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ABSTRACT

China has just implemented new drinking water quality standards, canceling the provisions detailed in the previous standards that allowed relatively lenient water quality standards in rural areas, and unifying the water quality requirements for urban and rural areas. In rural areas of China, lakes are important sources of drinking water, but their water typically contain high concentrations of organic pollutants. In addition, removal odorous substances from such sources is challening. In response to these issues, an ozone-biological activated carbon-ultrafiltration process is proposed and its efficiency in drinking water treatment is explored. The results indicate that O_3-BAC pretreatment significantly improved the efficiency of the membrane process in removing organic and odor substances. At an ozone dosage of 2 mg/L, with granular activated carbon as filler and an EBCT of 25 min, the ozone-BAC pretreatment allowed removal rates in the membrane system equal to 71.5% of COD_{Mn}, 84.2% of UV_{254}, as well as 92.2% and 92.5% of GSM and 2-MIB, respectively, the latter being typical odor compounds. In addition, the microbial communities in the reactors were evaluated under different pretreatment conditions at different times: microorganisms with specific functions were enriched in different membrane reactors, and some microorganisms contributing to the removal of organic and odorous substances were identified. The effluent from the combined O_3-BAC-UF process consistently met the new requirements for drinking water in China, implying that the combined system has significant potential for practical applications for drinking water treatment in rural areas.

KEYWORDS: Ozone; Biological activated carbon (BAC); Ultrafiltration; Geosmin (GSM); 2-methylisoborneol (2-MIB); Rural drinking water.

1. Introduction

As urbanization continues to progress globally, the development of urban areas has become a focus of attention, while rural areas, especially in developing countries, are facing significant challenges in terms of infrastructure and sanitation facilities (Du et al., 2021). The purity and safety of rural drinking water is a major issue related to the health of the majority of township residents, but also an important indicator of the improvement of rural living standards. In April 1, 2023, China officially implemented the “Standards for Drinking Water Quality” (GB 5749-2022). In these new standards, geographical limits have been eliminated, and the water quality requirements for small centralized water supply and decentralized water supply are no longer divided by the concept of "rural" and "urban" water quality standards. The unification of urban and rural standards means that the improvement of rural drinking water quality faces new challenges and opportunities. Currently, urban drinking water treatment technologies are well-established; they usually combine advanced treatment processes with traditional treatment processes to ensure high quality of urban drinking water (Wu et al., 2023). However, compared to urban areas, rural water supply is generally characterized by difficulties, such as poor water quality of drinking water sources, remote project locations, inadequate project scale, and weak operation and management (Qin et al., 2021). Therefore, providing clean and safe drinking water in rural areas should start with developing reliable, operable, and affordable water treatment systems (Du et al., 2021).

In rural areas of China, lakes serve as an important source of drinking water. However, as the issue of eutrophication in lakes becomes more prevalent worldwide, taste and odor (T&O) contamination resulting from the secondary metabolism of microorganisms has become a serious and widespread issue (Zhang et al., 2019). For the average consumers, T&O represents the main indicator of drinking water safety; therefore, the removal of odor substances is crucial for

successful drinking water treatment and supply (Srinivasan and Sorial, 2011). The primary sources of T&O are cyanobacteria (prokaryotes) and eukaryotic microorganisms, commonly known as "algae", which produce a variety of volatile metabolites with different chemical structures and odor characteristics (Christophoridis et al., 2021; Pivokonsky et al., 2021). Geosmin (GSM) and 2-methylisoborneol (2-MIB) are the most commonly detected T&O compounds in drinking water. They are both saturated cyclo-tertiary alcohols formed as secondary metabolites of actinomycetes and cyanobacteria (Abd El-Hack et al., 2022; Zhang et al., 2020). The odor threshold levels for GSM and 2-MIB are 1.3-4.0 ng/L and 6.3-15 ng/L, respectively (Wert et al., 2014), and are specified in many national drinking water standards. In China, the threshold concentration for both odor compounds in drinking water is 10 ng/L. The main challenges associated with GSM and 2-MIB are their extremely low odor threshold concentration and their persistence in conventional water treatment processes (Srinivasan and Sorial, 2011).

The main objectives of conventional water treatment processes, such as coagulation, sedimentation, and sand filtration, are to reduce the turbidity and the pathogenicity of water, and retain large molecules of organic matter, while also providing some removal of GSM and 2-MIB. Generally, due to the extreme resilience of GSM and 2-MIB to conventional water treatment processes, their removal efficiency is relatively poor (Montiel, 1983; Srinivasan and Sorial, 2011) . Kim et al. (Kim et al., 1997) showed that after coagulation-sedimentation-filtration of raw water, the effluent GSM decreased to 13.8 ng/L with a removal rate of 11.5%, while 2- MIB decreased to 65 ng/L with a removal rate of 20.7%. These results imply that conventional processes are not ideal for T&O removal. Membrane technology, especially ultrafiltration (UF), has shown suitable prospects in rural drinking water treatment because of its high efficiency, small footprint, and ease of operation and maintenance (Du et al., 2021). Due to the porous nature of the UF membrane,

soluble carbon and nutrients, such as ammonia and phosphorus, can pass through the membrane and reach the permeate product, which may result in poor microbial stability of the treated water and poor organic matter removal (Wu, 2019). Furthermore, studies have shown that membrane filtration is not highly effective in removing GSM and 2-MIB (Liato and Aider, 2017). Membrane separation is largely a size-exclusion mechanism, and contaminants that collect on the membrane surface will eventually lead to membrane contamination, reducing filtration efficiency and shortening membrane lifespan (Obotey Ezugbe and Rathilal, 2020). Therefore, proper pretreatment or synergistic processes are necessary to improve the removal efficiency of organic and odoriferous substances from drinking water and to optimize the membrane process.

Biological treatment is a cost-effective and efficient method for removing contaminants from drinking water in rural areas (Neoh et al., 2016; Tang et al., 2022b). Biological activated carbon (BAC) is a popular method for removing micropollutants, organic compounds, taste and odor compounds, and halogenated hydrocarbons (Hamid et al., 2019). The removal of organic matters is achieved through a combination of activated carbon adsorption and biodegradation by microorganisms attached to the carbon. BAC is preferred over granular activated carbon (GAC) as it does not require the disposal of waste carbon and can be used in several reactivation cycles (Hamid et al., 2019; Tak and Vellanki, 2020). BAC has shown to be effective (>80%) in removing GSM and 2-MIB, but its performance is influenced by water temperature, empty bed contact time (EBCT), and the accumulation of attached microbial biomass (Beniwal et al., 2018). BAC primarily targets the biodegradable fraction of dissolved organic carbon (DOC), but has difficulty metabolizing complex, refractory, and non-biodegradable carbon. Therefore, when BAC is used as a separate treatment technology, its efficiency in removing DOC is not satisfactory (Tak and Vellanki, 2020).

To improve the biodegradation of organic matter in BAC treatment, incorporating a chemical oxidation process prior to treatment is recommended (Lee et al., 2009). Ozone, a highly efficient and cost-effective oxidant commonly used in drinking water treatment, has been shown effective in breaking down organic matter into simpler forms and increasing the biodegradable fraction of dissolved organic carbon (Guo et al., 2014). Application of ozone prior to biofiltration has been shown effective in removing GSM, 2-MIB, and DBP precursors and improving biostability (Beniwal et al., 2018; Wang et al., 2019). GSM and 2-MIB have some antioxidant properties due to their saturated cyclic tertiary alcohol structure. Some oxidants such as chlorine, chlorine dioxide, and potassium permanganate are not effective in removing GSM and 2-MIB (Rosenfeldt et al., 2005). Ozone oxidation is more effective than other oxidants (Liato and Aider, 2017), since it act by breaking the double bonds of odor compunds, forming aldehydes, acids and ketones, and disrupting the metabolism of algae (Yuan et al., 2013). In addition, an ozone-BAC pretreatment process can mitigate membrane contamination and extend membrane lifespan by improving water quality and removing suspended matter (Tang et al., 2022b). In this study, the ozone-BAC and the UF processes are combined and applied to rural drinking water treatment testing real raw water from natural sources. The combined process shown in Fig. 1 is evaluated for the removal of organic matter and odor substances, while the influence of filler characteristics and microbial community on the effluent quality is also discussed. In addition, the mitigation of UF membrane fouling under different pretreatment conditions is evaluated.

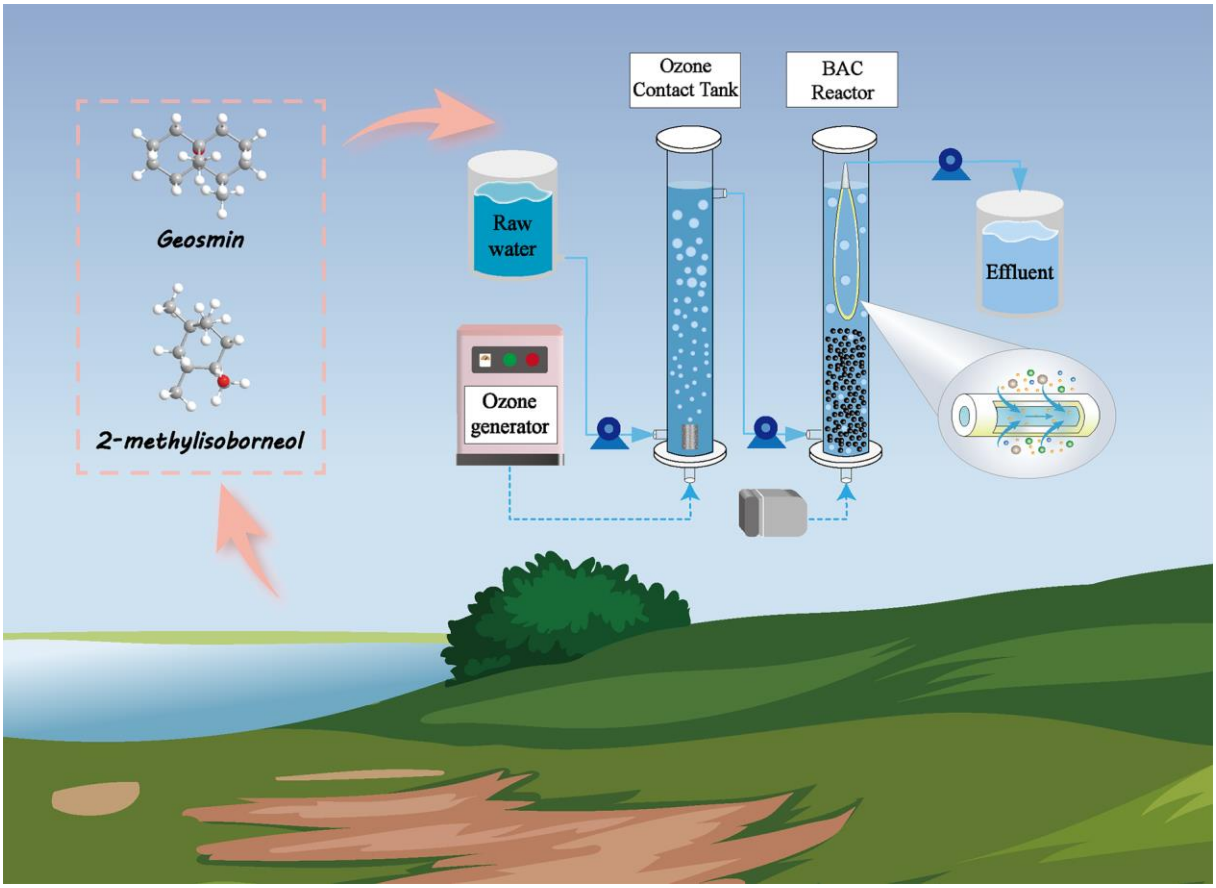

Figure 1. Diagram of the combined system comprising ozonation, BAC, and ultrafiltration.

2. Materials and methods

2.1. Chemical and materials

The raw water used in this study collected from a rural drinking water source reservoir in Zhongxian containing contaminants at low-medium concentrations (Chongqing, China). The standards of the target analytes 2-MIB and GSM were purchased from Sigma-Aldrich (USA). Ozone was generated using an ozone generator (Beijing Tonglin Co., Ltd., China) from dry oxygen (99%, v/v). The granular activated carbon (GAC) had a particle size of 12 × 40 mesh (0.425~1.70 mm) and an iodine value of >950 mg/g, and it was purchased from Calgon Carbon Corporation (USA). The UF system employed a submerged polyvinylidene fluoride (PVDF) hollow fiber UF

membrane module (Litree Purifying Technology Co., Ltd., China). Ultra-pure water (18.25 MΩ cm) (Ulupure, Chengdu, China) was used in this study.

2.2. Methods

2.2.1. Experimental setup

The target feed water concentration for 2-MIB and GSM spiking tests was 100 ng/L. A continuous flow ozone oxidation experiment was performed in a plexiglass contact column with a height of 80 cm and an inner diameter of 4 cm. The ozonated raw water was delivered to a BAC system using a peristaltic Pump (BT-300-2 J, longer Pump, China). The BAC system employed a granular activated carbon column with a height of 15 cm, an inner diameter of 2 cm, and an effective packing height of 4 cm; a schematic diagram of the reactors is shown in Fig. S1 of the Supporting Information (SI). The BAC was operated in up-flow mode to achieve a selected empty bed contact time (EBCT) of 25 minutes. During the BAC column domestication process, the raw water was gradually enriched in the activated carbon carrier by continuous batch feed and gradient dilution, resulting in biofilm formation on the activated carbon over 30 days. Details of the BAC system domestication process can be found in the SI (Text S1). The UF system employed a submerged PVDF hollow fiber UF membrane module. The effective membrane area was 30 cm^2, and the membrane pore size was 11.3-28.8 nm (Tang et al., 2022a). As a first step, UF treatment was conducted using raw water for 2-MIB and GSM removal without pretreatment. Three pretreatment scenarios were then tested: 1) UF receiving the effluent from the ozone treatment only (O_3-UF), 2) UF receiving the effluent from BAC treatment only (BAC-UF), 3) UF receiving combined O_3-BAC effluent (O_3-BAC-UF).

On the 30th day of the operation of the combined system, control experiments were conducted to measure the removal efficiency of T&O compounds at different process stages using a feed water GSM/2-MIB concentration of 100 ng/L. An aeration treatment was performed to determine the removal of T&O compounds from raw water due solely to aeration without pretreatment or ultrafiltration membrane. Similarly, an aeration treatment was performed on the raw water after different pretreatments without ultrafiltration, to determine the aeration-related removal after each pretreatment. The effluent from each process stage was collected to determine the removal rate of T&O compounds. In all cases, the 2-MIB/GSM concentrations in the inlet and outlet water were measured thrice, and the average concentrations of inlet and outlet were calculated to determine the average removal rates of 2-MIB and GSM.

2.2.2. Water quality analysis

The dissolved ozone concentration was determined by the indigo method (Bader and Hoigné, 1981). To measure the concentrations of 2-MIB and GSM, gas chromatography-mass spectrometer and tandem mass spectrometer (GC-MS/MS 8890-7010B, Agilent, USA) coupled with solid phase micro-extraction (SPME) fiber holder and SPME fiber assembly-divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) were employed. The GC/MS was equipped with an HP-5 MS capillary column (30 m × 0.25 mm × 0.25 mm film thickness). The detailed method is described in SI (Text S2 and Table S1). Standard chromatograms and 1-200 ng/L 2-MIB/GSM standard curves are shown in SI, Figure S2. COD_{Mn} was determined based on the protocol described in Water quality-Determination of permanganate index (GB 11892-89). The concentration of total organic carbon (TOC) was measured using a TOC analyzer (TOC-L CPH CN200, Shimadzu, Japan). The pH of the solution was measured by a pH-10 meter (Sartorious Scientific Instruments Co., Ltd., Germany). The values of turbidity and TDS were

181 determined using a turbidimeter (TL2100 Q, Hach Company, USA) and a portable
182 multifunctional meter (Ultrameter II 6PFC, Myron L Company, USA), respectively. The
183 fluorescent organics were determined by a three-dimensional excitation-emission matrix (3D EEM)
184 fluorescence spectrum (F-7000, Hitachi, Japan). UV absorbance was measured at 254 nm in a
185 quartz cuvette with a UV-vis spectrophotometer (Orion AquaMate 8000, Thermo Fisher Scientific
186 INC., MA, USA). Depending on the varied affinities between different resins and organics,
187 nonionic macroporous resins can be used for the fractionation of hydrophobic/hydrophilic organics
188 (Liu et al., 2021). Herein, XAD-8 resin (Supelite, USA) and XAD-4 resin (Amberlite, USA) were
189 used to adsorb hydrophobic and hydrophilic organics, respectively. Water samples were adjusted
190 to pH = 2.0 with 0.1 M HCl and then underwent adsorption in XAD-8 and XAD-4 column resins
191 at a flow rate of 15 times the bed volume per hour (BV/h). Soaking and rinsing were performed
192 with 0.1 M NaOH, 0.1 M HCl, methanol, and ultrapure water, respectively.
193 *2.2.3. Microbial diversity sequencing analysis*
194 Spatial and temporal changes in microbial communities and dominant functional
195 microorganisms were analyzed by sequencing microbial diversity on the BAC or membrane
196 surfaces of the four systems at different times during continuous operation mode. Specifically, 16S
197 rRNA sequencing was performed at day 15 and day 30 after the domestication phase ended. The
198 sequencing was conducted on 2 g of filler samples collected from the BAC-UF reactor and O_3-
199 BAC reactor, located approximately 5 cm from the top (backfilled with an equal amount of filler
200 immediately after removal), and about 2 cm of membrane samples from the UF reactor and O_3-
201 UF reactor (Liu et al., 2022; Tang et al., 2021b; Wu et al., 2023). Details of the microbial diversity
202 sequencing analysis can be found in the SI (Text S3).
203

3. Results and Discussion

3.1. Removal rates of organic matters

During the GAC domestication process, microorganisms presented in water adhere to the GAC surface and form biofilms. The GAC unit process can then effectively remove organic pollutants from water through both adsorption and biodegradation mechanisms, thus potentially prolonging the service life of the GAC material (Yuan et al., 2022a; Yuan et al., 2022b). In this work, DOC, UV_{254}, and COD_{Mn} values of the raw water and effluent streams were measured to characterize the organic matter present in water samples, and EEM was employed to determine the removal rate of various types of organic pollutants. As discussed hereforth, consistent results were obtained in the removal of the three organic matter indicators, overall suggesting the synergistic effect of pre-oxidation, BAC adsorption and biodegradation, and surface retention by membranes.

In detail, Fig. 2a and 2b present the DOC values and their average removal rates during the operation of the four investigated systems; please refer to chapter 2.2.1 for a description of the systems. The BAC-UF and O_3-BAC-UF systems gradually reached stabilization during the domestication period. During the operational period, the membrane filtration alone was not effective in removing DOC, with an average removal rate of only 21.7%, and the effluent quality fluctuated significantly in correlation with changes in raw water DOC. When BAC was as pretreatment, with or without ozone treatment, the average DOC removal rate in the system improved by 9.6% and 25.3%, respectively. On the other hand, pre-oxidation by ozone alone did not significantly improve DOC removal of the membrane filtration, likely due to the increased solubility of suspended organic matter from ozonation (Tang et al., 2020). Compared to BAC pretreatment alone, the combined pretreatment showed a synergistic effect in organic removal, and the O_3-BAC-UF system achieved an average DOC removal rate of 55.7% with stable effluent

quality. These results suggest that pre-oxidation can improve the removal efficiency of organics in the subsequent BAC-UF system, which may be due to the breakdown of recalcitrant organics such as aromatic compounds into simple and biodegradable organics (aldehydes, ketones, and carboxylic acids) by ozone (Loganathan et al., 2022; Loh et al., 2021), thereby improving their biochemical properties (Tang et al., 2020), and making them easily degradable in the BAC column.

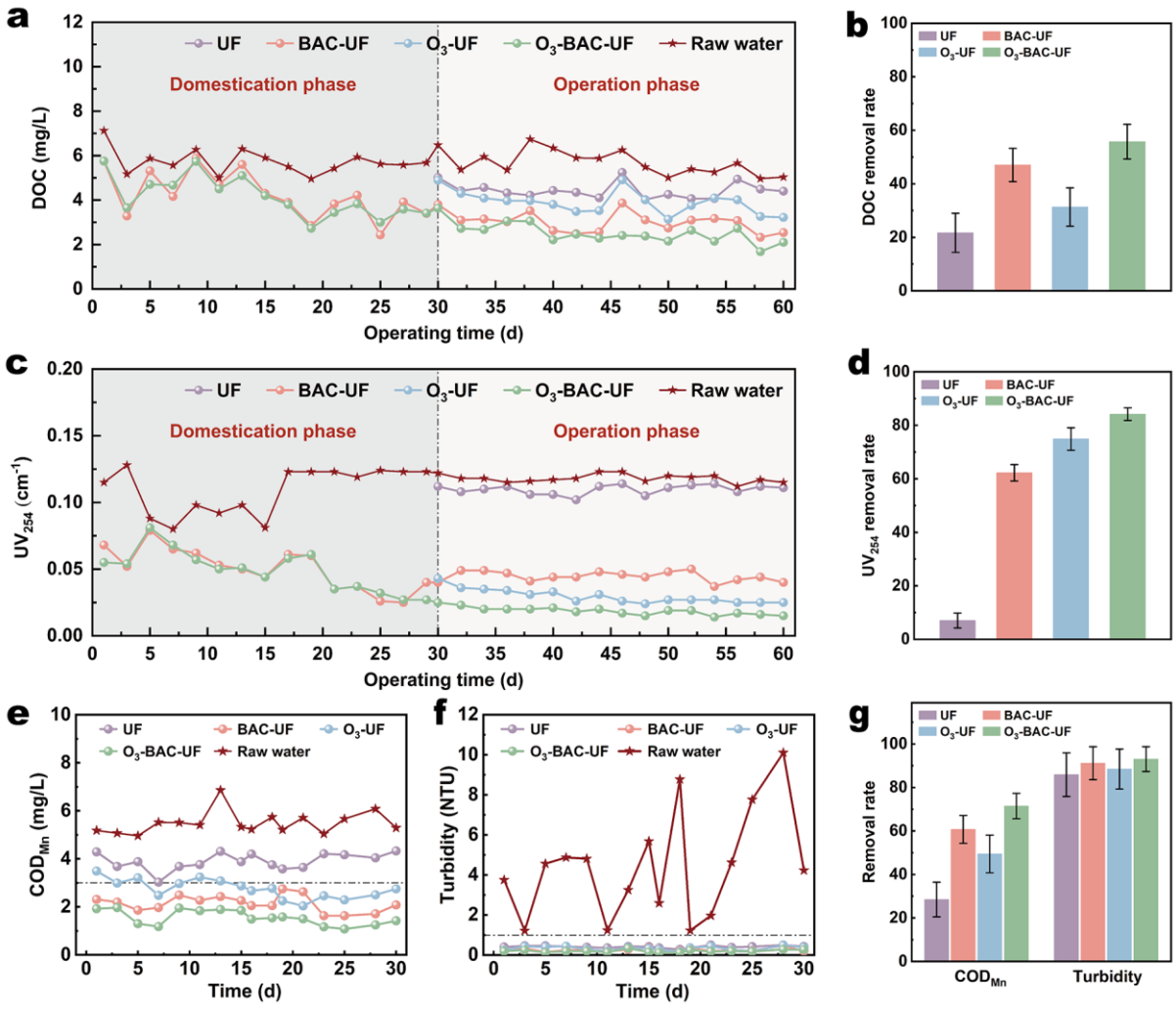

Figure 2. Water quality indexes of influent and effluent streams in different reactors during the operation period. (a) DOC values; (b) Corresponding DOC removal rates; (c) UV_{254} values; (d) Corresponding UV_{254} removal rates; (e) COD_{Mn} values; (f) Turbidity values; (g) Removal rates of COD_{Mn} and turbidity.

Fig. 2c and 2d present analogous results in terms of UV_{254}, a parameter that indicates the fraction of organic substances containing C=C double bonds and benzene ring structures, including humic macromolecules and aromatic compounds (Wu et al., 2023). The removal rates of UV_{254} were 7.0% (UF), 62.3% (BAC-UF), 74.9% (O_3-UF), and 84.2% (O_3-BAC-UF), respectively. Consistent with DOC analyses, the O_3-BAC-UF system is the most effective in removing UV_{254}. Results graphed in Fig. 2e indicate that membrane filtration alone did not result in sufficient removal of COD_{Mn} from the raw water to achieve the drinking water sanitation standard limit (3 mg/L). Pre-oxodation, although it improved removal, did not stabilize the effluent COD_{Mn} below 3 mg/L. The trend of COD_{Mn} removal was similar to that of DOC and UV_{254} removal, with average removal rates of 28.5% (UF), 60.7% (BAC-UF), 49.4% (O_3-UF), and 71.5% (O_3-BAC-UF) for the the four systems. In particular, the O_3-BAC-UF stabilized the effluent COD_{Mn} below 2 mg/L, thus greatly improving the efficiency of membrane treatment (Du et al., 2021; Obotey Ezugbe and Rathilal, 2020).

In addition, turbidity is another contamination indicator, related to the amount of suspended matter in water. The raw water turbidity ranged from 1.2 NTU to 10.1 NTU (as shown in Fig. 2f). Regardless of the raw water fluctuations, the effluent turbidity was significantly reduced in all four systems of all four systems to levels between 0.12 and 0.50 NTU), hence below the drinking water sanitation standard limit (1 NTU). Moreover, the average removal rates of the four systems were as follows: 85.9% (UF), 91.w% (BAC-UF), 88.5% (O_3-UF), and 93.1% (O_3-BAC-UF). These results demonstrate that all four systems were effective in intercepting particulate matter, which was mainly achieved through the effective removal of suspended particulate matter by the ultrafiltration membranes. The O_3-BAC-UF process also significantly demonstrated suitable performance in chromaticity removal with a removal rate of 94% (Fig. S3 of the SI).

3.2 Removal mechanism of organic compounds

To further explore the impact of different pretreatments on changes of organic matter in membrane filtration systems, fluorescence excitation-emission matrix (EEM) analysis was performed raw water and treated effluents from the different systems, and the maximum fluorescence intensity (F_{max}) of each component in the water before and after treatment was calculated (Fig. 3). The fluorescence spectra were categorized into five regions based on fluorescence region integration: region I and II are associated with aromatic proteins (AP1 and AP2). Region III, IV, and V are related to fulvic-like substances (FA), soluble microbial products (SMP), and humic-like substances (HA), respectively. The total removal rates of fluorescent organic matters were 6.6% with UF alone, 70.6% with BAC-UF, 81.9% with O_3-UF, and 74.3% in the O_3-BAC-UF system, respectively.

HA (region V) dominated the fluorescent organic matter in raw water. Membrane filtration alone showed inadequate removal of FA or HA. All the pretreatments showed a significant increase on membrane filtration efficiency for the removal of these substances (74.8% - 100 % and 65.7% - 79.4%, respectively). Region IV exhibited the second highest abundance of fluorescent organic compounds. Soluble microbial products (SMP), encompassing substances such as polycyclic aromatic hydrocarbons (PAHs), amino acids, polysaccharides, and hydrophobic organic acids were previously identified within this region (Liu et al., 2021). While all pretreatment combinations also allowed higher removal of substances in region IV, interestingly a lower removal rate for SMP was observed compared to humic substances. SMP produced and accumulated by microorganisms on BAC may flow into the effluent with microorganisms (Im et al., 2019; Wang et al., 2022). Furthermore, according to Nguyen and Roddick (Nguyen and

Roddick, 2010), the microorganisms under the effect of residual ozone may lead to an increase in SMP through the release of intracellular substances.

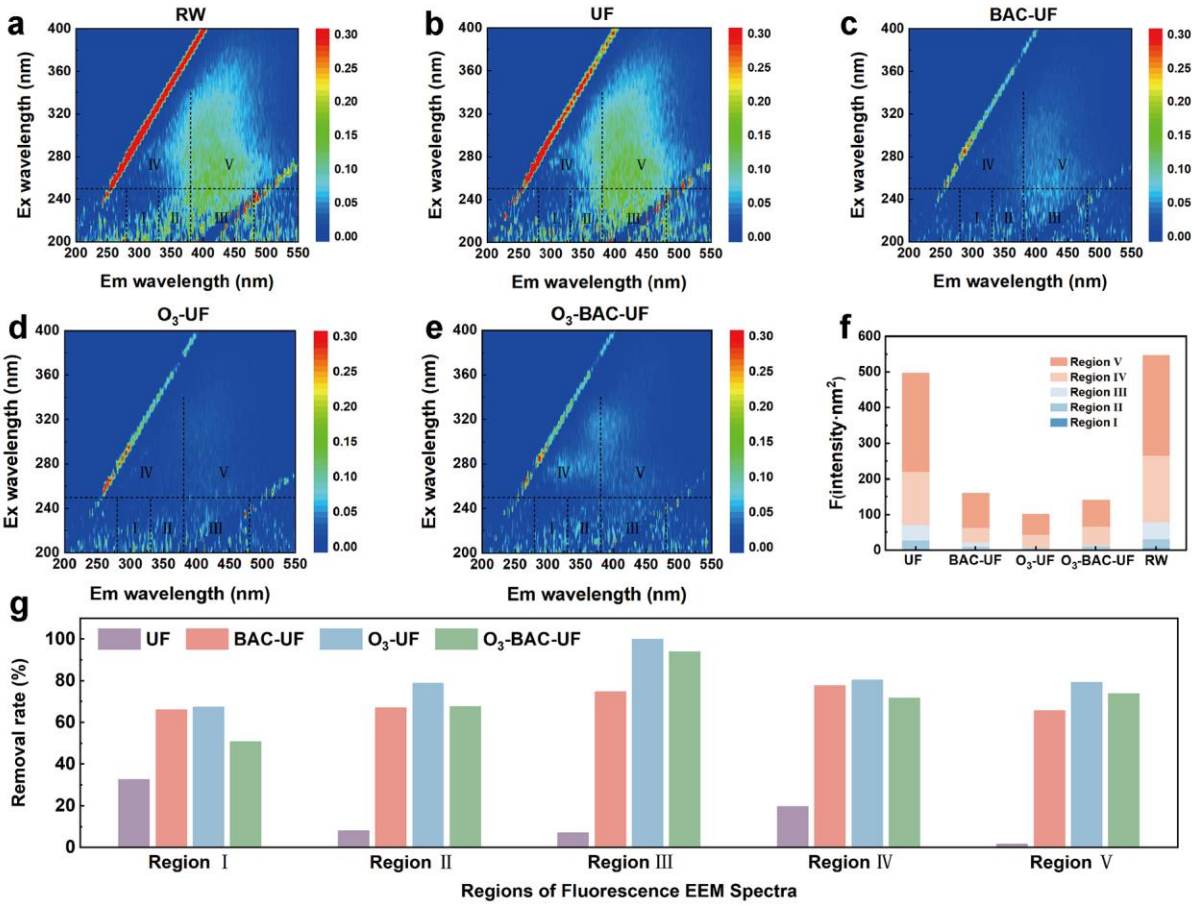

Figure 3. Fluorescence EEM spectra of influent and effluent streams in different reactors. (a) Raw water; (b):UF effluent; (c): BAC-UF effluent; (d): O_3-UF effluent; (e) O_3-BAC-UF effluent; (f): F_{max} calculated from fluorescence EEM spectra of influent and effluent streams; g): Removal rates of different reactors. (Region I: (Ex/Em = 220-250/280-330 nm, tyrosine protein-like substances), region II: (Ex/Em = 220-250/330-380 nm, tryptophan protein-like substances), region III: (Ex/Em = 220-250/380-480 nm, fulvic acid-like matters), region IV: (Ex/Em = 250-440/280-380 nm, soluble microbial by-product-like matters), and region V: (Ex/Em = 250-400/380-540 nm, humic acid-like components)).

As shown in Fig. 4, the majority of organic compounds in the raw water were found within the hydrophilic (HPI) fraction (70.8%). In addition, pre-oxidation led to a further increase in the

content of HPI, likely because ozonation promoted the formation of oxygen-containing functional groups, such as hydroxyl groups, aldehyde groups, and ketones (Loganathan et al., 2022). Indeed, it has been reported that pre-treatment with ozone result in an increase in the hydrophilic character of dissolved organic matter (DOM), making the removal of DOM by conventional processes relatively unsatisfactory (Yang et al., 2023). In this work, the HPO removal by BAC treatment alone was not ideal (24.4%), but significantly increased after pre-oxidation (88.4%), consistent with the oxidation activity of ozone and with the results presented in Figure 4.

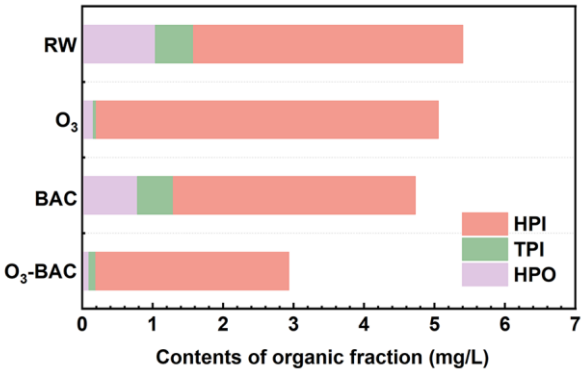

Figure 4. Distribution of organic fractionation by XAD chromatographic column. Illustration of hydrophilic (HPI), transphilic (TPI), and hydrophobic (HPO) fractions in raw water before and after pretreatment.

3.3. GSM and 2-MIB removal rates and mechanisms

During continuous operation, the concentrations of GSM and 2-MIB in the influent water fluctuated between 81.1-115ng/L and 86.4-112 ng/L, respectively. The experimental setup was in a non-fully sealed state (when in a fully sealed state, the pressure inside the reactor rises due to continuous aeration, and the resistance to water flow increases, resulting in a lower discharge rate), and a fraction of the odor compounds was lost due to natural volatilization. Control experiments indicated that natural volatilization accounted for 32.5% and 28.3% of the losses for GSM and 2-MIB, respectively, when the starting concentrations were 100 ng/L. These losses were subtracted

from the calculation of raw water concentration. As shown in the results graphed in Figs. 5a and 5b, pretreatment significantly improved the efficiency of odor removal in the membrane treatment system, and the GSM and 2-MIB concentrations in the effluent after pretreatment met the drinking water quality standards.

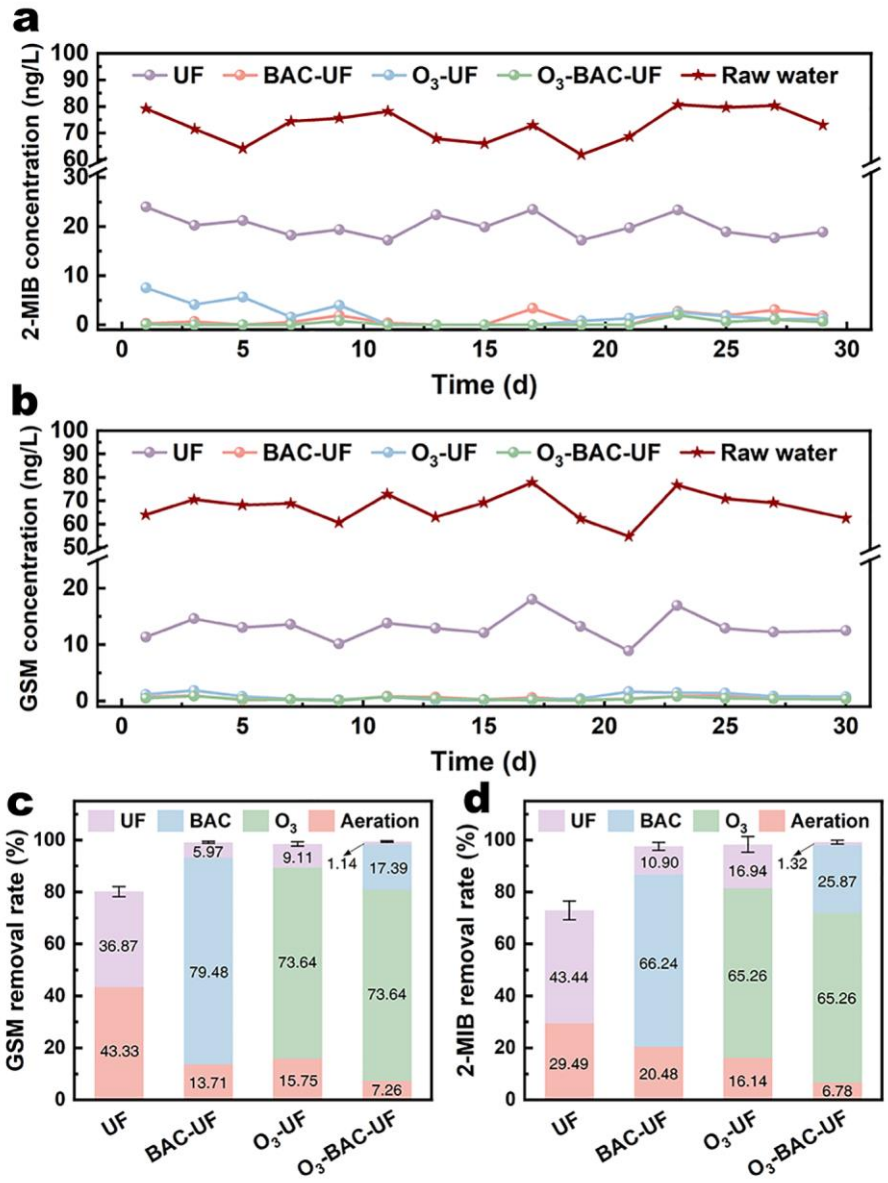

Figure 5. Removal of typical T&O substances: (a) GSM concentration in effluents of different reactors; (b) 2-MIB concentration in effluents of different reactors; (c) Contribution of different process stages to GSM removal rate; (d) Contribution of different process stages to 2-MIB removal rate.

Figs. 5c and 5d present the contribution of each process stage to the removal of GSM and 2-MIB in different systems. After deducting the loss due to volatilization, the total removal rates of GSM for the different systems were O_3-BAC-UF (92.2%), O_3-UF (82.8%), BAC-UF (85.5%), and UF (36.9%), and the total removal rates of 2-MIB were O_3-BAC-UF (92.5%), BAC-UF (82.2%), O_3-UF (77.1%), and UF (43.4%). Note that the volatilization effect was significantly higher in the individual UF system, with respect to all other systems, because without pretreatment the membrane was subjected to more severe fouling, resulting in a slower effluent rate that lengthened the filtration time, hence the volatilization time. The other factor contributing to odor compounds removal by UF membranes may instead be associated with cake layer filtration from the fouling layer and microorganisms attached and accumulated on the membrane surface during both the domestication process and the long-term continuous operation.

GSM and 2-MIB are hydrophobic compounds with $\log K_{ow}$ values of 3.57 and 3.31, respectively. Ozone oxidation had a slightly better degradation effect on GSM, partly attributed to its lower water solubility with respect to 2-MIB and its consequent easier transfer from the native liquid phase to the gas phase to react with ozone (Yuan et al., 2013). Similarly, the BAC treatment alone showed better removal efficiency for GSM. According to Doederer et al. (Doederer et al., 2019), adsorption is the main removal mechanism at the early stages of contact between the odourant and the BAC, beyond which biodegradation becomes the primary removal process. Compared to 2-MIB, GSM molecules have a more lipophilic and flatter structure, facilitating their interaction with GAC and biofilms, and encountering less direct competition with NOM molecules (Cook et al., 2001). It should be pointed out that, after ozone pre-oxidation, the subsequent BAC stage exhibited higher removal efficiency for 2-MIB compared to GSM. This result is consistent

with the discussion above, as higher oxidation of GSM would produce more hydrophilic products, which have less affinity with GAC. Also, Saadoun and EI-Migdadi (Saadoun and El-Migdadi, 1998) suggested that GSM is more recalcitrant to degradation by Gram-negative bacteria when used as the sole carbon source, in comparison to 2-MIB. Ozone treatment increased the proportion of Gram-negative bacteria in water, which may be one of the reasons for the above phenomenon.

3.4 Microbial diversity analysis

3.4.1 Microbial diversity

The abundance and diversity of microorganisms in the four reactors were analyzed with the Illumina sequencing method. A total of 32,133-56,154 valid sequences were obtained. Bioinformatics analysis of the valid sequences was performed at a 97% similarity level, and the results are summarized in Table 1. All samples had Coverage index values above 0.99 (Table 1), and the sparsity curve tended to increase with increasing sequence number (Fig. 6a), indicating that the sequence number was adequately large to represent nearly all microbial communities in each sample. Shannon and Chao index results showed that pretreatment increased microbial community diversity. Specifically, the Shannon index of the O_3-BAC-UF system was higher compared to the unoxidized BAC-UF system, which may be due to the increased availability of biodegradable organic carbon after ozone oxidation (Sauter et al., 2023; Tang et al., 2021a). Fig. 6b shows the number of OTUs that were unique and identical between the bacterial communities. The number of OTUs across all four reactors was 372, while the numbers for UF, BAC-UF, O_3-UF, and O_3-BAC-UF were 264, 96, 49, and 58, respectively. These results suggest that pretreatment significantly altered the community structure.

Table 1. Number of effective sequences, operational taxonomic units (OTUs), alpha diversity indexes for microbial communities in different reactors at different periods

Sample	Number of effective Sequences	OTU at 97% identity	Shannon	Chao	Coverage
UF-15d	32133	772	4.47	829.0	0.9963
UF-30d	44738	843	3.98	1038.9	0.9928
BAC-UF-15d	42960	1051	5.19	1238.4	0.9922
BAC-UF-30d	56154	971	5.02	1210.0	0.9913
O_3-UF-15d	47290	543	4.16	700.6	0.9950
O_3-UF-30d	51794	602	4.15	733.3	0.9950
O_3-BAC-UF-15d	44849	893	4.91	1102.5	0.9925
O_3-BAC-UF-30d	53216	976	5.05	1197.9	0.9920

Principal component analysis (PCA) is an important method for comparing bacterial diversity and assessing the similarity of microbial community composition. The closer two sample points are, the more similar would be the species composition of the two samples. The PCA at the level of microbial community OTUs (Fig. 6c) shows that the microbial community structure differed between the microbial communities of different reactors under long-term operating conditions. This result indicates that new dominant organisms were formed within the pretreated membrane reactor. In addition, it can be observed that the structure of the biotope did not differ significantly over time within the same reactor.

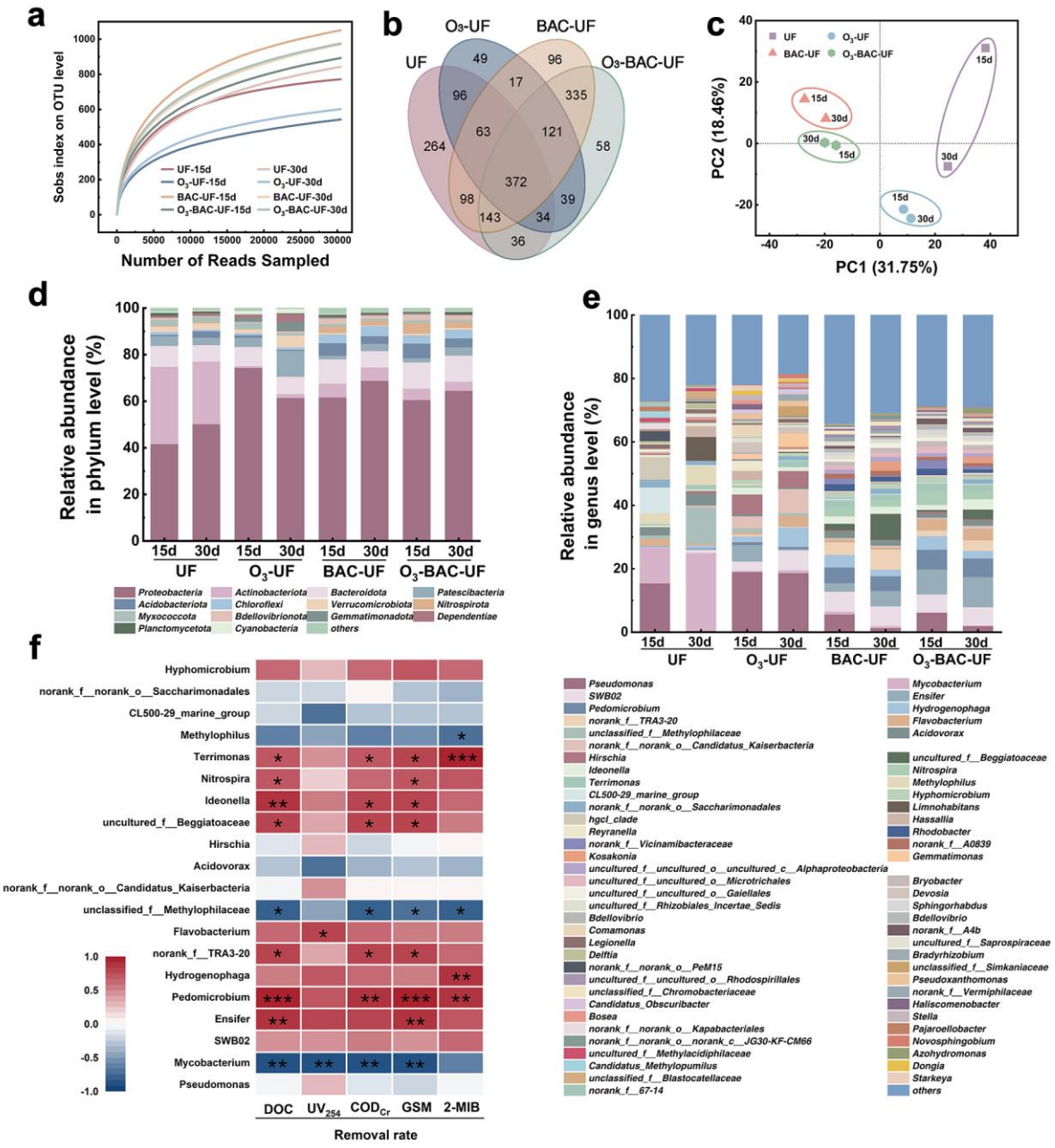

Figure 6. Results of microbial community characterization of water from different reactors at different operation times. a): Rarefaction curves of OTUs. b): Venn diagram at OTUs level; c): PCA analysis at OTUs level of microbial communities; d): Bacterial community compositions at the phylum level (> 0.1%); e): Bacterial community compositions at the genus level (> 0.12%). f): Correlation analysis between microbial community at the genus level (top 20) and environmental variables (organic matter removal rate, typical odor substances

removal rate). Here, "*" represents a value of $p < 0.05$, "**" represents a value of $p < 0.01$, "***" represents a value of $p < 0.001$.

3.4.2 Composition of the microbial community

Figs. 6d and 6e show the bacterial community composition at the phylum level and at the genus level for samples obtained at different times (day 15 and day 30) from raw water (RW), water undergone ozone pretreatment, and water undergone both biological treatment systems. At the phylum level (Fig. 6d), 14 bacterial phyla with relative abundances ≥1% were identified. Among all samples, the five most dominant phyla were *Proteobacteria* (41.68% - 74.32%), *Actinobacteriota* (0.81% - 33.16%), *Bacteroidota* (6.98% - 11.23%). These three phyla accounted for roughly 80% of the total bacterial abundance.

The ozone treatment significantly influenced the inactivation of *Actinobacteriota*, *Acidobacteriota*, *Nitrospirota*, and *Planctomycetota*, resulting in a notable reduction in the levels of these bacterial clades in the effluent after ozone oxidation. Specifically, the most significant reduction was observed for *Actinobacteriota* as a Gram-positive actinomycete, with the relative content decreasing from 33.2% to 0.81%. In addition, an increase in the relative content of the bacterial phyla *Gemmatimonadota*, *Cyanobacteria*, and *Dependentiae* was also observed. These results indicate that oxidative processes have a discernible impact on the bacterial community, leading to changes and adaptations in the composition of the phylum level.

The BAC-UF system exhibited an increase in both the abundance and diversity of bacteria in the effluent water, which also showed spatial and temporal variation. At the phylum level, after 30 days of operation, the proportion of *Proteobacteria*, *Chloroflexi*, and *Acidobacteriota* in the biomass of the BAC filter column increased by 27.1%, 3.13%, and 2.65%, respectively, compared to the raw water. *Proteobacteria* include a variety of as Gram-negative metabolizing bacteria that can play an important role in DOM decomposition and are the main bacteria for the removal of

dissolved biodegradable organic compounds (Du et al., 2020; Wang et al., 2022). Previous studies have also reported the prevalence of *Proteobacteria* in GAC or BAC filters in DWTPs (Chang et al., 2022; Du et al., 2020; Jiang et al., 2022). *Acidobacterta* and *Chroloflexi* can utilize a variety of carbohydrates (Wang et al., 2022), which could explain the better removal performance of DOC observed in the BAC treatment. In addition, a significant decrease in the relative content of *Actinobacteriota* (by 27.4%) was observed, a similar result for ozone oxidation. The biotope structure of the O_3-BAC-UF system differed from that of the BAC-UF system, although they shared similar core organisms at the phylum level. O_3-BAC-UF system had the highest relative content of *Bacteroidota* (11.2%) compared to the raw water and other treatment systems.

At the genus level, pre-oxidation caused a change in the bacterial community structure on the BAC filter. With continuous operation of the system, a large number of bacterial genera with low abundance in the raw water were gradually enriched on the BAC filter, such as *uncultured_f__Beggiatoaceae* (8.2%), *norank_f__TRA3-20* (6.3%), *SWB02* (6.2%), *Ensifer* (4.8%), and *Pedomicrobium* (4.7%). The genus *SWB02* is a potential symbiotic bacterium that can co-degrade volatile fatty acids with methanogenic bacteria (Feng et al., 2023; Lee et al., 2019). In contrast, after pre-oxidation, the relative content of *Ensifer* and *Pedomicrobium* on the BAC filter increased to 9.5% and 5.8%, respectively. Both bacteria belong to the *Alphaproteobacteria*, which are parthenogenic anaerobes that use organic matter in raw water as a carbon source while carrying out respiration and fermentation metabolism (Tian et al., 2014). In addition, *Flavobacterium* (3.6%) emerged as a new important genus in the ozone-BAC-UF system, belonging to the *Bacteroidota*, which can be involved in protein degradation and amino acid fermentation, with a strong metabolism of complex organic compounds and lipids (Jiang et al., 2022).

Fig. 5f shows the correlation analysis between bacterial genera (top 20 in abundance) and environmental variables (organic matter removal rate, odorant substance removal rate). The analysis identified several bacterial genera associated with DOC removal, namely, *Pedomicrobium*, *Ensifer*, and *Ideonella*. Among them, *Pedomicrobium* with an abundance of 0.4%-6.2% was significantly and positively associated with DOC removal ($P < 0.001$). Some studies reported that *Pedomicrobium* may be associated with the biodegradation of phenolic compounds (Deng et al., 2021). Significant correlations were also observed between *Pedomicrobium* and COD_{Mn} ($P < 0.01$), 2-MIB ($P < 0.01$), and GSM ($P < 0.001$) removal. *Ensifer* was associated with GSM removal. Bacterial genera that were significantly and positively correlated with 2-MIB removal included *Terrimonas* ($P < 0.001$) and *Hydrogenophaga* ($P < 0.01$).

4. Conclusion

The combined O_3-BAC-UF system was employed for the treatment of drinking water in rural areas, and its practical application potential was assessed by examining changes in water quality indicators (e.g., organic matter, turbidity) and odor compound indicators (GSM, 2-MIB) during continuous operation. Ozone oxidation altered the biochemical properties of organic matter, facilitating the subsequent BAC process to efficiently remove organic matter and odorous substances from the water. The ultrafiltration membrane effectively blocked microorganisms from the BAC-treated effluent and reduced the turbidity of the water. During continuous operation after the domestication phase, the combined O_3-BAC-UF process was able to achieve a COD_{Mn} removal rate of 71.5% and a UV_{254} removal rate of 84.2%. In terms of T&O removal, the combined process also showed a stable removal capacity with an average removal rate of 92.2% for GSM and 92.5%

for 2-MIB. Ozone oxidation and BAC degradation were the primary removal mechanisms, with air stripping and membrane filtration providing additional removal of T&O compounds.

The combined O_3-BAC-UF process exhibited promising applicability for the treatment of rural drinking water with high organic concentrations and significant odor issues. However, it is important to note that the presented results were obtained at the laboratory scale. Further large-scale experiments are necessary to evaluate the broader applicability and feasibility of this process for drinking water treatment in rural areas.

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