, toluene, ethylbenzene, and xylene (BTEX); methylene blue; and Sudan II dye.

■ EXPERIMENTAL SECTION

Materials. The MAX phase, that is, Ti_3AlC_2 99% (Nanoshel, UK), hydrofluoric acid 48%, sodium hydroxide, PVA M wt 72,000, Sudan II dye, methylene blue, BTEX, chrysene, mesitylene, biphenyl and bisphenol A (Sigma-Aldrich), n-octadecyltrichlorosilane (95%), n-octyltrichlorosilane (95%), and triphenylchlorosilane (95%) were provided by Alfa Aesar Co., Germany. GA and MCE membrane filters having a pore size of 0.22 μm were provided by Merck, Germany.

Silane Grafting Procedure. The synthesis of the MXene was carried out using the reported procedure[9] as follows: 1.0 g of the MAX phase was taken in a Teflon beaker; 10 mL of 48% hydrofluoric acid was added slowly, and it was kept under stirring for 24 h at 60 °C to ensure complete etching of the aluminum layer. The resulting suspension was washed with DI water, and centrifugation was done for 10 min at 5000 rpm to obtain the settled material. The process of washing was repeated three to four times until the pH reached around 7. The MXene was finally obtained after oven drying overnight at 60 °C. The MXene was dispersed in water and then ultrasonicated for 1 h to obtain a few/single-layer flakes as the result of delamination. The resulting MXene further went through alkaline treatment with 2 g of NaOH for 2 h with constant stirring. The obtained $Ti_3C_2(OH)_2$ was separated through centrifugation and dried in oven overnight at 60 °C. Silane grafting resulted when 1:1 MXene, that is, $Ti_3C_2(OH)_2$, and silanes (1 g) were placed under reflux for 48 h in 30 mL of toluene and HCl gas (as a byproduct) was allowed to escape time to time. After washing with toluene, methanol, and water several times, followed by filtration and oven drying at 60 °C for 4 h, the grafted hydrophobic materials were obtained and were labeled as MODCS, MNOCS, and MTPCS, indicating MXene grafting with n-octadecyltrichlorosilane, n-octyltrichlorosilane, and triphenylchlorosilane, respectively.

Fabrication of MCE Filter Paper-Supported Silane-Grafted MXene Membranes. PVA was used as a binder to prepare MXene polymer membranes.[24] In order to prepare 1% solution of PVA, 1 g of PVA was added in 100 mL of water and left for stirring for 3 h at 90 °C. Homogeneous dispersions were obtained after 2 h stirring by adding 0.1 g each of the MXene, MODCS, MNOCS, and MTPCS separately in 100 mL of 1% PVA solution. The dispersions were then passed through an MCE membrane filter (0.22 μm as a support)

through vacuum filtration assembly. The uniform layers of unmodified MXene and modified materials (i.e., silane-grafted MXenes) were deposited over the MCE filter paper.

Fabrication of silane-grafted MXene membranes with PVA/GA cross-linked (without the filter paper support).

Using PVA as a binder and glutaraldehyde (GA) as a cross-linker, silane-grafted MXene membranes were fabricated. Casting solutions were prepared by adding 0.5 mL of GA in 4 mL of 1% PVA and then dispersing 0.1 g each of the MXene, MODCS, MNOCS, and MTPCS separately in the solutions. They were then poured into Teflon Petri dishes (70 mm diameter) and placed for 3 h in an oven at 40 °C.

Procedure for Pollutant Removal by Silane-Grafted Membranes. The prepared membranes were tested for pollutant removal, which included mesitylene, PAHs (chrysene, as a model), biphenyl, bisphenol A, BTEX, methylene blue dye, and Sudan dye. Methylene blue was the only water-miscible analyte, whereas the others had low solubility in water. Therefore, 10% methanolic solution in water with the respective concentrations of pollutants was prepared (except for biphenyl, which was prepared in 50% methanolic solution in water). Thereafter, 50 ppm (methanolic water solutions) each of Sudan II, methylene blue, PAHs, bisphenol A, biphenyl, mesitylene, and BTEX was used for the removal by prepared membranes. The membranes (both MCE and PVA cross-linked with GA) were fitted in vacuum-filtration assembly and individually tested for the removal of every pollutant by using UV−visible (UV−vis) spectrophotometry (Shimadzu double beam 1800).

■ RESULTS AND DISCUSSION

Characterization. *FT-IR Analysis of the Silane-Grafted MXene.* FT-IR spectral analysis was performed in the range of 4000−400 cm^{-1} for the unmodified MXene and the modified silane grafted MXene, that is, to validate the functionality. No functional group peaks were observed in case of MXenes, whereas new peaks appeared in the range of 2950−2800 cm^{-1} and 1470−1350 cm^{-1}, corresponding to C−H stretching and bending, respectively, showing the successful silane grafting on the MXene (Figure 1). The formation of the Si−O−Ti bond in the modified material was also indicated by the peaks observed in the range of 950−700 cm^{-1}.[25] All these peaks confirmed the modification of the MXene and successful silane grafting.

The major peaks corresponding to wide OH stretching, CH$_2$ stretching, C═O carbonyl stretching, and C−O stretching were observed at 3280, 2920, 1690, and 1050 cm^{-1}, respectively, suggesting the presence of PVA.[26] The MXene and silane-grafted MXene were transformed into a membrane using PVA as a binder; also, the previously described peaks for modified materials can be seen in Figure 2.

The characteristic peaks appearing at 3350, 2860, 1723 cm^{-1} and 1087 cm^{-1} were assigned to broad −OH stretching, stretching (symmetric and asymmetric) vibrations of the −CH$_2$ group, C═O stretching, and −C−O−C− linkage,[26] respectively, as illustrated in Figure 3.

Powder X-ray Diffraction Analysis. The obtained XRD was found in agreement with the reported literature.[27] Figure 4a represents MAX phase XRD. In the MXene, good Al etching and exfoliation of the MAX phase were indicated by the vanishing and shifting of the main diffraction peak at $2\theta \approx 9.6°$, corresponding to the (002) basal plane of the MAX phase (Ti$_3$AlC$_2$). In the MXene, the broad peak indicated increased interlayer spacing (Figure 4b). In the MAX phase (Ti$_3$AlC$_2$),
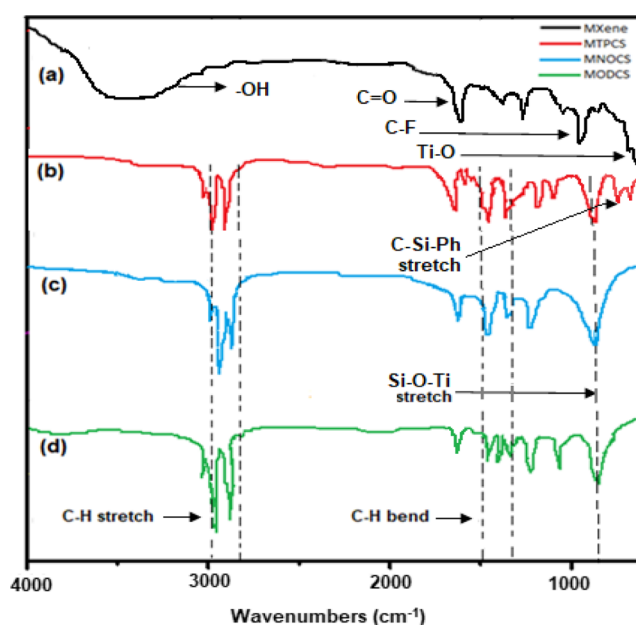

Figure 1. FT-IR spectra of (a) unmodified MXene, (b) MTPCS modified, (c) MNOCS modified, and (d) MODCS modified. FT-IR analysis of MCE filter paper-supported MXene membranes with the PVA binder.
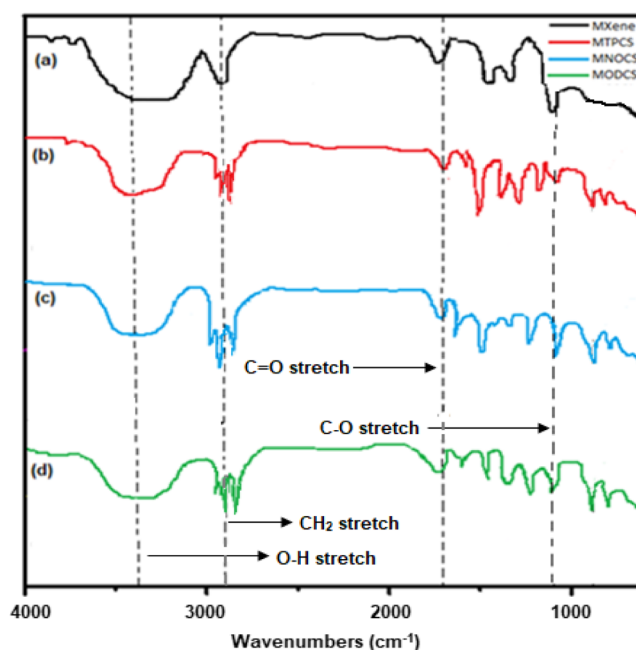

Figure 2. FT-IR spectra of MCE filter paper-supported membranes with the PVA binder: (a) MXene, (b) MTPCS modified, (c) MNOCS modified, and (d) MODCS modified. FT-IR analysis of silane-grafted MXene membranes with PVA/GA cross-linked.

the most intense peak is at $2\theta \approx 39°$, which corresponds to the (104) suppressed in the MXene, indicating the etching of Al from the structure. The decrease in peak intensity showed the loss of crystallinity after the removal of aluminum from the MAX phase.[28]

SEM Analysis. It is evident from SEM images of the MAX phase (Ti$_3$AlC$_2$) (Figure 5) that it had a compact structure where no distinct layers could be seen. However, after etching, multi-layered MXene structures are formed (Figure 6), thus
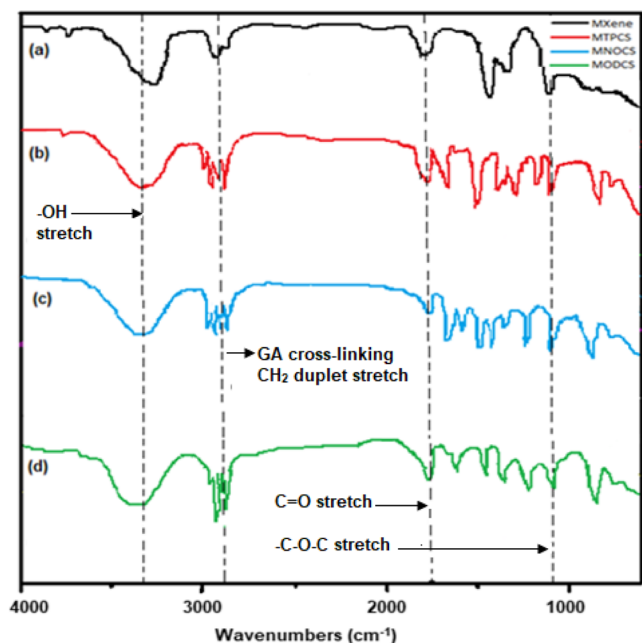
Figure 3. FT-IR spectra of the PVA/GA cross-linked modified membrane (without the filter paper support): (a) MXene, (b) MTPCS, (c) MNOCS, and (d) MODCS.

Figure 5. SEM morphological images of the MAX phase (Ti_3AlC_2) precursor at (a) 100 nm and (b) 300 nm scales.

validating successful etching of Al from the MAX phase. After grafting, the MXene surface was found to be entirely covered with the silane materials (Figure 7). SEM images indicated the MXene surface modification and successful silane grafting.

Flexibility of Membranes. MXene-incorporated PVA membranes were found to be less flexible compared to silane-grafted MXenes. It was observed that the grafting resulted in more flexible attachments of MXenes with added PVA, which enhance the use in water purification applications. Figure 8 shows the MXene membranes with and without silane modifications.

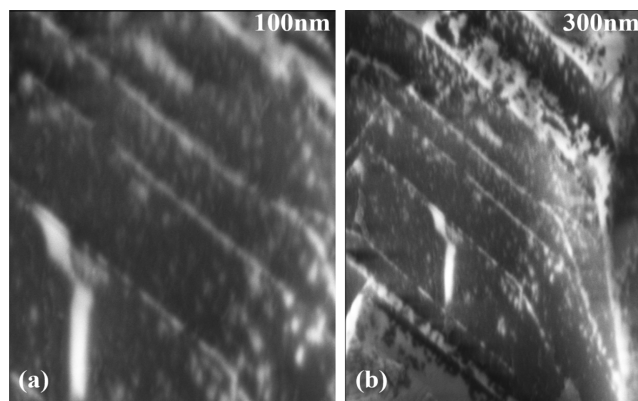**Pollutant Removal Studies.** UV−vis spectra were recorded for the samples prior to filtration. Afterward, the filtrate was subjected to record the UV−vis spectrum in order to figure out the remaining concentration of the pollutant. The removal performance was evaluated out of reduced concentrations from the calibration curve. A range of quantity of materials was tested in order to achieve optimum pollutant removal. The removal efficiency data with varying amounts of the MXene, MNOCS, MODCS, and MTPCS incorporated in PVA/GA membranes are represented in Figure 9. It was observed that 0.1 g of the grafted MXene was suitable for membrane fabrication after optimization.

UV−visible spectra of all studied pollutants are represented in Figures S1 and S2 (Supporting Information). In each case, the highest spectral curve corresponds to the initial value of absorbance by the respective pollutant in the solution. Subsequent spectral curves indicated a decreased concentration of pollutants and hence the absorbance after being passed through MNOCS, MODCS, and MTPCS membranes. The lowest spectral curves are for pollutant removal by MTPCS membranes, which indicate maximum removal by MTPCS membranes as compared to MNOCS and MODCS membranes.
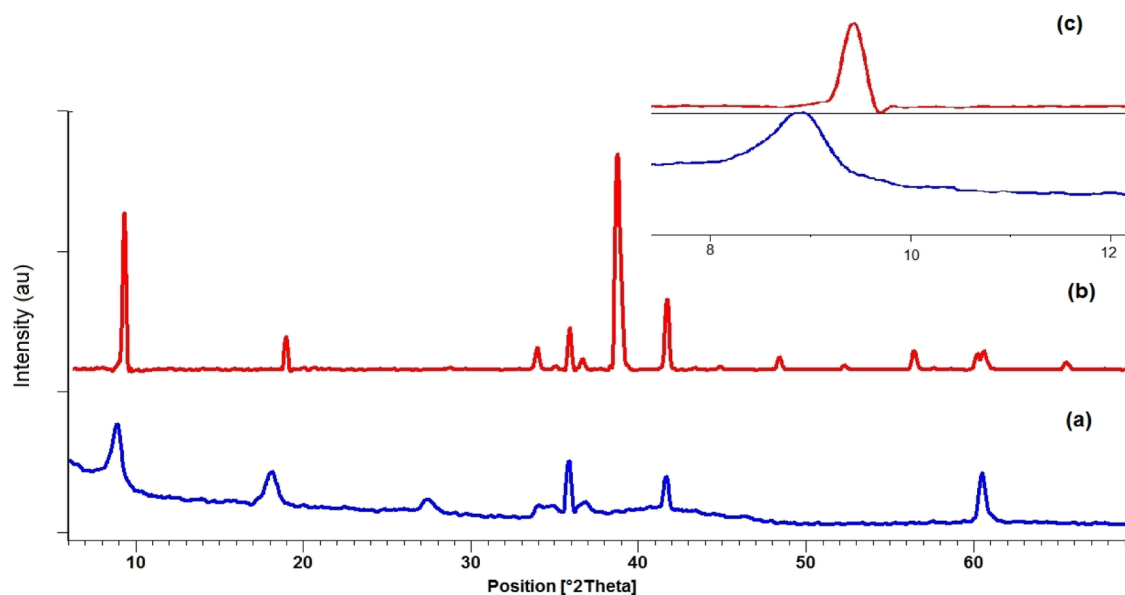

Figure 4. pXRD spectrum of (a) MXene ($Ti_3C_2T_x$) and (b) MAX phase (Ti_3AlC_2) and (c) inset showing the peak shift.
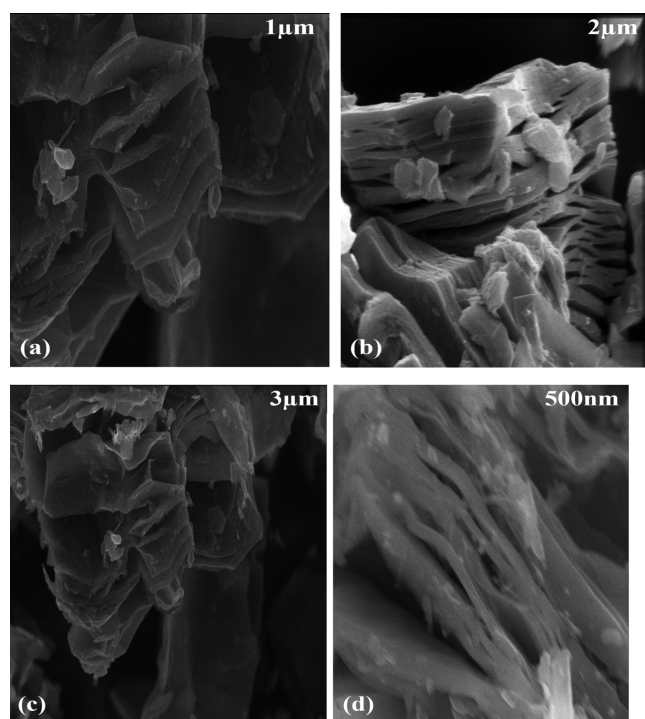
Figure 6. SEM morphological images of the MXene $(Ti_3C_2T_x)$ after etching at (a) 1 μm, (b) 2 μm, (c) 3 μm, and (d) 500 nm scales.
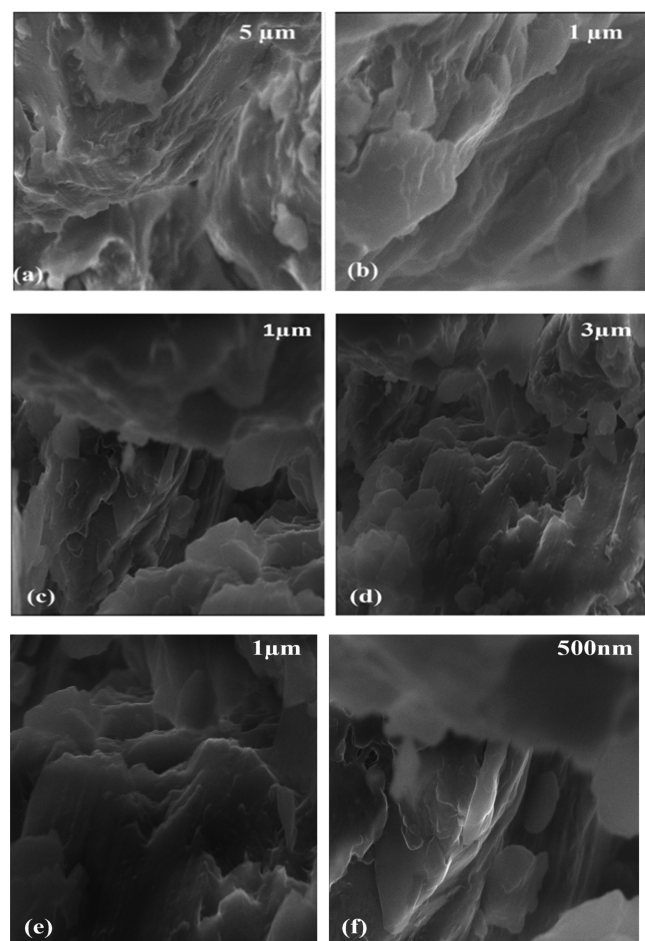

Figure 7. SEM images of silane-grafted MXenes: (a,b) MNOCS, (c,d) MODCS, and (e,f) MTPCS.
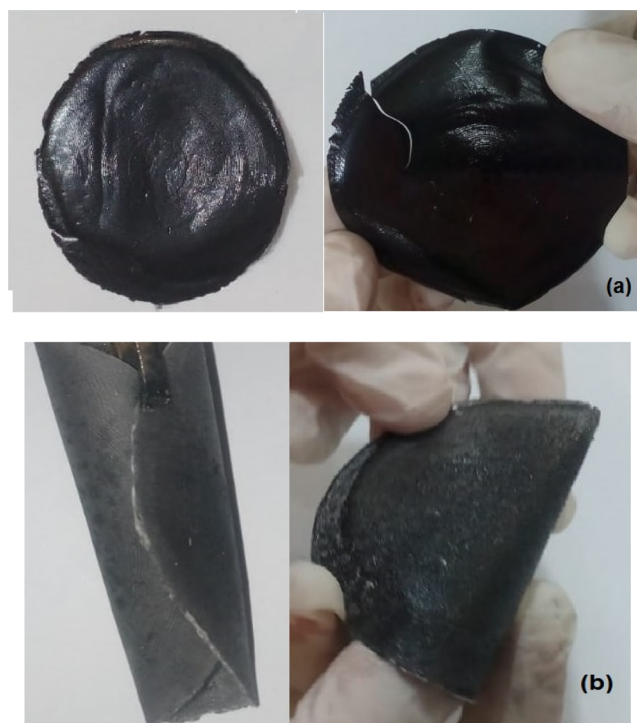

Figure 8. (a) MXene-incorporated and (b) silane-grafted MXene-incorporated PVA/GA membranes.

Calculating Pollutant Removal Performance. To measure the membrane pollutant removal performance, 50 ppm (methanolic water solutions) each of Sudan II, methylene blue, PAHs, bisphenol A, biphenyl, mesitylene, and BTEX was used for their removal by prepared membranes. The removal efficiency (R %) for pollutants is expressed as follows

$$R\ (\%) = \frac{C_f - C_p}{C_f} \times 100$$

whereas C_f is the feed concentration and C_p is the permeated concentration of pollutants in mg/L or ppm[29] evaluated from the Beer–Lambert law using corresponding absorbance and molar absorptivity in each case.

Pollutant Removal. Figures 10 and 11 show that both types of membranes, MCE filter paper-supported membranes and membranes without the support, are excellent in removal of Sudan II, methylene blue, PAHs, bisphenol A, biphenyl, mesitylene, and BTEX. Due to the hydrophobic nature of these membranes, the pollutants with less water solubility and organic moiety in their structure (*i.e.*, Sudan II dye) were removed efficiently. Out of all these membranes, MTPCS membranes showed the maximum removal. Furthermore, MNOCS and MODCS membranes were also very efficient in pollutant removal next to MTPCS membranes. Unmodified MXene membranes were also found to be effective; however, they were found to be least effective compared with modified membranes.

Generally, the efficiency for pollutant removal increased in the case of PVA/GA cross-linked membranes as compared to their complementary MCE filter paper-supported membranes incorporated with similar grafted materials. The reason was attributed to the fact that the cross-linking of PVA by GA had resulted in the formation of a hydrophobic network where the silane-grafted MXene is attached and surrounded by multiple
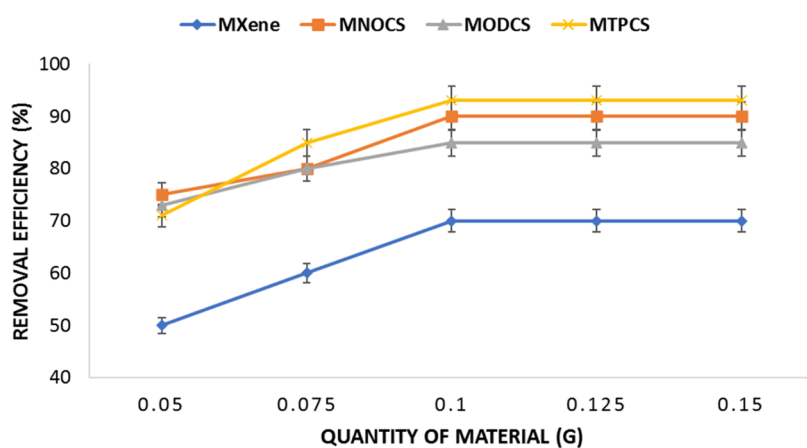
Figure 9. Optimization of the modified MXene PVA/GA material for membrane fabrication.
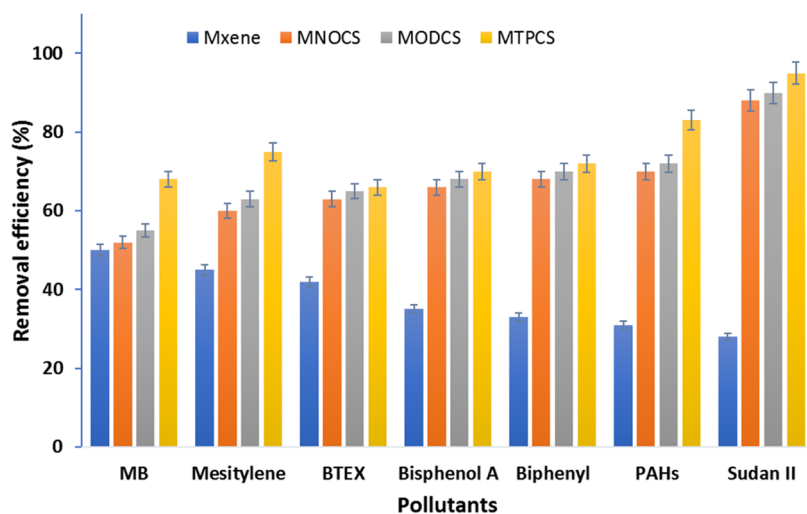

Figure 10. Graphical representation of % removal of the pollutants by MCE filter paper-supported MXene membranes.
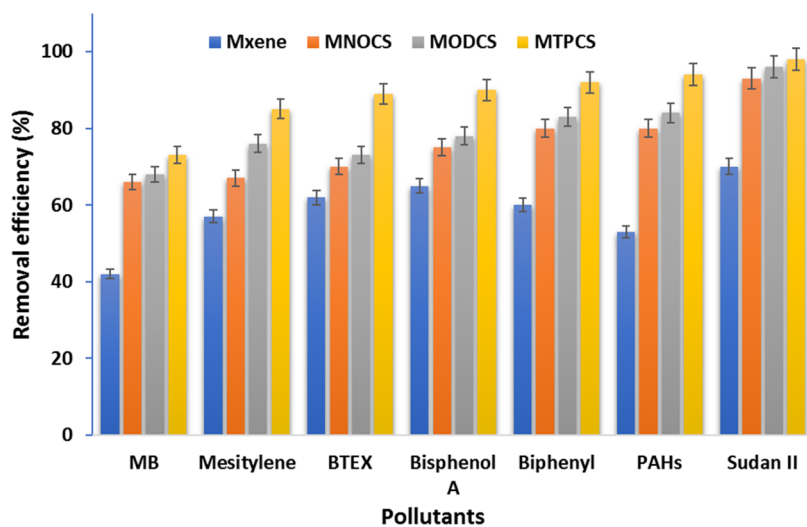
Figure 11. Graphical representation of % removal of the pollutants by PVA with GA cross-linked MXene membranes.

PVA/GA bonds. Thus, hydrophobic silane-grafted MXenes incorporated in hydrophobic PVA/GA membranes exhibited the best removals for hydrophobic pollutants by entrapping and adsorbing them onto their surface. Exceptionally, MXene-incorporated MCE filter paper-supported membranes showed better removal for MB as compared to PVA and GA membranes because of the hydrophilic nature of both the MXene and MCE membrane. Table 1 compares the removal performances of various pollutants by newly synthesized membranes.

Table 1. Comparison of Removal of Pollutants for Different Membrane Materials[a]

| | MXene[a] | | MNOCS | | MODCS | | MTPCS | |
| | membrane materials | | | | | | | |
Pollutants	MCE filter paper-supported (%)	PVA/GA cross-linked (%)	MCE filter paper-supported (%)	PVA/GA cross-linked (%)	MCE filter paper-supported (%)	PVA/GA cross-linked (%)	MCE filter paper-supported (%)	PVA/GA cross-linked (%)
MB	50	42	52	66	55	68	68	73
mesitylene	45	57	60	67	63	76	75	85
BTEX	42	62	63	70	65	73	66	89
bisphenol A	35	65	66	75	68	78	70	90
biphenyl	33	60	68	80	70	83	72	92
PAHs	31	53	70	80	72	84	83	94
Sudan II	28	70	88	93	90	96	95	98

removal percentages

[a]*Without silane grafting.

Comparison with Previously Reported Studies (MXene-Based Membranes). Lamellar membranes based on 2D MXene nanosheets supported on the aluminum oxide substate with a favorable removal rate (over 90%) for Rhodamine B and Evans blue as model pollutants were reported earlier.[30] Similarly, the hydrophilic MXene supported on the polyethersulfone ultrafiltration membrane was demonstrated for the removal of Congo red dye (92.3% at 0.1 MPa), having permselectivity in the separation of dyes from salts shown earlier.[31] The removal of dyes such as methyl red, methylene blue, rose Bengal, and brilliant blue carried out in thin (90 nm), laminated porous $Ti_3C_2T_x$–graphene oxide membranes was demonstrated by Kang et al..[32] The author shows the removal performance (under 5 bar pressure) for hydrated radii above 5 Å with removal performance of 68–100% for these dyes. Similarly, the removal rate for four different dyes, that is, Rhodamine B, methyl blue, crystal violet, and neutral red, was shown to be >97%[33] by another study in which the MXene nanosheets were used to produce TiO_2 nanoparticles *via in situ* oxidation which intercalated with graphene oxide (GO) to produce GO-based nanofiltration membranes. In another study, the composite membrane was developed using GO and MXene. The author demonstrated that the heterogeneous structure of the GO/MXene membrane produced a synergistic effect in terms of substrate removal and permeability. The removal performance of common organic dyes (chrysoidine G, neutral red, methylene blue, crystal violet, brilliants blue) was found to >99.5%.[34] Table 2 shows the comparison of various membranes in terms of support materials and removal performance with the reported grafted membranes.

Membrane Reusability and Disposal. The reusability of membrane was tested using $Ti_3C_2T_x$–triphenylchlorosilane (MPTCS) PVA/GA cross-linked membranes for removal of various pollutants (Figure 12) after washing with ethanol (50 mL × 5). It was observed that the membranes exhibit reusability up to five cycles. The removal efficiency dropped in the range of 8–15% of the original values after five cycles. The used membranes can be disposed off as usual as the material for membrane fabrication is environmentally friendly and the MXene and PVA matrix do not show any environmental problems.

■ **CONCLUSIONS**

The commercially available MAX phase (Ti_3AlC_2) was successfully etched with HF and exfoliated and delaminated using ultrasonication as confirmed by powder X-ray diffraction (pXRD) analysis. The modifications of the MXene $(Ti_3C_2T_x)$ with silane grafting reaction for membrane preparation for enhances water purification were investigated. The MXene was successfully grafted with *n*-octadecyltrichlorosilane (MODCS), *n*-octyltrichlorosilane (MNOCS), and triphenylchlorosilane (MTPCS) in order to make a hydrophobic MXene that could be able to bind with the organic matrix/polymers. The grafting was confirmed with FT-IR analysis. The modified MXenes were transformed into thin membranes by forming an MXene/PVA composite over a filter paper support, that is, MCE filter paper. MXene membranes were also formed without the MCE support by using PVA/GA, where GA was used as a cross-linker to stabilize PVA and make it water-resistant. The conditions of membrane formation were optimized to investigate optimum compatible conditions with the modified materials. 0.1 g of the MXene was sufficient

Table 2. Comparison with Previously Reported Studies for the Removal of Selected Pollutant Species by MXene-Based Membranes

MXene	support layer	pollutants	key removal (%)	ref.
$Ti_3C_2T_x$	anodic aluminum oxide	Rhodamine B, Evans blue	85, 90	30
	polyethersulfone	Congo red, Gentian violet	92, 80	31
$Ti_3C_2T_x$–Ag	polyvinylidene difluoride	Rhodamine B, methyl green	79.9, 92.3	35
$Ti_3C_2T_x$–graphene oxide	polycarbonate and nylon	brilliant blue, rose Bengal	95.4, 94.6, 40	32
		methylene blue		
	mixed cellulose ester (200 nm)	Rhodamine B, methyl blue crystal violet, neutral red	>97 for all dyes	33
	mixed cellulose ester (450 nm)	Chrysoidine G, neutral red, methylene blue, crystal violet, brilliant blue	>99 for all dyes	34
	porous nylon membrane	methyl orange, methylene blue, acid yellow 14, indigo carmine, eosin	>95 for all dyes	36
$Ti_3C_2T_x$	mixed cellulose ester (220 nm)	methylene blue	50%	Current studies
		mesitylene	45%	
		BTEX	42%	
		bisphenol A	35%	
		biphenyl	33%	
		PAHs	31%	
		Sudan II	28%	
	polyvinyl acetate and GA	methylene blue	42%	
		mesitylene	57%	
		BTEX	62%	
		bisphenol A	65%	
		biphenyl	60%	
		PAHs	53%	
		Sudan II	70%	
$Ti_3C_2T_x$–n-octadecyltrichlorosilane (MODCS)	mixed cellulose ester (220 nm)	methylene blue I	52%	Current studies
		mesitylene	60%	
		BTEX	63%	
		bisphenol A	66%	
		biphenyl	68%	
		PAHs	70%	
		Sudan II	88%	
	polyvinyl acetate and GA	methylene blue	66%	
		mesitylene	67%	
		BTEX	70%	
		bisphenol A	75%	
		biphenyl	80%	
		PAHs	80%	
		Sudan II	93%	
$Ti_3C_2T_x$–n-octyltrichlorosilane (MNOCS)	mixed cellulose ester (220 nm)	methylene blue	55%	Current studies
		mesitylene	63%	
		BTEX	65%	
		bisphenol A	68%	
		biphenyl	70%	
		PAHs	72%	
		Sudan II	90%	
	polyvinyl acetate and GA	methylene blue	68%	
		mesitylene	76%	
		BTEX	73%	
		bisphenol A	78%	
		biphenyl	83%	
		PAHs	84%	
		Sudan II	96%	

Table 2. continued

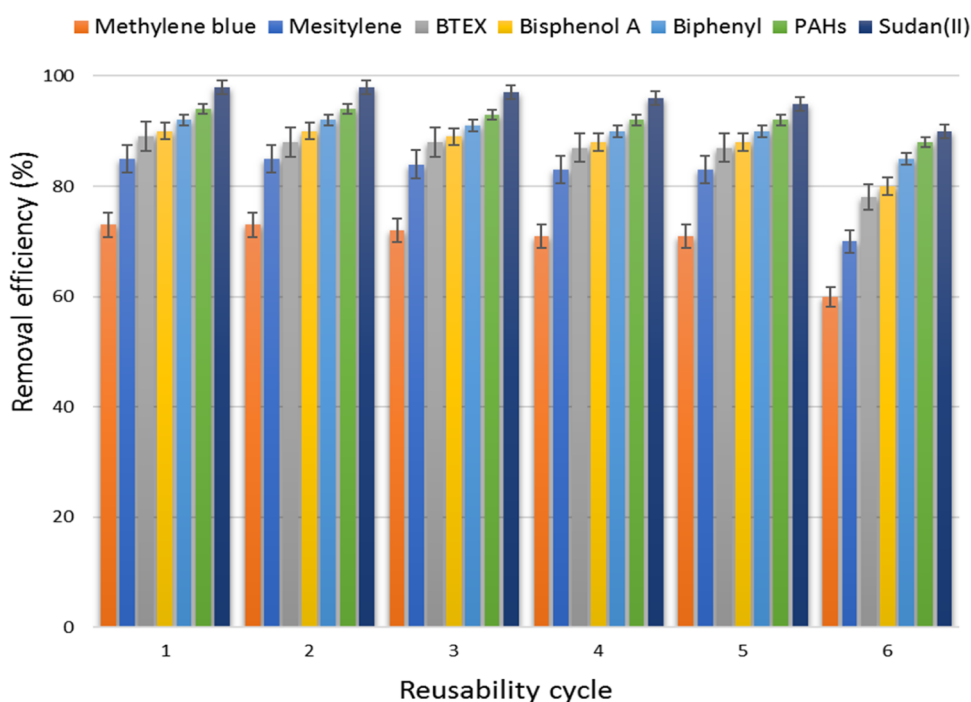| MXene	support layer	pollutants	key removal (%)	ref.
Ti$_3$C$_2$T$_x$−triphenylchlorosilane (MPTCS)	mixed cellulose ester (220 nm)	methylene blue	68%	Current studies
		mesitylene	75%	
		BTEX	66%	
		bisphenol A	70%	
		biphenyl	72%	
		PAHs	83%	
		Sudan II	95%	
	polyvinyl acetate and GA	methylene blue	73%	
		mesitylene	85%	
		BTEX	89%	
		bisphenol A	90%	
		biphenyl	92%	
		PAHs	94%	
		Sudan II	98%	

Figure 12. Reusability of the MXene membrane [Ti$_3$C$_2$T$_x$−triphenylchlorosilane (MPTCS) PVA/GA cross-linked] for the removal of various pollutants.

to develop the membrane with a high efficiency for removal. The resulting membranes were tested for removal for various organic pollutants that included mesitylene (or trimethylbenzene), PAHs (chrysene, as a model), biphenyl, bisphenol A, BTEX, methylene blue, and Sudan II dyes. MTPCS PVA/GA cross-linked membranes showed the best results for pollutant removal up to 98% efficiency. Overall, all six types of membranes showed a removal efficiency in the range of 52−98%, which is better than that of the bare MXene membrane (28−50% removal efficiency). It was observed that the membranes exhibit reusability up to five cycles.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01143.

Membrane performance of two different types in terms of UV−vis spectra for pollutant removal of methylene blue, mesitylene, BTEX, bisphenol A, biphenyl, PAHs, and Sudan II (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Amir Waseem − Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan; ⓞ orcid.org/0000-0001-8414-0374; Email: waseemq2000@hotmail.com, amir@qau.edu.pk

Authors

Tayyaba Yousaf − Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

Aneeqa Areeb − *Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan*

Maida Murtaza − *Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan*

Akhtar Munir − *Department of Chemistry, University of Sialkot, Sialkot 51310, Pakistan*

Yaqoob Khan − *Nanosciences & Technology Department, National Centre for Physics, Islamabad 44000, Pakistan*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c01143

Notes

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■ REFERENCES

(1) Shao, L.; Chen, G. Q. Water Footprint Assessment for Wastewater Treatment: Method, Indicator, and Application. *Environ. Sci. Technol.* **2013**, *47*, 7787−7794.

(2) Rasool, K.; Pandey, R. P.; Rasheed, P. A.; Buczek, S.; Gogotsi, Y.; Mahmoud, K. A. Water treatment and environmental remediation applications of two-dimensional metal carbides (MXenes). *Mater. Today* **2019**, *30*, 80−102.

(3) Wahab, N.; Saeed, M.; Ibrahim, M.; Munir, A.; Saleem, M.; Zahra, M.; Waseem, A. Synthesis, Characterization, and Applications of Silk/Bentonite Clay Composite for Heavy Metal Removal From Aqueous Solution. *Front. Chem.* **2019**, *7*, 654 Original Research.

(4) Madsen, H. T. Membrane Filtration in Water Treatment—Removal of Micropollutants. In *Chemistry of Advanced Environmental Purification Processes of Water: Fundamentals and Applications*; Søgaard, E. G., Ed.; Elsevier, 2014; pp 199−248.

(5) Ojajuni, O.; Saroj, D.; Cavalli, G. Removal of organic micropollutants using membrane-assisted processes: a review of recent progress. *Environ. Technol. Rev.* **2015**, *4*, 17−37.

(6) Hube, S.; Eskafi, M.; Hrafnkelsdóttir, K. F.; Bjarnadóttir, B.; Bjarnadóttir, M. Á.; Axelsdóttir, S.; Wu, B. Direct membrane filtration for wastewater treatment and resource recovery: A review. *Sci. Total Environ.* **2020**, *710*, 136375.

(7) Lipatov, A.; Alhabeb, M.; Lukatskaya, M. R.; Boson, A.; Gogotsi, Y.; Sinitskii, A. Effect of Synthesis on Quality, Electronic Properties and Environmental Stability of Individual Monolayer Ti3C2MXene Flakes. *Adv. Electron. Mater.* **2016**, *2*, 1600255.

(8) Ranck, J. M.; Bowman, R. S.; Weeber, J. L.; Katz, L. E.; Sullivan, E. J. BTEX Removal from Produced Water Using Surfactant-Modified Zeolite. *J. Environ. Eng.* **2005**, *131*, 434−442.

(9) Naguib, M.; Kurtoglu, M.; Presser, V.; Lu, J.; Niu, J.; Heon, M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-dimensional nanocrystals produced by exfoliation of Ti3 AlC2. *Adv. Mater.* **2011**, *23*, 4248−4253.

(10) Salim, O.; Mahmoud, K. A.; Pant, K. K.; Joshi, R. K. Introduction to MXenes: synthesis and characteristics. *Mater. Today Chem.* **2019**, *14*, 100191.

(11) Magnuson, M.; Mattesini, M. Chemical bonding and electronic-structure in MAX phases as viewed by X-ray spectroscopy and density functional theory. *Thin Solid Films* **2017**, *621*, 108−130.

(12) Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y. 25th anniversary article: MXenes: a new family of two-dimensional materials. *Adv. Mater.* **2014**, *26*, 992−1005.

(13) Poonam; Sharma, K.; Arora, A.; Tripathi, S. K. Review of supercapacitors: Materials and devices. *J. Energy Storage* **2019**, *21*, 801−825.

(14) Ihsanullah, I.; Ali, H. Technological challenges in the environmental applications of MXenes and future outlook. *Case Stud. Chem. Environ. Eng.* **2020**, *2*, 100034.

(15) Ronchi, R. M.; Arantes, J. T.; Santos, S. F. Synthesis, structure, properties and applications of MXenes: Current status and perspectives. *Ceram. Int.* **2019**, *45*, 18167−18188.

(16) Al-Hamadani, Y. A. J.; Jun, B.-M.; Yoon, M.; Taheri-Qazvini, N.; Snyder, S. A.; Jang, M.; Heo, J.; Yoon, Y. Applications of MXene-based membranes in water purification: A review. *Chemosphere* **2020**, *254*, 126821.

(17) Zhao, J.; Yang, Y.; Yang, C.; Tian, Y.; Han, Y.; Liu, J.; Yin, X.; Que, W. A hydrophobic surface enabled salt-blocking 2D Ti3C2 MXene membrane for efficient and stable solar desalination. *J. Mater. Chem.* **2018**, *6*, 16196−16204.

(18) Cao, W.-T.; Feng, W.; Jiang, Y.-Y.; Ma, C.; Zhou, Z.-F.; Ma, M.-G.; Chen, Y.; Chen, F. Two-dimensional MXene-reinforced robust surface superhydrophobicity with self-cleaning and photothermal-actuating binary effects. *Mater. Horiz.* **2019**, *6*, 1057−1065.

(19) Zhang, Q.; Yi, G.; Fu, Z.; Yu, H.; Chen, S.; Quan, X. Vertically Aligned Janus MXene-Based Aerogels for Solar Desalination with High Efficiency and Salt Resistance. *ACS Nano* **2019**, *13*, 13196−13207.

(20) Zhang, J.; Liu, Y.; Lv, Z.; Zhao, T.; Li, P.; Sun, Y.; Wang, J. Sulfonated Ti3C2Tx to construct proton transfer pathways in polymer electrolyte membrane for enhanced conduction. *Solid State Ionics* **2017**, *310*, 100−111.

(21) Hao, L.; Zhang, H.; Wu, X.; Zhang, J.; Wang, J.; Li, Y. Novel thin-film nanocomposite membranes filled with multi-functional Ti3C2Tx nanosheets for task-specific solvent transport. *Composites, Part A* **2017**, *100*, 139−149.

(22) Lim, S.; Park, H.; Yang, J.; Kwak, C.; Lee, J. Stable colloidal dispersion of octylated Ti3C2-MXenes in a nonpolar solvent. *Colloids Surf., A* **2019**, *579*, 123648.

(23) Liu, M.; Zhou, C.; Dong, B.; Wu, Z.; Wang, L.; Yu, S.; Gao, C. Enhancing the permselectivity of thin-film composite poly(vinyl alcohol) (PVA) nanofiltration membrane by incorporating poly-(sodium-p-styrene-sulfonate) (PSSNa). *J. Membr. Sci.* **2014**, *463*, 173−182.

(24) Anasori, B.; Gogotsi, Y. *2D Metal Carbides and Nitrides (MXenes)*; Springer International Publishing, 2019.

(25) Gao, L.; Li, C.; Huang, W.; Mei, S.; Lin, H.; Ou, Q.; Zhang, Y.; Guo, J.; Zhang, F.; Xu, S.; et al. MXene/Polymer Membranes: Synthesis, Properties, and Emerging Applications. *Chem. Mater.* **2020**, *32*, 1703−1747.

(26) Figueiredo, K. C. S.; Alves, T. L. M.; Borges, C. P. Poly(vinyl alcohol) films crosslinked by glutaraldehyde under mild conditions. *J. Appl. Polym. Sci.* **2009**, *111*, 3074−3080.

(27) Pandey, R. P.; Rasheed, P. A.; Gomez, T.; Azam, R. S.; Mahmoud, K. A. A fouling-resistant mixed-matrix nanofiltration membrane based on covalently cross-linked Ti3C2TX (MXene)/cellulose acetate. *J. Membr. Sci.* **2020**, *607*, 118139.

(28) Zhang, H.; Wang, Z.; Shen, Y.; Mu, P.; Wang, Q.; Li, J. Ultrathin 2D Ti3C2Tx MXene membrane for effective separation of oil-in-water emulsions in acidic, alkaline, and salty environment. *J. Colloid Interface Sci.* **2020**, *561*, 861−869.

(29) Iqbal, M. A.; Ali, S. I.; Amin, F.; Tariq, A.; Iqbal, M. Z.; Rizwan, S. La- and Mn-Codoped Bismuth Ferrite/Ti3C2 MXene Composites for Efficient Photocatalytic Degradation of Congo Red Dye. *ACS Omega* **2019**, *4*, 8661−8668 Article.

(30) Ding, L.; Wei, Y.; Wang, Y.; Chen, H.; Caro, J.; Wang, H. A Two-Dimensional Lamellar Membrane: MXene Nanosheet Stacks. *Angew. Chem., Int. Ed. Engl.* **2017**, *56*, 1825−1829.

(31) Han, R.; Ma, X.; Xie, Y.; Teng, D.; Zhang, S. Preparation of a new 2D MXene/PES composite membrane with excellent hydrophilicity and high flux. *RSC Adv.* **2017**, *7*, 56204−56210.

(32) Kang, K. M.; Kim, D. W.; Ren, C. E.; Cho, K. M.; Kim, S. J.; Choi, J. H.; Nam, Y. T.; Gogotsi, Y.; Jung, H.-T. Selective Molecular Separation on Ti3C2Tx-Graphene Oxide Membranes during Pressure-Driven Filtration: Comparison with Graphene Oxide and MXenes. *ACS Appl. Mater. Interfaces* **2017**, *9*, 44687−44694.

(33) Han, R.; Wu, P. High-performance graphene oxide nano-filtration membrane with continuous nanochannels prepared by the in situ oxidation of MXene. *J. Mater. Chem.* **2019**, *7*, 6475−6481.

(34) Liu, T.; Liu, X.; Graham, N.; Yu, W.; Sun, K. Two-dimensional MXene incorporated graphene oxide composite membrane with enhanced water purification performance. *J. Membr. Sci.* **2020**, *593*, 117431.

(35) Pandey, R. P.; Rasool, K.; Madhavan, V. E.; Aïssa, B.; Gogotsi, Y.; Mahmoud, K. A. Ultrahigh-flux and fouling-resistant membranes based on layered silver/MXene (Ti3C2Tx) nanosheets. *J. Mater. Chem.* **2018**, *6*, 3522−3533.

(36) Wei, S.; Xie, Y.; Xing, Y.; Wang, L.; Ye, H.; Xiong, X.; Wang, S.; Han, K. Two-dimensional graphene Oxide/MXene composite lamellar membranes for efficient solvent permeation and molecular separation. *J. Membr. Sci.* **2019**, *582*, 414−422.