



Article Mitigation Mechanism of Membrane Fouling in MnFeOx Functionalized Ceramic Membrane Catalyzed Ozonation Process for Treating Natural Surface Water

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Abstract: In order to efficiently remove NOMs in natural surface water and alleviate membrane pollution at the same time, a flat microfiltration ceramic membrane (CM) was modified with MnFeO_X (Mn-Fe-CM), and a coagulation-precipitation-sand filtration pretreatment coupled with an in situ ozonation-ceramic membrane filtration system (Pretreatment/O₃/Mn-Fe-CM) was constructed for this study. The results show that the removal rates of dissolved organic carbon (DOC), specific ultraviolet absorption (SUVA) and NH_4^+ -N by the Pretreatment/O₃/Mn-Fe-CM system were 51.1%, 67.9% and 65.71%, respectively. Macromolecular organic compounds such as aromatic proteins and soluble microbial products (SMPs) were also effectively removed. The working time of the membrane was about twice that in the Pretreatment/CM system without the in situ ozone oxidation, which was measured by the change in transmembrane pressure, proving that membrane fouling was significantly reduced. Finally, based on the SEM, AFM and other characterization results, it was concluded that the main mitigation mechanisms of membrane fouling in the Pretreatment/ O_3 /Mn-Fe-CM system was as follows: (1) pretreatment could remove part of DOC and SUVA to reduce their subsequent entrapment on a membrane surface; (2) a certain amount of shear force generated by O_3 aeration can reduce the adhesion of pollutants; (3) the loaded MnFeO_X with a higher catalytic ability produced a smoother active layer on the surface of the ceramic membrane, which was conducive in reducing the contact among Mn-Fe-CM, O₃ and pollutants, thus increasing the proportion of reversible pollution and further reducing the adhesion of pollutants; (4) Mn-Fe-CM catalyzed O_3 to produce ·OH to degrade the pollutants adsorbed on the membrane surface into smaller molecular organic matter, which enabled them pass through the membrane pores, reducing their accumulation on the membrane surface.

Keywords: ceramic membrane filtration; in situ ozone oxidation; transmembrane pressure; membrane pollution

1. Introduction

As a result of the superior demand for improving the quality of drinking water in daily life and the raw water used in industrial manufacturing, such as the biopharmaceutical or food industries [1], some advanced treatment methods similar to membrane filtration and advanced oxidation have been widely applied to remove more traditional



Citation: Guo, H.; Chi, Y.; Jia, Y.; Li, M.; Yang, Y.; Yao, H.; Yang, K.; Zhang, Z.; Ren, X.; Gu, P.; et al. Mitigation Mechanism of Membrane Fouling in MnFeOx Functionalized Ceramic Membrane Catalyzed Ozonation Process for Treating Natural Surface Water. *Separations* **2022**, *9*, 372. https://doi.org/10.3390/ separations9110372

Academic Editor: Piotr Paweł Wieczorek

Received: 18 October 2022 Accepted: 9 November 2022 Published: 15 November 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and emerging pollutants from water or wastewater, for example antibiotic contaminants [2]. Trimethoprim (TMP) is a common antibiotic drug, which is difficult to biodegrade using conventional water treatment processes and it can accumulate and spoil the ecosystem. TMP has been commonly detected in natural rivers, lakes and wastewater plants and poses a threat to human health and the safety of ecosystems. Moreover, some natural organic matters (NOMs), such as macromolecular polysaccharides and proteins etc., also need to be removed to reduce the generation of disinfection by-products (DBPs) during the disinfection process. However, some NOMs can be deposited on the surface of the membrane through both the adsorption bridging and the net capture to form a gel layer in the membrane filtration process, leading to membrane pollution, and a decrease in both the permeate flux and the lifespan of the membrane [2]. As one of the most widely used advanced oxidation technologies, ozonation is applied to alleviate membrane fouling due to the strong degradation ability of the organic foulants, generally through an in situ combination of ozonation and membrane filtration; especially in the Al_2O_3 (ceramic membrane), which possesses stronger stability, wider availability and a lower cost when compared to other ceramic membranes (e.g., SiO_2 and ZrO_2). Moreover, due to a good mechanical strength and a particular ability to catalyze ozone, the in situ ozonation, along with the Al_2O_3 ceramic membrane filtration, enhances the removal efficiency of organic pollutants and the lifespan of the membrane. The results of Song et al. [3] show that the addition of O_3 in the in situ catalytic ozonation and the Al_2O_3 membrane filtration can increase the removal efficiency of COD and UV_{254} by 20% and 18% when compared with ozonation alone, demonstrating an improved NOM removal performance and a particular catalytic ability of the Al_2O_3 ceramic membrane for ozone. However, the catalytic ability of pristine ceramic membranes was relatively low, resulting in a limited increase in the degradation of the organic pollutants. Karnik [4] et al. loaded iron oxide nanoparticles onto ceramic membranes to catalyze O_3 to generate OH on the membrane surface, which not only improved the pCBA removal efficiency, but also significantly reduced membrane contamination. Cheng [5] et al. and Corneal [6] et al. used manganese oxide as a loading layer on ceramic membranes for in situ catalytic O_3 oxidation to obtain the enhanced removal of organics and the mitigation of membrane contamination. In our previous studies, Mn-Fe binary oxides (MnFeOx) were used to modify the pristine ceramic membranes to further improve its catalytic ozonation ability, which obtained a better removal and degradation ability for antibiotic contaminants similar to trimethoprim (Shown in Figure S4) [7]. The anti-membrane fouling ability and cyclic usage performance of the ceramic membrane were also strengthened, resulting in a longer lifespan of the membrane to a certain extent. However, when compared to normal pristine membrane filtration the major substance and characteristic (reversibility), and formation mechanism of membrane fouling in the combined process change due to the participation of the ozonation oxidation, which needs to be further studied.

Not only can in situ catalytic ozonation and the membrane filtration process can not only retain NOMs, bacteria and other organic mixture matter, but they can also remove or degrade emerging organic pollutants in water, and it is for these reasons that its application in the field of advanced surface water treatment for good-quality drinking water has gradually increased in recent years [2,3]. However, some researchers have discovered that [4,5], when the transmembrane pressure is rapidly increased this results in the ceramic membrane needing to be continuously cleaned at its actual surface during water treatment with the combined catalytic ozonation and membrane filtration process. This is due to raw water containing numerous NOMs, which can block the pore or channel of the ceramic membrane and greatly increasing the cost of water treatment. Therefore, it is necessary to explore a novel and efficient method that can shorten the membrane cleaning cycle. The pretreated methods, such as coagulation–precipitation–sand filtration, can remove some macromolecular suspended solids, colloidal substances, dissolved organic substances, etc., in the raw water, which can reduce the pressure on the ceramic membrane filtration [7,8]. In addition, the oxidation degradation rate and the ability of the combined catalytic ozonation and membrane filtration process are influenced by the operation conditions, such as ozone concentration and flow velocity, which have a significant effect on the formation of membrane fouling. Consequently, a suitable pretreated method and operation conditions should be determined, and their influence mechanism on the membrane fouling also needs to be further studied.

Therefore, to address the need for efficiently removing TMP and NOMs in natural surface water and to alleviate membrane pollution at the same time, the treatment process of coagulation–precipitation–sand filtration pretreatment coupled with an in situ ozonation-ceramic membrane filtration was used for the advanced treatment of real surface water in this study. The removal efficiency of typical organic matters in the surface water under different ozone concentrations was studied. The main substance and character of MnFeOx functionalized ceramic membrane fouling with different combined treatment process systems under different operation conditions were observed and analyzed through scanning electron microscope (SEM) and atomic force microscope (AFM). Based on the removal and membrane fouling results, the mitigation mechanism of the combined treatment systems and operation conditions on membrane fouling was comprehensively analyzed, which provided a theoretical basis for the application of the combined in situ ozonation-membrane filtration system in practical surface water treatment for drinking water, and a new idea for effectively controlling membrane fouling.

2. Materials and Methods

2.1. Materials

The Al₂O₃ flat ceramic membrane used in this experiment was purchased from Shenzhen Huahuai New Materials Co., Ltd. (Guangdong, China), with a pore size of 100 nm, an effective filtration area of 0.075 m² and a pure water flux of 10 m³/m₂·d. The functionalized ceramic membrane (Mn-Fe-CM) was co-impregnated with ferromanganese nitrate solution and precipitated with high temperature firing, whose detailed fabrication methods are shown in our previous study [9]. The characterization of prepared Mn-Fe-CM, such as SEM and TEM (Figure S1) [10], EDS and XRD (Figure S2) [9], XPS (Figure S3) [5] etc., was added in the supplementary material. Potassium iodide was purchased from Sinopharm Chemical Reagent Co., Ltd of shanghai, China (city, country). The coagulant is 30% polyaluminum chloride. The sand filter material is quartz sand with a particle size of 2 to 4 mm. The natural surface water is taken from Xiaoli Lake of Jiangnan University in Wuxi, and the basic water quality indicators are shown in Table 1.

Index	Raw Water	0 mg/L	0.5 mg/L	1.0 mg/L	2.0 mg/L
pH	7.39	7.32	7.21	7.05	6.86
DOC(mg/L)	7.57	5.98	4.28	3.42	3.05
SUVA (L/mg·m)	1.45	1.42	0.63	0.41	0.25
NH_4^+ -N (mg/L)	0.35	0.28	0.25	0.19	0.12
Fe (mg/L)	0.05	0.05	0.06	0.07	0.09
Mn (mg/L)	0.03	0.03	0.04	0.06	0.08

 Table 1. Variation in each index in the combined process under different ozone concentration conditions.

2.2. Process Parameter Setting

A small test device of "conventional treatment (coagulation–precipitation–sand filtration)" combined with "O₃-CM" was adopted, and the treated water volume was 2–4 L·h⁻¹. The process is shown in Figure 1. The coagulant was added by the wet method of polyaluminum chloride, the dosage was 12–20 mg·L⁻¹, the low-speed stirring was 20 r/min, and the coagulation time was 30 min; the sand filter column was 1.2 m and the hydraulic retention time was 5–8 min; the dissolved O₃ concentration was 0.5 mg·L⁻¹, the contact time was 20 min, and the exhaust gas was absorbed by 2% KI solution. The influent water enters the membrane module in the way of "external suction and internal pressure". The initial transmembrane pressure was 2.0 kPa, and the membrane flux was $25.0 \pm 2.0 \text{ L/(m}^2 \cdot \text{h})$. During the continuous operation of the reactor, the transmembrane pressure of the ceramic membrane was recorded regularly. The effluent was collected every day, and the dissolved organic carbon (DOC) and specific absorbance UV₂₅₄ to judge the stability of the device operation was measured. Relevant index analysis was focused on by collecting influent water, pretreatment effluent, and ceramic membrane effluent. The membrane cleaning method was performed as follows: a. backwashing, the washing time was 5 min, and the washing intensity was $48.0 \pm 2.0 \text{ L/(m}^2 \cdot \text{h})$; b. chemical cleaning, the membrane after use was soaked in NaOH solution (pH = 11, at a constant temperature 35 °C) for 2 h, and then backwashed with ultrapure water several times for 2 h, and the cleaning intensity was $6.0 \text{ L/(m}^2 \cdot \text{h})$.



Figure 1. Diagram of the combined process device.

2.3. Characterization of Membrane Rejection Performance and Membrane Fouling

The retention performance of the ceramic membranes is mainly characterized by the removal rate of DOC and the specific ultraviolet absorption rate SUVA (SUVA = $UV_{254} \times 100/DOC$) before and after filtration. Membrane fouling is mainly characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM) by scraping the surface of the ceramic membrane before and after use. The water contact angle analysis and BET analysis were used for the hydrophilic characteristic and surface area of the ceramic membranes.

3. Results and Discussions

3.1. Effect of Different Treatment Process on the Removal of DOC, UV_{254} and Fluorescent Substances

The most commonly used parameters that can represent NOM, DOC and SUVA are considered to be closely related to membrane fouling. Generally speaking, surface water with a high SUVA content often contains some hydrophobic organics, e.g., aromatic organics, etc. Water with higher values of SUVA indicates a higher possibility for resulting in membrane fouling [11]. The change in DOC and SUVA concentrations in the effluent of the different combined treatment process is shown in Figure 2. When compared with the initial influent, the concentrations of DOC and SUVA in the effluent of the coagulation–precipitation–sand filtration pretreated system were reduced by 14.2% and 26.7%, respectively. The in situ ozonation/Mn-Fe-CM filtration system (O_3 /Mn-Fe-CM) removal performance without pretreatment for DOC and SUVA were 44.6% and 58.6%, respectively. The addition of in-situ ozonation and the ceramic membrane filtration process after pretreatment further reduced the DOC and SUVA concentrations. Among these combined treatment systems, the combined pretreatment process and the in situ

ozonation/Mn-Fe-CM filtration system (Pretreatment/O3/Mn-Fe-CM) possessed the best removal performance for DOC (51.1%) and SUVA (67.9%). This was because the interception function of the ceramic membrane channel, and the adsorption or electrostatic interaction on the membrane surface or pores, further increased the removal efficiency of organic matters. On the other hand, based on the results of the quenching experiments and EPR tests [7] (shown in Figures S7 and S8) in our previous study, it can be concluded that the direct oxidation of O_3 and the O_3 adsorbed onto the ceramic membrane surface was promoted by Mn-Fe-CM catalytic ozone oxidation, which generates a series of chain reactions to produce more OH and ¹O₂, which can degrade more macromolecular organic matters of NOMs into smaller molecular substances, even to CO_2 and H_2O [10]. The synergistic effect enhanced the removal of organic matter [4,6]. Additionally, the loaded MnFeOx made the ceramic membrane possess a stronger adsorption and catalytic ability, resulting in the best removal performance of the Pretreatment/ O_3 /Mn-Fe-CM system. When compared with the pristine O_3 /Mn-Fe-CM system, the ratios of DOC and SUVA were increased by 6.5% and 9.3%, respectively, which might be due to some organic compounds containing unsaturated bonds and aromatic bonds that can be appropriately removed by the pretreatment of raw water [11]. Additionally, the removal of TMP in the Pretreatment/ O_3 /Mn-Fe-CM system is shown in Figure S4.



Figure 2. Water discharge along the course: (**a**) DOC variation characteristics, (**b**) SUVA variation characteristics.

Fluorescence electron spectroscopy (EEM) is also considered an efficient method to analyze the main components in surface water that can aggravate membrane fouling [10]. Therefore, EEM was used to analyze the fluorescent organic components in the final effluent of the different combined treatment systems. The obtained spectrum can be divided into four regions, namely region I ($E_{x200\sim250}/E_{m200\sim380}$, aromatic protein-like substances), region II ($E_{x200~250}/E_{m380~550}$, fulvic acid-like organic compounds); region III ($E_{x250~280}/E_{m200~380}$, soluble microbial products (SMPs)); region IV ($E_{x250\sim400}/E_{m380\sim550}$, humic substances and their analogues) [6]. As shown in Figure 3, when compared with the initial influent and the effluent after the pretreatment process, the effluent fluorescence intensity for region I and I,I after only adding ozone oxidation, was greatly decreased, indicating that ozone oxidation can effectively reduce macromolecular organic substances, such as aromatic proteins and SMPs-like substances [12]. When combining the results with the transmembrane pressure variation in different combined treatment systems, it can be inferred that the reduction in aromatic proteins and SMPs-like substances by ozonation was an important factor for the mitigation of Mn-Fe-CM membrane contamination. According to Figure 3d, all the fluorescence intensity of the four regions in the effluent of the Pretreatment/ O_3 /Mn-FeCM system was decreased and corresponded with the removal trend of SUVA, indicating that the significant reduction in SUVA in the effluent of O_3 /Mn-Fe-CM is related to the decrease in macromolecular humic analogues and aromatic compounds [13]. All these phenomena proved that the combined Pretreatment/ O_3 /Mn-Fe-CM system had an excellent removal performance for organic matters and a strong ability to mitigate membrane fouling. Hence, the influence of the operation condition was studied and performed with the Pretreatment/ O_3 /Mn-Fe-CM system.



Figure 3. EEM characteristics of effluent along the route, (a) the raw water, (b) the conventional process effluent, (c) the conventional process+ O_3 effluent, (d) the conventional process+ O_3 /Mn-Fe-CM effluent.

3.2. Effect of Ozone Concentration on Removal Performance and Transmembrane *Pressure Variation*

The typical water quality index in the effluent of the combined Pretreatment/ O_3/Mn -Fe-CM system under different ozone concentration conditions was tested, and the results are shown in Table 1. With an increase in ozone concentration, the removal efficiency of DOC, SUVA and NH4⁺-N continually improved. The removal rate of DOC, SUVA and NH_4^+ -N can reach up to 60.0%, 82.8% and 65.7% at an ozone concentration of $2.0 \text{ mg} \cdot \text{L}^{-1}$, which were about 16.6%, 26.2% and 32.4% higher than those at the concentration of $0.5 \text{ mg} \cdot \text{L}^{-1}$. Although the leaching amount of Fe and Mn from Mn-Fe-CM also increased, they were all lower than the national drinking water standard limit of China (Fe \leq 0.3 mg/L, Mn \leq 0.3 mg/L, GB5749-2006). In addition, the Mn-Fe-CM transmembrane pressure was measured to study the influence of O_3 concentration on membrane fouling, and the results are shown in Figure 4. In the ultrafiltration process without ozone oxidation, the transmembrane pressure was increased by about 13.4 kPa within 120 h. When the O₃ concentration was $0.5 \text{ mg} \cdot \text{L}^{-1}$, the transmembrane pressure was increased by about 6.6 kPa during the whole test; however, the transmembrane pressure was only slightly increased by 3.3 kPa at 2.0 mg·L⁻¹ of ozone. Generally speaking, as the ozone concentration continually increased, the growth rate of the transmembrane pressure for the ceramic membrane decreased, indicating that the anti-pollution performance of the membrane improved [14,15]. This was because the bubbles generated by O_3 aeration would generate a certain shear force, which would split the pollutants that were adhered to the ceramic membrane, thereby reducing membrane fouling and increasing the membrane flux [16]. In addition, Mn-Fe-CM catalyzed O_3 to generate more $\cdot OH$ so that the

Pretreatment/O₃/Mn-Fe-CM system, with the stronger oxidizing ability, could degrade the pollutants adsorbed on the membrane surface into smaller molecular organic compounds, thus, enabling them to pass through the membrane pores. Hence, only a small amount of polluted substance was accumulated on the membrane surface [2]. Therefore, the synergistic effect of the in situ O₃/Mn-Fe-CM system not only promoted the degradation of organics on the membrane surface, but also alleviated the membrane fouling to a certain extent [17]. Although the added ozone dose of 2.0 mg·L⁻¹ was not enough to totally control membrane fouling, it could ensure the long-term stable operation of the ceramic membrane. Consequently, the added ozone dose can be appropriately increased to further prolong the operating time of the membrane [18]. Considering the cost and the membrane fouling results, the ozone concentration of 0.5 mg/L was determined as the suitable added dose in the Pretreatment/O₃/Mn-Fe-CM system.



Figure 4. Transmembrane pressure of Mn-Fe-CM under different ozone concentrations in the combined process.

3.3. Analysis of Membrane Fouling during Long-Term Operation

3.3.1. Transmembrane Pressure Variation in Different Combined Treatment Process

As shown in Figure 5, the transmembrane pressure of the Pretreatment/CM system was increased to 12.0 kPa after 40 h without ozone oxidation. If the membrane was not regularly rinsed, the transmembrane pressure would increase faster, indicating that the formation rate of membrane fouling in the Pretreatment/CM system was relatively quick [19,20]. After adding ozone $(0.5 \text{ mg} \cdot \text{L}^{-1})$, the transmembrane pressure in both the Pretreatment/O₃/CM and the Pretreatment/O₃/Mn-Fe-CM systems was only increased to 9.8 kPa and 7.9 kPa, respectively, after a long-term operating time of 120 h. The membrane working time for one time was approximately three times that of the Pretreatment/CM system without the in situ ozonation treatment. According to the flat curve for the growth of the transmembrane pressure, it can be speculated that the generation rate of membrane fouling in both the Pretreatment/ O_3 /CM and the Pretreatment/ O_3 /Mn-Fe-CM systems was quite slower than the Pretreatment/CM system, especially for the Pretreatment/O₃/Mn-Fe-CM system. The nano-scale porous structure of the ceramic membrane can increase the contact probability and the reaction time of the ozone and organic pollutants, thereby enhancing the degradation of the macromolecule organic pollutants, which increases a proportion of the reversible pollution to a large extent, making the membrane flux easier to be recovered by a hydraulic backwashing [16–18]. Our previous study showed that organic matter was not only oxidized in the reactor, but also degraded in the membrane pores [19]. Due to the stronger ability of Mn-Fe-CM for catalyzing ozone, more free radicals can be immediately generated in the inner interface of the membrane pores, which

accelerates the decomposition rate and the extent of the adsorbed organic pollutants in the membrane channels. In this way, the degraded macromolecules easily fell away from the ceramic membrane and the flow resistance induced by the fouling layer in the membrane channel was reduced. All these changes further alleviated membrane fouling in the Pretreatment/O₃/Mn-Fe-CM system [20]. Generally speaking, the combined in situ ozonation and the ceramic membrane with a catalytic function greatly alleviates membrane pollution during the drinking water ultrafiltration process and prolongs the working time of the membrane.



Figure 5. Variation in transmembrane pressure in Pretreatment/CM, and Pretreatment/O₃/CM, and Pretreatment/O₃/Mn-Fe-CM in combined process.

3.3.2. Characterization Analysis and the Anti-Membrane Fouling Mechanism Analysis

SEM and AFM were used to further analyze the main components and characters of membrane fouling in both the Pretreatment/ O_3 /CM and Pretreatment/ O_3 /Mn-Fe-CM systems [21]. Figure 6 shows that obvious contamination layers existed on both pristine CM and Mn-Fe-CM after they were used for 120 h. Some of the membrane pores in pristine CM were completely blocked, while the membrane pores of Mn-Fe-CM can still be clearly observed. It is shown that Mn-Fe-CM had a better resistance to contamination than the unmodified ceramic membranes due to its better ozone catalytic ability. The ozonation action can reduce the molecular weight of the organic matter and can increase the hydrophilicity of the organic matter, thus reducing the retention rate of the membrane [22]. After simple hydraulic flushing with pure water, the membrane flux of pristine CM and Mn-Fe-CM was recovered by 82.4% and 95.7%, respectively, indicating that most of the membrane fouling was reversible, especially for the Pretreatment/ O_3 /Mn-Fe-CM system. However, the corresponding membrane flux in the Pretreatment/CM system was only recovered by about 66%, showing that the addition of ozonation greatly decreased the generation rate and the extent of permanent membrane pollution. The combination of in situ ozone with ceramic membranes, catalyzed ozone decomposition and the accelerated generation of hydroxyl radicals, further enhanced the oxidation of accumulated fouling substance on the membrane surface and in the membrane pores, thus effectively mitigating reversible and irreversible contamination [23–25]. After the substances trapped on the membrane surface were rinsed, the effluent was studied by three-dimensional fluorescence and the results indicated that the filter-cake layer was mainly composed of aromatic-like proteins, SMPs and colloidal substances in the water, which were consistent with the organic pollution removal results of the Pretreatment/ O_3 /Mn-Fe-CM system [26].



Figure 6. SEM characterization of ceramic membranes before and after use in the combined process: (**a**,**d**) are the cross-sections of CM and Mn-Fe-CM before use, (**b**,**e**) are the cross-sections of CM and Mn-Fe-CM after use, (**c**,**f**) are the surfaces of CM and Mn-Fe-CM after use.

AFM was used to study the morphology and roughness of CM and Mn-Fe-CM before and after use, which could veritably reflect the surface contamination of the ceramic membrane. The 3D AFM surface images (Figure 7a–d) shows significant changes in the surface morphology of Mn-Fe-CM film after MnFeOx doping. The roughness of (497 nm) after loading with $MnFeO_x$ was decreased when compared with that of pristine CM (528 nm), indicating that the surface of Mn-Fe-CM became smoother than pristine CM. The change in roughness increases the mass transfer flux of the membrane [27]. This was because the loaded $MnFeO_x$ form a smooth active layer on the membrane surface or the inner-surface membrane channel, which restulted in a better stain resistance [7]. After use for ultrafiltration for 120 h, it was found, from Figure 7b,d, that the surface roughness of used CM was as high as $1.3 \mu m$, about twice that of used Mn-Fe-CM, indicating that a smoother membrane surface greatly reduces the accumulation of pollutants and retard membrane fouling [14,22,28]. When compared with other similar combined in situ ozonation systems in the reported research in Table 2, the Pretreatment/O₃/Mn-Fe-CM system in this study showed a relatively higher degradation efficiency for DOC and SUVA removal and a stronger membrane anti-fouling ability. Moreover, Figure S6 and Table S1 shows the N2 adsorption-desorption isotherms and the BET results of the original CM and Fe-Mn-CM. After MnFeOx loading, the BET surface area and total pore volume of Fe-Mn-CM became $1.6353 \text{ m}^2/\text{g}$ and $0.0096766 \text{ cm}^3/\text{g}$, which was slightly lower than the original CM (1.7401 m^2/g , 0.0095672 cm^3/g). This was due to the deposition of the MnFeOx catalyst on the surface of the ceramic membrane, which blocked some internal voids. The decreased surface area and total pore volume may decrease the contact between Fe-Mn-CM and macro-NOMs to some extent [29]. Water contact angle analysis (Figure S5) shows that the hydrophilicity of Fe-Mn-CM became better when compared to pristine CM, which further decreased the adsorption or adherence of organic matters on Fe-Mn-CM and reducing membrane fouling [21,30,31]. Hence, according to the characterization analysis of membrane fouling and Mn-Fe-CM before and after use, the anti-membrane fouling mechanism for the Pretreatment/ O_3 /Mn-Fe-CM system was mainly ascribed to that Mn-Fe-CM with a smoother and more hydrophilic surface activity layer that reduced the adhesion of pollutants and catalyzed O3 to generate more ·OH, which in turn degraded the pollutants adsorbed on the membrane surface into smaller molecular organic compounds that were able to pass through the membrane pores. Additionally, part of the DOC and SUVA concentrations can be removed by pretreatment to reduce the subsequent entrapment of them on the membrane surface, which also contributes to the better mitigation of membrane fouling in the Pretreatment/ O_3 /Mn-Fe-CM system.



Figure 7. AFM characterization of ceramic membranes before and after use in the combined process: (**a**,**c**) CM and Mn-Fe-CM before use; (**b**,**d**) CM and Mn-Fe-CM after use, (**e**) roughness variation.

Table 2. Removal performance and membrane fouling change in different ozonation-ceramic membrane filtration systems.

Systems	DOC Removal	SUVA Removal	TMP Variation	Membrane Flux Recovery with Simple Hydraulic Flushing
CM $(DOC = 9.0 \text{ mg} \cdot \text{L}^{-1},$ $SUVA = 1.0 \text{ L/mg} \cdot \text{m}, \text{ The ozone}$ $concentration \text{ of } 0.5 \text{ mg} \cdot \text{L}^{-1})$	5.3%	6.1%		
$O_3/CM [7]$ (DOC = 9.0 mg·L ⁻¹ , SUVA = 1.0 L/mg·m, The ozone concentration of 0.5 mg·L ⁻¹)	4.6%	43.0%	Increased 45.4% after 120 h operation	82.4% recovery after 120 min operation
$O_3/Mn-Fe-CM$ (DOC = 9.0 mg·L ⁻¹ , SUVA = 1.0 L/mg·m, The ozone concentration of 0.5 mg·L ⁻¹)	46.7%	58.6%		93.0% recovery after 120 min operation
$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	60.0%	82.8%	Increased 40.0% after 120 h operation	95.7% recovery after 120 min operation

Systems	DOC Removal	SUVA Removal	TMP Variation	Membrane Flux Recovery with Simple Hydraulic Flushing
$O_3/CuMn_2O_4 / CM [9]$ (DOC= 10 mg·L ⁻¹ , SUVA = 0.9 L/mg·m, The ozone concentration of 2 mg·L ⁻¹)	10.0%	81.1%		85.1% recovery after 120 min operation
$\frac{O_3/CMF/BAC [32]}{(DOC = 2.3-4.9 \text{ mg} \cdot \text{L}^{-1},}$ SUVA = 0.058–0.114 L/mg·m, The ozone concentration of 2 mg·L ⁻¹)	47.5%	73.3%	Increased 30.0% after 120 h operation	74.0% recovery after 60 min operation
$\begin{array}{c} O_3/\text{TiO}_2\text{-CM [33]}\\ (\text{DOC} = 5.0 \text{ mg} \cdot \text{L}^{-1},\\ \text{SUVA} = 1.0 \text{ L/mg} \cdot \text{m}, \text{ The ozone}\\ \text{concentration of 8 mg L}^{-1}) \end{array}$	44.0%	80.0%	Increased 40.0% after 60 h operation	70.0% recovery after 10 min operation

Table 2. Cont.

4. Conclusions

A coagulation-precipitation-sand filtration pretreatment, coupled with an in situ ozonation-ceramic membrane filtration system (Pretreatment/O₃/Mn-Fe-CM) was constructed to efficiently remove pollutants in natural surface water and to help alleviate membrane pollution. The results indicated that pretreatment of raw water could appropriately improve the removal ability of the combined process for organic compounds containing unsaturated bonds and aromatic bonds. The Pretreatment/O₃/Mn-Fe-CM system can effectively remove macromolecular organic compounds, such as aromatic proteins and SMPs, whose removal rates for DOC and SUVA were 51.1% and 67.9%, respectively. Additionally, with an increase in the ozone concentration, the removal efficiency of the organic matter continued to increase, and the growth rate of the transmembrane pressure decreased accordingly. When the ozone concentration was $0.5 \text{ mg} \cdot \text{L}^{-1}$, the working time of Mn-Fe-CM was about double that without the in situ ozone oxidation, effectively mitigating membrane fouling. AFM and SEM characterization further confirmed that aromatic-like proteins, SMPs and colloidal substances played an important role in membrane fouling. Most membrane fouling was reversible in the Pretreatment/O₃/Mn-Fe-CM system and 95.7% of the membrane flux could be recovered after hydraulic cleaning. In the Pretreatment/ O_3 /Mn-Fe-CM system the bubbles generated by O_3 aeration could form a certain shear force reducing the adhesion of pollutants on the membrane surface, thereby improving the membrane flux. In addition, Mn-Fe-CM catalyzed O_3 to produce OH, which has a strong oxidation capacity to decompose macromolecular organic substances into smaller molecular substances that can pass through the membrane pores. The formation of an active loading layer allowed for a smoother membrane surface, thus, reducing the adhesion of organic substances. The synergistic effect of in situ ozonation and Mn-Fe-CM greatly reduced membrane pollution and verified the feasibility of the process for practical water treatment.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/separations9110372/s1, Figure S1: Characterizations of CMs (a) SEM image of pristine CM, (b) and (c) SEM images of Mn-CM and Fe-CM, (d) and (e) the surface of Mn-Fe-CM, (f) the cross section of Mn-Fe-CM, (g) and (h) TEM of Mn/FeOx, (i) the cyclic voltammetry of CMs, Figure S2: (a) The EDS and (b) XRD image of modified-ceramic membrane, Figure S3: XPS spectra of (a) The full survey spectrum, (b) O 1 s spectrum, (c) and (e) Mn 2p spectrum of Mn-Fe-CM before and after catalytic ozonation, (d) and (f) Fe 2p spectrum of Mn-Fe-CM before and after catalytic ozonation, Figure S4: The concentration changes of TMP in the effluent of different processes, Figure S5: The water contact angle of (a) the original ceramic membrane and (b) the Mn-Fe-CM, Figure S6: N₂ Adsorption-Desorption Isotherm of (a) original ceramic membrane and (b) the Mn-FeCM. And the pore diameter distribution of (c) original ceramic membrane and (d) the Mn-Fe-CM, Figure S7: Effect of radical scavengers on the degradation of TMP, Figure S8: EPR spectra in different systems: (a) DMPO-·OH, (b) TEMP-1O2. Table S1: The BET tests of (a) the original ceramic membrane and (b) the Mn-Fe-CM, Text S1: Effectiveness of the combined process on the removal of TMP.

Author Contributions: All the authors contributed to the preparation of this manuscript. H.G. performed all the laboratory experiments and prepared the draft manuscript. Y.C., Y.J., M.L., Y.Y. and H.Y., analyzed the experimental data and reviewed manuscript. K.Y. designed the framework for the experiments. Z.Z., X.R. and P.G. helped with the manuscript preparation. H.M. conceptualized the research and corrected the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would be grateful to the National Key Research and Development Program of China (No. 2019YFC1906303), National Natural Science Foundation of China (42177376), Fundamental Research Funds for the Central Universities (JUSRP122022), and Wuxi Science and Technology Development Funds (No. N20201007).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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