Can pre-ozonation be combined with gravity-driven membrane filtration to treat shale gas wastewater?

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Abstract: Low-cost gravity-driven membrane (GDM) filtration combined with appropriate pre-treatment processes has major potential to efficiently manage shale gas wastewater (SGW). In this work, the feasibility of combining low dosage pre-ozonation with the GDM process was evaluated in the treatment of SGW. The results showed that pre-ozonation significantly increased the stable flux (372%) of GDM filtration, while slightly deteriorating the quality of the effluent water in terms of organic content (−14%). These results were mainly attributed to the conversion of macromolecular organics to low-molecular weight fractions by pre-ozonation. Interestingly, pre-ozonation markedly increased the flux (198%) in the first month of operation also for a GDM process that comprised the addition of GAC (GGDM). Nevertheless, the flux of O_3-GGDM systems dropped sharply around the 25th day of operation, which might be due to the rapid accumulation of pollutants in the high flux stage and the formation of a dense fouling layer. Pre-ozonation remarkably influenced the microbial community structure and O_3-GDM systems were characterized by distinct core microorganisms, which could degrade specific organics in SGW. Furthermore, O_3-GDM outperformed simple GDM as a pretreatment for RO. These findings can provide valuable references for combining oxidation technologies with the GDM process in treating refractory wastewater.

Keywords: Shale gas wastewater; Pre-ozonation; Gravity driven membrane filtration; Mechanism

1. Introduction

Horizontal drilling and hydraulic fracturing technologies are applied to overcome the challenge of shale gas extraction. Nevertheless, a large amount (~5200-25,870 m^3 per well) of shale gas wastewater (SGW) is produced during hydraulic fracturing (Kondash and Vengosh, 2015). SGW is typically characterized by high salinity and high concentrations of toxic metals and organics (Butkovskyi et al., 2017). If not treated properly, its discharge would seriously threaten the water environment and human health. At present, hybrid membrane technologies are regarded as suitable and effective means to treat SGW (Tong et al., 2019). Specifically, low-pressure membrane processes, such as ultrafiltration (UF), are investigated and implemented as pretreatment steps for the subsequent desalination (Chang et al., 2019b; Guo et al., 2018; Miller et al., 2013). However, operational problems associated with membrane fouling seriously reduce the efficicacy and economy of UF (Shang et al., 2019; Tang et al., 2020).

Gravity driven membrane filtration (GDM), a recently developed membrane technology, has been proposed to replace traditional UF in the pretreatment of SGW (Chang et al., 2019a). The main rationale is that GDM filtration does not need cleaning and can obtain a stable flux driven solely by gravity with the advantages of simple operation, low cost, and low energy consumption (Pronk et al., 2019). The feasibility of the GDM process as a pretreatment option for SGW desalination was verified in a number of research efforts (Chang et al., 2019a; Tang et al., 2021a).

While underlining the potential of GDM filtration, these studies highlighted the current need for significant improvements in stable flux values and contaminant removal rates of this technology (Chang et al., 2019a; Tang et al., 2021a).

Some processes, including adsorption, aeration, and coagulation were successfully combined with GDM to the purpose of improving its performance (Ding et al., 2016; Lee et al., 2021; Tang et al., 2021c). As a strong oxidant, ozone was shown to effectively alleviate membrane fouling when used as a pretreatment process for UF and for membrane bioreactors (MBR) (Sathya et al., 2019; Tang et al., 2020; Wang et al., 2017; Zhang et al., 2020), owing to a reduction of organics molecular size, an enhancement of foulants hydrophilicity, and a decrease of biofouling (Wang et al., 2017). Therefore, we hypothesize that pre-ozonation should also effectively increase the performance of GDM filtration. Generally, it is not recommended to combine pre-ozonation with GDM in the treatment of drinking water, because pre-ozonation has the risk of deteriorating water quality and may produce toxic by-products (Tang et al., 2021b). On the other hand, these issues should not impact the application of GDM filtration to treat wastewater, because this technology would not act as a final polishing step, but instead as pretreatment for subsequent tertiary or desalination processes. The high potential of applying advanced oxidation in the specific treatment of SWG and other producted waters has been recently highlighted and it is of great significance to study synergy of ozonation and GDM filtration, two of the most promising processes for efficient SGW management.

Therefore, in this study pre-ozonation is investigated in combination with GDM filtration to treat SGW with the aim of increasing stable flux and contaminant removal values in GDM, and improving the quality of the final desalinated effluent. Six GDM systems are examined to understand the effect of pre-ozonation with low ozone dosage on the performance of GDM systems with and without the presence of an additional treatment step through activated carbon adsorption. The integration between pre-ozonation and GDM filtration is thus discussed, also in the light of the effect on microbial communities that drive membrane fouling and organics removal and biodegradation within the GDM unit.

2. Materials and methods

2.1 Water samples and water quality analysis

SGW samples were collected from the Weiyuan shale gas play (Sichuan Basin, China). The water quality parameters of the SGW are summarized in Table 1. The analytical methods for the determination of turbidity, dissolved organic carbon (DOC), UV_{254}, fluorescent organics, and total dissolved solid (TDS) can be found in Text S1 of the Supporting Information (SI) and in our previous study (Tang et al., 2020).

Table 1. Water quality characteristics of the raw water and the raw water treated by O_3 at different dosages.

Parameter	Raw water	Raw water treated by O_3		
		20 mg/L	40 mg/L	80 mg/L
DOC (mg/L)	17.48	17.91	18.95	18.54

UV_{254} (cm^{-1})	0.095	0.097	0.100	0.098
Turbidity (NTU)	8.2	7.7	7.2	9.6
TDS (g/L)	19.85	20.14	20.71	19.86

2.2 Experimental setups and procedures

The schematic diagrams and the parameters of the six GDM systems utilized in this work are shown in Fig. S1 and Table 2, respectively. The systems were operated in parallel at room temperature (10-26 °C, Fig. S2) with a hydrostatic pressure of 70 mbar as driving force. The characteristics of the poly(vinylidene fluoride) hollow fiber UF membranes (Litree Purifying Technology Co., Ltd., China) with an effective membrane area of 10 cm^2 employed in this study can be found in a previous report (Chang et al., 2019a). The systems ran continuously for 90 days, and the flux was monitored through the electronic balance.

The system referred to as GDM1 treated raw water without any pre-preatment and represented the control unit. On the other hand, the feed water of four of the six GDM systems (namely, GDM-3, 4, 5, 6) was raw water treated by O_3 at different dosages. Low ozone dosages (20-80 mg/L) were applied and the detailed description of the pre-ozonation process can be found in our previous work (Tang et al., 2020). Before the subsequent GDM filtration, the residual ozone in water was quenched by heating the ozonated effluent at 50 °C for 30 min.

Granular activated carbon (GAC, CPG LF 12, Calgon Carbon Co., Ltd., USA) adsorption was included in four of the six GDM systems, specifically, GDM-2, 3, 5, 6. The four systems comprising adsorption are referred to as GGDM units. The GAC was cleaned with deionized water and dried before use. A dosage of 4 g was used to pre-treat the influent water to the GDM system, a much smaller quantity than that used in our previous study (Tang et al., 2021a), to slightly reduce the adsorption effect and highlight the effect of microbial degradation in the membrane reactor.

Reverse osmosis (RO) filtration experiments were carried out to verify the effect of different GDM pre-treatment systems on the desalination performance. The RO process was operated at a constant applied pressure of 5.5 MPa (55 bar) with 50% recovery. The RO setup and membrane are described in detail in our previous work (Tang et al., 2020).

Table 2. The parameters of six GDM systems.

No.	Aeration	The addition of GAC	Pre-ozonation
GDM1 (GDM)	10 ml/min	-	-
GDM2 (GGDM)	10 ml/min	4 g	-
GDM3 (O_3^{20}-GGDM)	10 ml/min	4 g	20 mg/L O_3
GDM4 (O_3^{40}-GDM)	10 ml/min	-	40 mg/L O_3
GDM5 (O_3^{40}-GGDM)	10 ml/min	4 g	40 mg/L O_3
GDM6 (O_3^{80}-GGDM)	10 ml/min	4 g	80 mg/L O_3

2.3 Analysis of the membrane fouling layers

The measurement and calculation methods of hydraulic resistance of the membrane fouling layers, namely, the reversible resistance (R_{re}) and the irreversible resistance (R_{ir}), were identical to our previous study (Chang et al., 2019a). The pure water contact angles and Fourier transform infrared (FTIR) spectra of membrane fouling layers were measured with a KRÜSS DSA 25S instrument (KRÜSS GmbH, Germany) and with an attenuated total reflectance FTIR spectrometer (Nicolet IS 20, Thermo Fisher Scientific Inc., USA), respectively. The surface and the cross-section of the fouled membrane samples, as well as the thickness of membrane fouling layers, were observed and measured by scanning electron microcopy (SEM) (FE-SEM, Regulus-8230, Hitachi, Japan). The surface roughness of the fouled UF membrane samples was determined with atomic force microscopy (AFM, Icon, Bruker, Germany). The extracellular polymer substances (EPS) extraction was conducted using a heating and sonication method and the EPS measuring protocol can be found in our recent studies (Tang et al., 2021d). The fluorescent compounds comprised in the EPS matrix were measured by fluorescence excitation-emission (EEM) (F7000, Hitachi, Japan)

2.4 Microbial diversity analysis

The variation of the microbial community and the dominant functional microorganisms were analyzed through microbial diversity sequencing of the raw water and membrane fouling layers. The amplified primer sets of 16S rRNA genes for bacteria was 338F/806R. Details about microbial diversity sequencing and analysis are presented in Text S2 of the SI and in our previous study (Tang et al., 2021a).

3. Results and discussion

3.1 Permeate flux and organic matter removal performance

The hypothesis of this study is that pre-ozonation performance should influence the behavior of the subsequent GDM filtrations, with possibly higher productivity achievable in the membrane step. As presented in Table 1, the DOC and UV_{254}

parameters in the raw stream did not decrease upon oxidation, most likely due to the competing effect of mineralization and solubilization of organics (Tang et al., 2021b). Our previous research showed that pre-ozonation mainly changed the organic composition and characteristics of SGW, rather than translating into mineralization of compounds (Tang et al., 2020; Tang et al., 2021b). For example, pre-oxidation significantly improved the biodegradability of SGW (Liu et al., 2018; Tang et al., 2020). The composition and relative content of fluorescent organic matter components in SGW are shown in Fig. S3. The soluble microbial by-product-like matters (region IV) and humic acid-like matters (region V) were the dominant fluorescent organic components in SGW: 3.1%-38.6% of fluorescent organic components were removed by O_3.

The flux profiles measured in the six GDM systems are presented in Fig. 1a and analyzed in the light of the pre-oxidation results. The flux trends can be divided into three stages. During the initial filtration stage (stage 1, 0-30 days), a monotonic decline of flux occurred in all the units. However, the flux of GDM systems treating pre-ozonized SGW dropped very slowly and was significantly higher than that of the control GDM system and of the GGDM system without pre-oxidation (GDM2). Specifically, the average flux in the O_3^{40}-GDM system was 2.8 times that of GDM and 2.0 times that of GGDM. This result may be attributed to the degradation of macromolecular organic compounds by O_3 into low molecular-weight and more hydrophilic molecules that take more time to deposit on the membrane surface (Tang et al., 2020). However, on the 25th day of operation, the fluxes of O_3-GDM systems also dropped sharply and this phenomenon may be due to the rapid accumulation of pollutants due to the relatively high flux upon the formation of a more homogeneous coating layer at this point of the experiment.

Later, the fluxes in the systems continually decreased (second stage, 30-60 days), and ultimately tended to converge to roughly the same steady value (third stage, 60-90 days), due to the formation of stable fouling layers on the membrane surfaces. The final stable flux values in the GDM, GGDM, O_3^{20}-GGDM, O_3^{40}-GDM, O_3^{40}-GGDM, and O_3^{80}-GGDM units were 0.18, 1.17, 0.85, 0.67, 0.97, and 0.98 L $m^{-2}h^{-1}$ (LMH), respectively. These results suggest that pre-treatment significantly increased the productivity of the GDM filtration and that: (i) the productivity increased non-linearly but monotonically with ozone dosage; (ii) GAC adsorption significantly helped increasing the GDM flux.

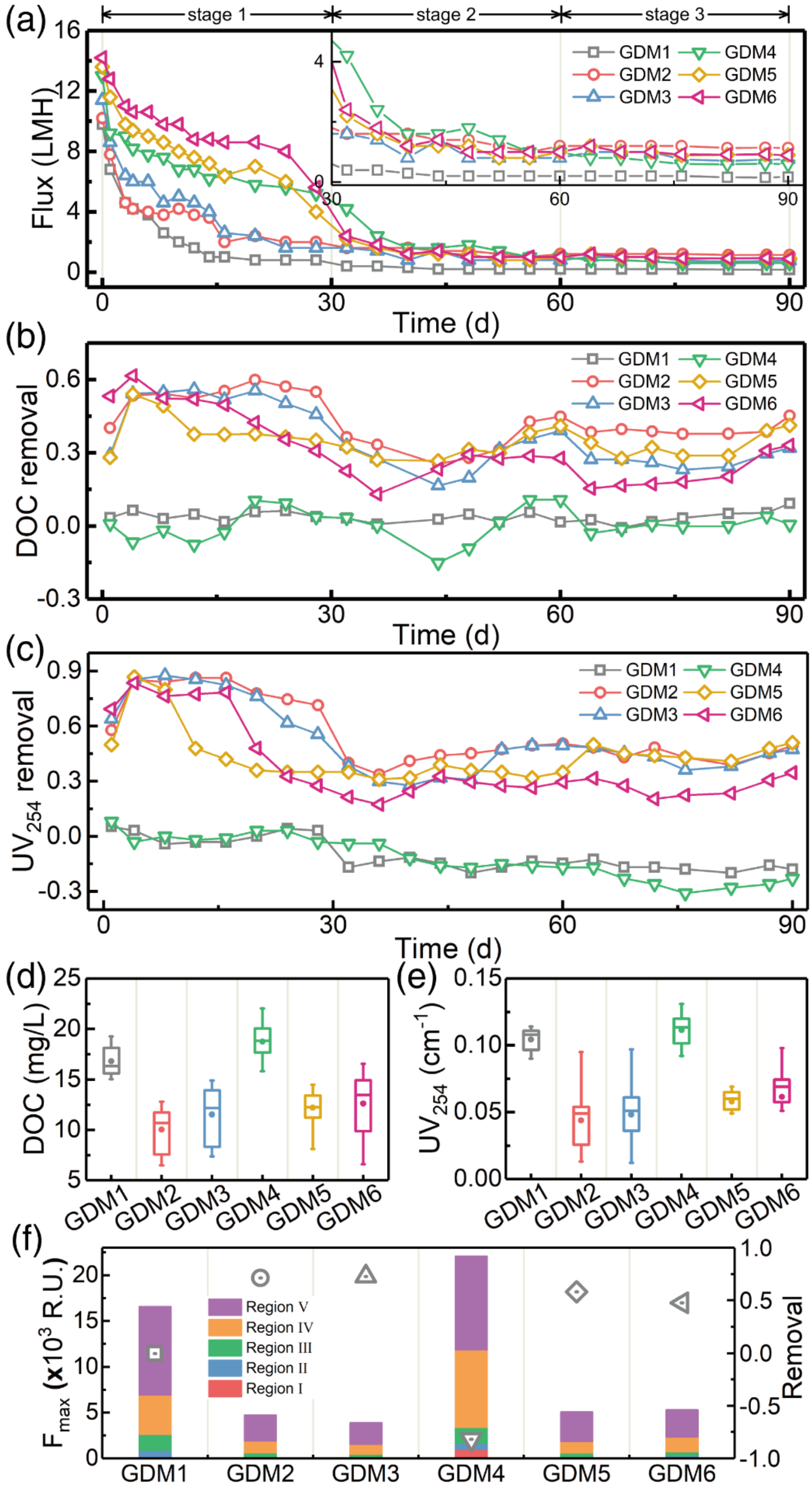

Fig. 1. (a) Flux profile; (b) DOC removal; and (c) UV_{254} removal measured in the six GDM systems. Values of (d) DOC, (e) UV_{254} in the six effluents. (f) Removal rate and

content of fluorescent organics in the effluent of the six systems. GDM1, GDM2, GDM3, GDM4, GDM5, and GDM6 represent control GDM, GGDM, O_3^{20}-GGDM, O_3^{40}-GDM, O_3^{40}-GGDM, and O_3^{80}-GGDM units, respectively.

Fig. 1b and Fig. 1c present the variation of DOC removal and UV_{254} removal rates in the six GDM systems. This rate decreased firstly, then increased, and gradually stabilized. The gradual decrease of GAC adsorption sites is considered to be the main reason for the decline of removal rate in the initial stage; note that the two systems that did not comprise an adsorption process had near zero organics removal in the beginin of the experiments. On the other hand, the increase in removal rate in the second part of the tests may be attributed to the enhancement of microbial degradation and the formation of denser membrane fouling layers (Tang et al., 2021c; Tang et al., 2021d). Instead, the control GDM system and the O_3^{40}-GDM system (no GAC adsorption) showed no or decreasing removal rates of organics components, which reached netagive values for UV_{254} compounds.

Overall, these observations also support the conclusion that O_3 degraded macromolecular organics into low molecular weight fractions which, when not pre-adsorbed, could directly and more easily pass through into the permeate or undergo biodegradation within the fouling layers, thus further enhancing the passage through the membrane pores. Fig. 1f presents the composition and the relative content of fluorescent organic compounds in the effluent of the six GDM systems. The four

GGDM systems were associated with fluorescent organic compounds (47.6-72.8%). However, the removal rate of fluorescent organic compounds, indicative of soluble microbial by-product-like matters, was negative in the O_3^{40}-GDM system. A factor that should also be considered when analyzing removal results is the phenomenon of concentration (Tang et al., 2021a). Since our GDM systems were based on dead-end filtration, contaminants would be concentrated in the reactor and this concentration would be more important for systems associated with higher flux values. We assessed the DOC value in the GDM reactors. (Fig. 1d and Fig. 1e): adsorption effectively reduced the amount of organics in the feed streams to the membranes, and this amount was the highest in the O_3^{40}-GDM system, thus also contributing to a more challenging separation and overall negative values of organics removal. Not surprisingly, the higher the productivity of the systems the larger was the observed DOC concentration.

To summarize, pre-ozonation produced improvied productivity in GDM filtration systems, which in fact increased as a function of oxonation strength. Smaller and more biodegradable organic compounds in the oxidized effluent would translate into a somewhat facilitated passage of organics into the permeate stream, also exacerbated by faster solubilization within the fouling layer. When adsorption of the oxidized effluent was included as an intermediate pre-treatment step, a higher removal rate of organics was consistently obtained compared to the treatment of the raw effluent without pre-ozonation. As suggested by these results, different properties and a different composition of the membrane fouling layers should be expected following the different pre-treatment combinations, as fouling layers are a direct consequence of feed stream characteristics and water flux values.

3.2 Characteristics of membrane fouling layers

Fig. S4, Fig. S5, and Fig. 2 present surface and cross-sectional micrographs of fouled membrane samples collected from the six GDM systems. A dense fouling layer was always observed, also corroborated by the fact that the typical IR peaks of virgin PVDF membrane disappeared in the FTIR spectra of fouled membranes (Fig. S6c). The layer thickness and roughness were the largest for the control GDM unit, while the distribution on the surface was very uneven. In addition, some pollutants were also deposited within the membrane pores. Compared with GDM and GGDM, the fouling layers of O_3-GDM systems were consistently thinner.

As summarized in Fig. S6a, the membrane fouling resistance of GDM systems is mainly reversible, with reversibility accounting for above 90% of the total resistance value. The pure water contact angles of fouling layers (Fig. S6b) indicated that pre-ozonation increased the hydrophilicity of the fouling layers by increasing the hydrophilicity of pollutants, while simultaneously GAC adsorption decreased the hydrophilicity of the fouling layers by absorbing hydrophilic pollutants.

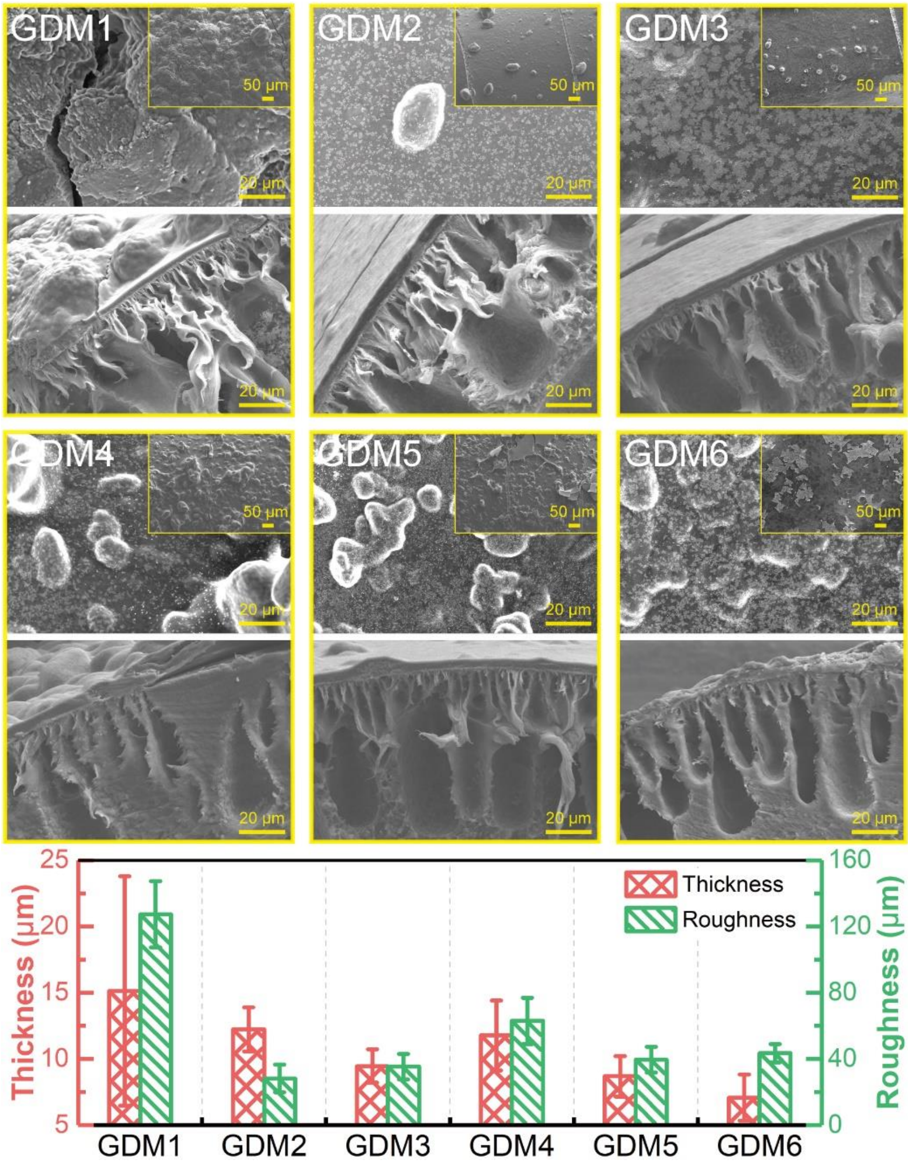

Fig. 2 Surface (top; 500 × and 100 ×) and cross-sectional (bottom; 500 ×) micrographs of the fouled membrane samples from the six GDM systems, as well as thickness and roughness values measured for the membrane fouling layers. GDM1, GDM2, GDM3, GDM4, GDM5, and GDM6 represent control GDM, GGDM, O_3^{20}-GGDM, O_3^{40}-GDM, O_3^{40}-GGDM, and O_3^{80}-GGDM units, respectively.

The results presented in Fig. 3a suggest that the accumulation of overall organic contaminants on the membrane of control GDM and O_3^{40}-GDM systems was the lowest and the largest, respectively. This observation is corroborated by the amount of EPS detected on the membranes and by the EEM analysis (Fig. 3b, c). The EPS content of the fouling layer in the four O_3-GDM systems was higher than that observed in GDM and GGDM units, and highest in the O_3^{40}-GDM unit. The same conclusion can be also drawn for fluorescent organic compounds. In particular, thse compounds were distributed in region II (aromatic protein) and especially in region IV (soluble microbial by-product-like matters), suggesting the important contribution of transformation phenomena occurring within the fouling layer.

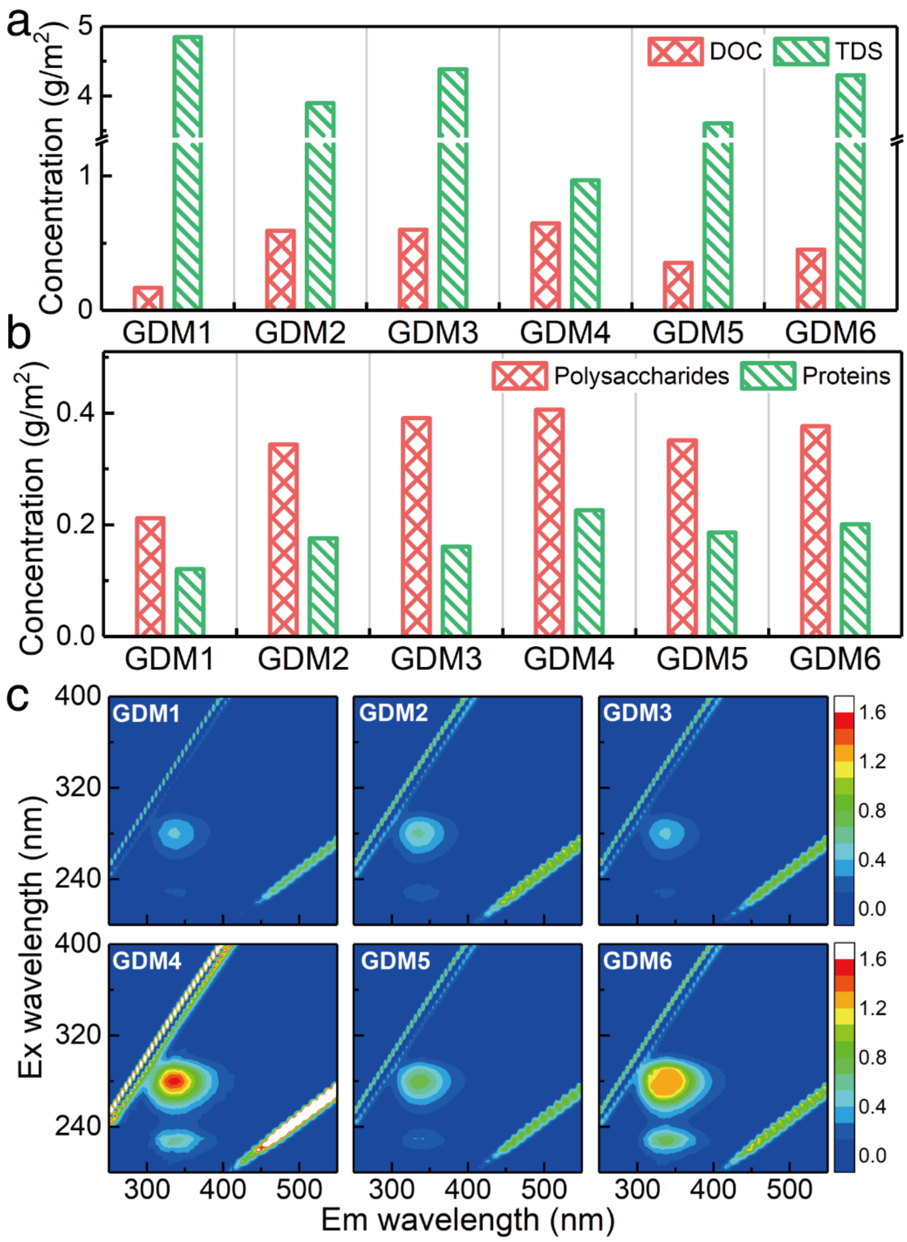

Fig. 3 Concentration of (a) DOC and TDS, (b) EPS (includes polysaccharides and proteins) in the fouling layers. (c) EEM spectra of compounds in the fouling layers. GDM1, GDM2, GDM3, GDM4, GDM5, and GDM6 represent control GDM, GGDM, O_3^{20}-GGDM, O_3^{40}-GDM, O_3^{40}-GGDM, and O_3^{80}-GGDM units, respectively.

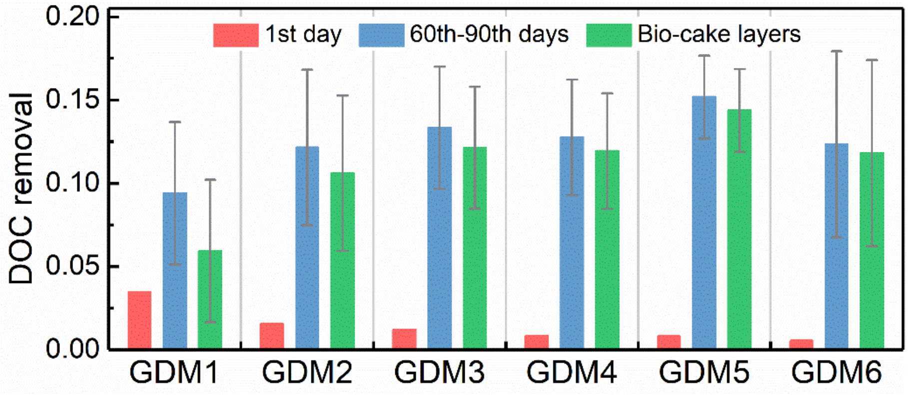

Fig. 4 DOC removal of UF membrane of six GDM systems at 1st day and 60th-90th days of operation and DOC removal of fouling layers at 60th-90th days. GDM1, GDM2, GDM3, GDM4, GDM5, and GDM6 represent control GDM, GGDM, O_3^{20}-GGDM, O_3^{40}-GDM, O_3^{40}-GGDM, and O_3^{80}-GGDM, respectively.

The relative DOC removal rates of UF membranes can be obtained from the varying concentrations of DOC in the reactor and effluent at any time to understand the role of fouling layers as they form during operation (Fig. 4). The fouling layers perform three functions, namely., physical interception, adsorption, and biodegradation, which increase the contaminants removal in GDM systems (Tang et al., 2021d). Specifically, the DOC removal attributable to the fouling layer can be estimated by subtracting the DOC removal of the 1st day (no fouling layer present) from that observed during the stable flux stage (days 60-90) . The DOC removal of the fouling layer was 5.9% and 10.6% in control GDM and GGDM systems, respectively. This parameter was significantly higher in all units treating pre-ozonized streams. As mentioned above, the thickness of the fouling layer of GDM and GGDM was thick and one would expect higher DOC removal by physical exclusion. Therefore, the higher DOC removal assessed in the four O_3-GDM systems might be attributed to the higher biodegradation function of the fouling layers. In our work, we did not directly appraised the relative proportion of physical interception and biodegradation mechanisms resulting in organic removal. However, previous research indirectly determined the importance of these phenomena by adding biological inhibitors, such as sodium azide (Tang et al., 2021d), with results consistent with the present observations.

3.3 Microbial diversity analysis

The number of effective sequences, alpha diversity indexes, OUTs, and rarefaction curves for microbial communities in the raw water and in the fouling layer of the six GDM systems are presented in Table 3 and Fig.S7. The richness and diversity of microbial communities in the raw water were higher than those on membranes. The coverage values and rarefaction curves suggested the sequencing depth were sufficient.

Principal component analysis (PCA) at OUT level (Fig. S8) provides information on the affinity relationships of microbial community between the raw water and the fouling layers in the six GDM systems, as well as among the six GDM systems. The microbial community composition in the raw water was vastly different from that observed in the samples from the six GDM systems, indicating new dominant microorganisms had been formed in the filtration reactors. Also, pre-ozonation seemed to have a large effect in the microbial community. The microbial community compositions from the four GDM systems treating pre-ozonized SGW as feed water were all similar, but different from the composition of the other two GDM systems This result also indicates that GAC had little effect on the microbial community.

Table 3 Number of effective sequences, OTUs, alpha diversity indexes for microbial communities in the raw water and on the membrane of the six GDM systems.

Sample Name	Number of effective Sequences	OTUs at 97% identity	Shannon	Chao	Coverage
Raw water	36178	316	3.83	334.6	0.9988
GDM1	36064	115	2.50	119.2	0.9996
GDM2	30672	113	2.68	121.3	0.9994
GDM3	28903	88	2.52	107.4	0.9993
GDM4	29351	62	2.75	66.2	0.9997
GDM5	29713	92	2.93	105.0	0.9994
GDM6	24814	81	3.01	84.0	0.9997

Fig. 5a and Fig. 5b show the microbial community composition at the phylum and genus level, respectively. *Proteobacteria* (44.1%), *Firmicutes* (17.5%), *Campilobacterota* (8.4%), *Desulfobacterota* (5.9%), and *Bacteroidota* (4.2%) were the major phyla in the raw water, comprising 80.1% of bacteria. After operation, *Proteobacteria* (74.8%-86.5%) and *Bacteroidota* (5.6%-18.2%) became the absolute dominant microbial phyla in GDM reactors. The major genera in the raw water were *unclassified_o_Rhizobiales*, *norank_f_Izemoplasmataceae*, *Parvibaculum*, *Sulfurospirillum*, and *Desulfuromonas*. A large amount of relatively low abundance microorganisms (<0.5%) was enriched in GDM systems, like *Porphyrobacter* (4.8-32.8%), *Roseovarius* (7.0-23.2%), *unclassified_f_Rhodobacteraceae* (0.8-33.3%), *SM1A02* (3.6%-9.4%), *Pyruvatibacter* (0.6%-13.0%) and *Rehaibacterium* (0.5-15.2%). Some research showed that members of *Porphyrobacter* can degrade organics, such as polycyclic aromatic hydrocarbons (Balázs et al., 2020; Fan et al., 2016). *Roseovarius*, as an iodine oxidation bacterium, can promote the formation of large amounts of iodinated organic compounds (Almaraz et al., 2020). *Rhodobacteraceae* were widely reported in various environments with ability of degrading organic matter and removing nitrogen (Chen et al., 2021; Ma et al., 2020). Some works proved that *Pyruvatibacter* as a halophilic bacterium can degrade acetoacetic acid and pyruvate (Wang et al., 2016). *Rehaibacterium* was reported as a thermotolerant, halophilic, and strictly aerobic bacterium with the function of degrading some organic compounds (Yu et al., 2013).

In this work, O_3-GDM systems had their own characteristic microorganisms. Specifically, *Porphyrobacter* and *norank_c_Gammaproteobacteria*, were enriched in the two GDM systems treating non-ozonized SGW as feed water. *Thalassospira* (5.0-15.5%), *Pyruvatibacter* (3.2-13.0%), and *Erythrobacter* (7.2-10.9%) were enriched in three of the O_3-GDM systems. It was reported that some species of *Thalassospira* can degrade quaternary ammonium compounds, which are often used as biocides in SGW (Acharya et al., 2020). *Pyruvatibacter* as an aerobic marine bacterium can degrade some organics, such as pyruvate (Wang et al., 2016). As aerobic phototrophs, *Erythrobacter* often exist in organic-rich environments, and can degrade PAHs, one of the main organic pollutants in SGW (Butkovskyi et al., 2017; Kahla et al., 2021).

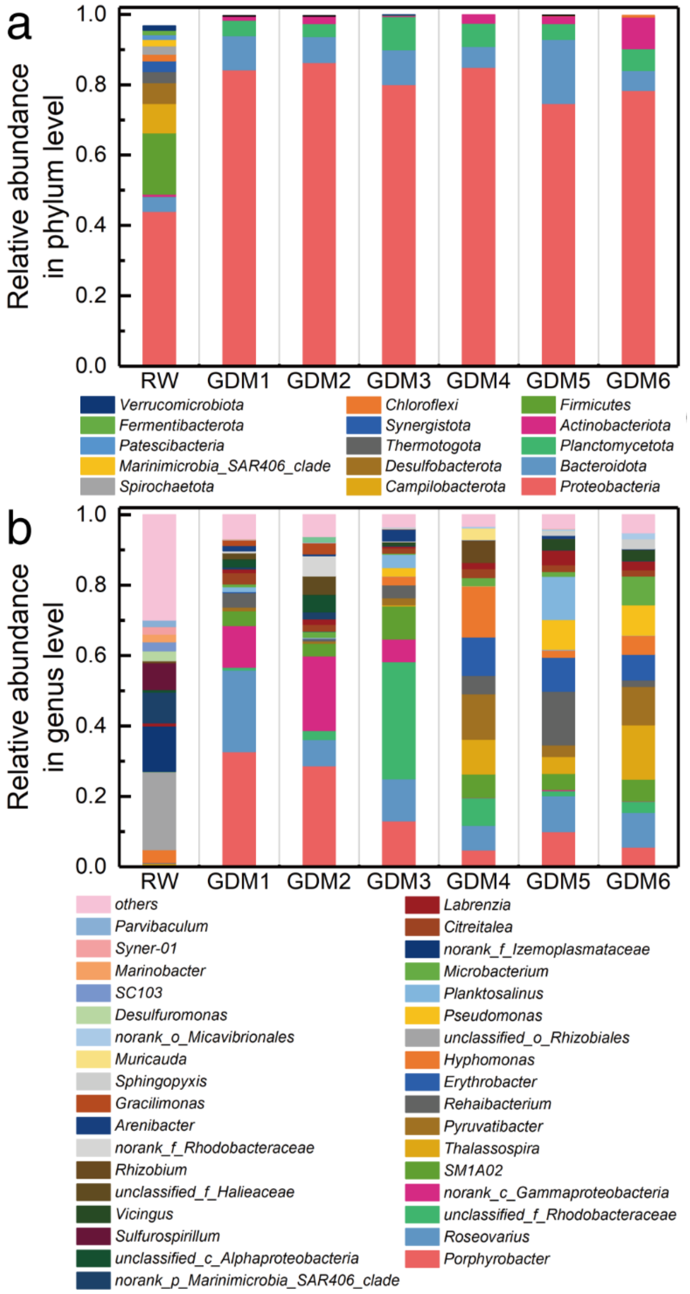

Fig. 5 Bacterial community compositions at (**a**) the phylum (> 1%) and (**b**) the genus level (> 1.5%) in raw water and on the membrane of the six GDM systems. GDM1,

GDM2, GDM3, GDM4, GDM5, and GDM6 represent control GDM, GGDM, O_3^{20}-GGDM, O_3^{40}-GDM, O_3^{40}-GGDM, and O_3^{80}-GGDM units, respectively.

3.4 Summary on mechanisms and effect of pre-ozonation on GDM systems and desalination

The rapid decline of flux in GDM system should be attributed to the blocking of membrane pores by the rapid formation of dense fouling layer (Fig. 1 and Fig. 2). Pre-ozonation significantly increased the initial flux (245%) but deteriorated the quality of effluent water in terms of DOC concentration (−14%) (Fig. 1). These results are mainly attributed to the conversion of macromolecular organics to low fractions by pre-ozonation (Fig. 1 and Fig. 4). EPS played an important role in flux development of GDM, and a large number of studies found negative correlation between EPS content and stable flux (Pronk et al., 2019; Tang et al., 2021d). However, some contradictory results were observed in this study. O_3-GDM system had higher EPS concentration compared to GDM (Fig. 3), while the stable flux of O_3-GDM system was 3.7 times of GDM. This observation suggests that there were other factors that played roles in stabilizing the flux. Compared with GDM, it was observed that the thickness of the fouling layer of O_3-GDM system was thinner, the hydrophilicity of the fouling layer was higher, and biodegradation ability of the fouling layer was enhanced (Fig. 2, Fig. S6, and Fig. 4). All these factors might play a positive function in the improvement of stable flux. However, we hypothesize that the reduction of organics molecular size may be the main result of pre-ozonation that increased the stable flux.

Compared with GDM, GGDM had higher stable flux (637%), likely because GAC adsorption reduced the concentration of organic matters blocking membrane pores. For GGDM systems, pre-ozonation also markedly increased the flux (198%) in the first month of operation. Pre-ozonation improved the stable flux by reducing organics molecular size and GAC adsorption improved the stable flux by reducing the concentration of organic matters blocking membrane pores, also simultaneously improving the quality of the effluent.

The permeate of the six GDM systems was collected and fed individually to the RO system to study the effect of pretreatment on RO performance. The RO flux was higher when treating effluents that were previously ozonized, despite the fact the the DOC level in these streams was not necessarily lower than that from the control system (Fig. 6). Considering that the RO unit was operating in dead-end mode, the observed increase (9%) can be considered significant (Chang et al., 2019a). Some research found that pre-ozonation reduced RO membrane fouling by improving the hydrophilicity of foulants and weakening the adhesion forces between foulants and the membrane and among foulants (Yin et al., 2020a,b). Furthermore, the use of GAC significantly increased the flux of GDM-RO (13.6%) and slightly improve the flux of O_3-GDM-RO. GAC adsorption may further reduce RO membrane fouling by decreasing the overall content of organic foulants (Monnot et al., 2017). Table S1 presents the effluent quality of six GDM-RO systems and indicates that within the range of errors, the water quality of the six systems was almost the same. In general, O_3-GDM outperformed GDM in terms of productivity.

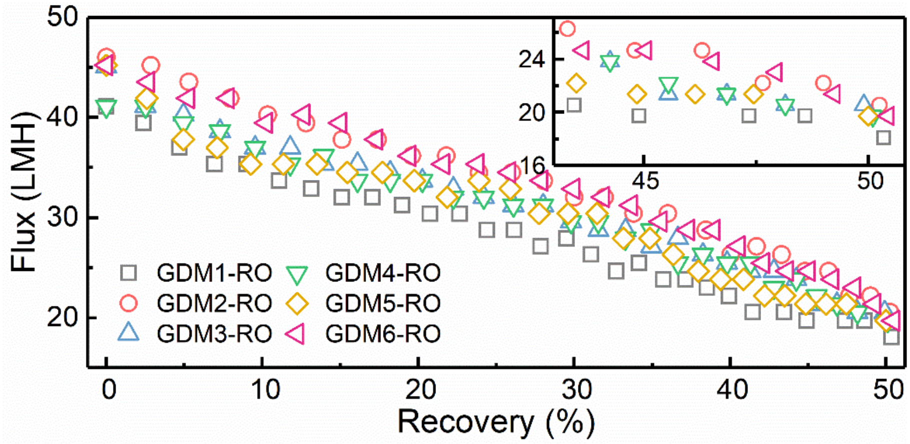

Fig. 6 Effect of pretreatments on the RO desalination performance. GDM1, GDM2, GDM3, GDM4, GDM5, and GDM6 represent control GDM, GGDM, O_3^{20}-GGDM, O_3^{40}-GDM, O_3^{40}-GGDM, and O_3^{80}-GGDM units, respectively.

4. Conclusions

Pre-ozonation was investigated in combination with GAC adsorption and with GDM system to treat SGW. Pre-ozonation changed the properties and molecular weight of organic compounds. Macromolecular organics are oxidized by ozonation to low fractions organics, which have a lower fouling tendency, can more easily pass through the membrane pores, and can be more readily biodegraded the the microorganisms in the fouling layers. At the same time, the decrease of the molecular weight of organic matter also led to the deterioration of the effluent quality of O_3-GDM in terms of organic content. The higher concentration of organic compounds in the feed solution and the laerger amount of EPS in the fouling layers of O_3-GDM systems may be the reason why the stable flux of the systems treating ozonized effluents without adsorption was lower than that of systems including GAC. A large number of microorganisms with the ability to degrade organics and of denitrification were generally enriched in the membrane fouling layer. The O_3-GDM systems had distinct core microorganisms that may help degrade characteristic organic compounds in SGW, such as quaternary ammonium compounds and PAHs. The contribution of microorganisms in the degradation of organic matter needs further investigation.

Supporting Information

The Supporting Information is available free of charge on the website.

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