

Integration of Aerobic Riverbank Filtration and Ultrafiltration for Advanced Water Treatment and Membrane Ageing Reduction

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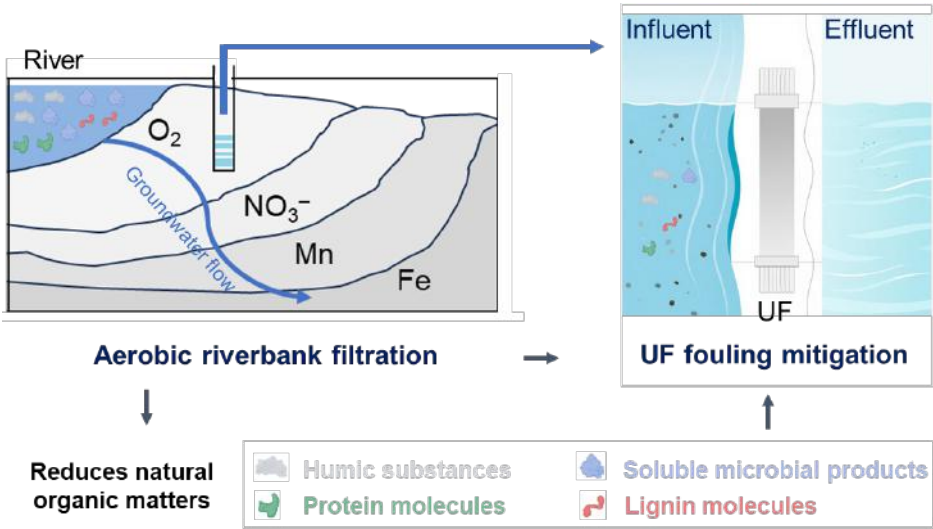
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Highlights

- Proposes a chemical-free, short-process aerobic RBF-UF water purification system.
- The aerobic RBF without Mn/Fe release issues reduces UF membrane fouling.
- Fouling reduction is due to less humic substances and soluble microbial products.
- Reduced proteins and lignin molecules may contribute to fouling mitigation.
- Synergistic NOM removal via adsorption and biodegradation (e.g., *Streptomyces*).

Graphical Abstract



Abstract

Reduced chemical usage and the development of cost-effective water treatment technologies are key priorities for safeguarding public health, particularly in the context of global carbon neutrality goals. Integrating nature-based riverbank filtration (RBF) with ultrafiltration (UF) offers an efficient and environmentally friendly approach for drinking water supply. However, traditionally deployed RBF systems operating across aerobic, anoxic, and anaerobic zones face practical challenges, including ion release and groundwater depletion. Focusing solely on the aerobic RBF may address these limitations; however, its impact on UF performance, particularly in relation to natural organic matter (NOM) as a major membrane foulant, remains poorly understood. As microbe-mediated processes in RBF also critically influence membrane performance, this study examined aerobic RBF's influence on UF membrane fouling through comprehensive NOM and microbial analyses. The results showed that aerobic RBF pretreatment reduced UF fouling by approximately 77%, primarily through decreased organic accumulation on membrane surfaces. This mitigation was attributed to reductions in dissolved organic carbon, UV₂₅₄, humic acid-like substances, and soluble microbial products (e.g., proteins). NOM molecular analysis revealed decreased quantities of proteins, lignin/carboxylic-rich alicyclic molecules (CRAM)-like compounds, and condensed aromatic structures (CAS). Adsorption accounted mainly for the removal of persistent compounds (e.g., CAS), while the removal of proteins and lignin was attributed to microbially mediated biotransformation by genera such as *Streptomyces* and *Pseudomonas*. These findings provide novel molecular-level insights into the dynamics of NOM in RBF and demonstrate the significant potential of aerobic RBF as an effective pretreatment step for UF towards advanced water treatment applications.

Keywords: Aerobic zone; Biofilm regulation; Nature-based solution; Short process water purification; UF membrane

1. Introduction

The increasing frequency of global extreme weather events calls for urgent climate action across all sectors (Grant et al., 2025; Hoy et al., 2023). In response, the drinking water treatment industry must accelerate its shift toward sustainable, low-carbon processes. This shift demands the development of purification methods that reduce energy consumption, chemical use, and operational complexity (Li et al., 2025; Reid et al., 2023; Zhai et al., 2022). Riverbank filtration (RBF), a century-old nature-based pretreatment technology, has proven effective in Europe and North America (Hollender et al., 2018; Hoppe-Jones et al., 2010; Ray, 2008), and shows promise for addressing water security challenges in Asia, including China and South Korea (Zhao et al., 2025). RBF's proven ability to remove a wide range of contaminants, such as turbidity, microorganisms, natural organic matter (NOM), and emerging pollutants like pharmaceuticals, makes it a valuable tool for modern water treatment (von Rohr et al., 2014; Zhao et al., 2025). RBF's pollutant removal capabilities enable the development of short, chlorine-free water treatment processes. Integrating RBF with membranes can reduce energy use, chemical demand, and simplify treatment processes (Li et al., 2025; Wang et al., 2024; Zhai et al., 2022). RBF is commonly combined with reverse osmosis (RO) or ultrafiltration (UF) in drinking water plants (Haas et al., 2019; Zhai et al., 2022). RBF-RO systems provide high-quality permeate and effective contaminant removal, but their widespread application is constrained by high energy consumption and operational costs. Although simulation studies suggest promising potential for RBF combined with nanofiltration (NF) (Li et al., 2025), real-world implementations remain limited, also largely due to cost considerations. In contrast, UF is increasingly adopted in large-scale plants due to its favorable balance of high permeate quality, lower energy demand, and cost-effectiveness compared to RO and NF (Haas et al., 2019; He et al., 2025; Li et al., 2023; Wu et al., 2023). Given its practical and economic advantages, this study focuses specifically on the RBF-UF combination.

However, integrating RBF with membrane processes presents challenges. RBF requires long infiltration paths (tens to hundreds of meters) that guide water through aerobic, anoxic, and anaerobic zones (Covatti and Grischek, 2021; Zuo et al., 2022). These extended paths can significantly increase

groundwater abstraction, contributing to concerns about over-exploitation and saltwater intrusion (Aeschbach-Hertig and Gleeson, 2012; Shamrukh and Abdel-Wahab, 2008). Additionally, the drawdown in pumping wells often raises concentrations of hardness (Ca, Mg), dissolved manganese (Mn), and iron (Fe) in the water (Covatti and Grischek, 2021; Salamon and Goda, 2019). The elevated Mn and Fe levels, particularly from anoxic zones, contribute to membrane fouling, requiring chemical cleaning (Haas et al., 2019). The long residence time needed to reach the anoxic/anaerobic zones also limits the production capacity of RBF-membrane systems. The aerobic zone of RBF, being the most biogeochemically active, plays a crucial role in degrading NOM and organic micropollutants (Hollender et al., 2018; von Rohr et al., 2014; Zhao et al., 2022). Given that NOM removal helps mitigate membrane fouling (Li et al., 2025; Wang et al., 2024), utilizing only the aerobic zone as pretreatment for the membrane stage could reduce groundwater abstraction, limit the mobilization of problematic ions (e.g., Fe, Mn), and enhance process efficiency. However, the feasibility of this approach remains largely unexplored.

The impact of RBF pretreatment on membrane performance is a critical aspect of integrated RBF-membrane systems. Studies confirm that RBF pretreatment enhances membrane flux and reduces resistance due to fouling compared to direct river water treatment by membranes (Haas et al., 2019). Scanning electron microscopy (SEM) analyses indicate that RBF decreases the accumulation of NOM and particulate foulants on membrane surfaces (Wang et al., 2024). Understanding the 3D nanostructure of the fouling cake layer is vital, as it governs water transport and thereby permeate flux in processes like UF (Lu et al., 2021). However, conventional characterization techniques (e.g., SEM) lack the resolution and chemical structure specificity for precise nanoscale 3D analysis. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), offering ~5 nm depth resolution and suitability for distinguishing different organic substances, is ideal for resolving this 3D cake layer structure (Wu et al., 2023). Yet, its application to characterize foulant layers in RBF-UF systems has not yet been explored. Regarding NOM, research using techniques like three-dimensional excitation-emission matrix (3D-EEM) and Fourier transform infrared spectroscopy (FT-IR) suggests that RBF primarily alters NOM content rather than its composition, with humic acids identified as key foulants whose concentration is significantly reduced by RBF (Wang et al., 2024). However, contradictory

observations exist: some studies report that RBF selectively removes protein-like components but has limited effect on humic substances (Li et al., 2025). Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS), with its unparalleled resolution, is essential for definitively characterizing NOM molecular transformations (Guo et al., 2025). Crucially, the application of FT-ICR MS to elucidate RBF-induced NOM changes and their specific impact on membrane fouling has not yet been reported.

Recent studies on integration of RBF-membrane systems often employ RBF (incorporating aerobic, anoxic, and anaerobic zones) or short-distance RBF combined with UF (Table S1). In contrast, based on the redox zonation theory and the identified critical role of the aerobic zone in pollutant removal (Hollender et al., 2018; Zhao et al., 2025; Zuo et al., 2022), this study proposes a water treatment process coupling aerobic RBF with UF. Furthermore, previous research has not utilized ToF-SIMS to analyze the UF membrane cake layer after RBF pretreatment, nor applied FT-ICR MS to investigate changes in dissolved organic matter (DOM) during RBF and their relationship with membrane fouling. This study integrates ToF-SIMS, FT-ICR MS, and metagenomics to provide deeper insights into the mechanisms by which the aerobic RBF zone influences UF membrane fouling.

This study aims to investigate, with natural river water as feed, the impact and underlying mechanisms of RBF aerobic zone pretreatment on UF performance, using a one-meter sand column to simulate the aerobic zone. It further examines the resulting membrane fouling behavior in the UF process through various analysis methods, such as SEM and ToF-SIMS. Analysis methods including 3D-EEM, FT-IR, and FT-ICR MS are employed to characterize NOM and reveal information on molecular-level transformations induced by the pretreatment. Additionally, metagenomic sequencing is used to identify the functional microbial communities responsible for driving changes in NOM composition. Together, this work provides new insights into the role of the RBF aerobic zone in influencing UF fouling and clarifies the molecular mechanisms through which RBF affects membrane filtration processes.

2. Materials and Methods

2.1. River water

River water was collected weekly from the Yongding River (39°59'58"N, 116°44'7"E, Beijing). Key water quality parameters were measured weekly, including: dissolved oxygen (DO, 6.1 ± 3.4 mg/L), Ca^{2+} (63.8 ± 4.9 mg/L), K^+ (6.2 ± 0.9 mg/L), Mg^{2+} (33.2 ± 1.4 mg/L), dissolved organic carbon (DOC, 4.8 ± 1.7 mg/L), UV_{254} (0.066 ± 0.015), $\text{NH}_4^+\text{-N}$ (0.12 ± 0.04 mg/L), F^- (0.53 ± 0.05 mg/L), Cl^- (61.9 ± 4.0 mg/L), and SO_4^{2-} (133.6 ± 19.5 mg/L).

2.2. Experimental setup and design

The setup comprised one column, 1.0 m in length and 36 mm in internal diameter, made from polyvinyl chloride. Natural riverbank sand with a particle size ≤ 2 mm and a median diameter (d_{50}) of 1 mm was used to pack the column. [Table S2](#) presents the results of the key physicochemical properties of the natural riverbank sand, including grain size distribution, organic carbon content, and pH. Filtration was performed in an upflow mode at a flow rate of 0.25 L/d, controlled by a peristaltic pump (BT100-2J, LongerPump, China), resulting in a hydraulic retention time of approximately 36 h. The experimental setup was maintained at 20-25 °C. Before setting up the RBF-UF system, the column was preconditioned with river water for 16 months to cultivate stable microbial communities, thereby exceeding typical 2-6 months' acclimation period to better simulate the RBF aerobic zone ([Bertelkamp et al., 2016](#); [Wang et al., 2024](#); [Zhao et al., 2025](#)). Following stabilization, sand samples (5 g each) were taken from the bottom (inlet_{-sand}), middle (50 cm_{-sand}), and top (100 cm_{-sand}) of the column and stored at -80 °C before DNA extraction and analysis.

2.3. UF experiment protocol

A polyvinylidene fluoride (PVDF) UF membrane was selected for this work due to its well-established properties and continued relevance in drinking water treatment ([Robinson and Bérubé, 2020](#); [He et al., 2025](#)). To establish a consistent initial membrane flux (J_0), a flat-sheet PVDF UF membrane (76 mm in diameter) with a nominal pore size of 30 nm and a molecular weight cut-off (MWCO) of 100 kDa (Ande Membrane Separation Technology & Engineering (Beijing) Co., Ltd., China) was preconditioned by filtering 300 mL of ultrapure water. The ultrapure water flux was

determined to be $222.05 \pm 8.37 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ at 0.1 MPa. Subsequently, 2000 mL samples of river water and RBF filtrate were filtered separately using a 400 mL stirred cell (Amicon 8400, Millipore) connected to a 5 L pressure tank and driven by nitrogen gas at a constant pressure of 0.1 MPa. No stirring was applied during filtration. The filtration time and absolute flux (J_t) were continuously recorded via a digital balance (AR2202CN, Ohaus, NJ, USA) connected to a data acquisition system. The specific flux (J_t / J_0) was calculated for each sample. After filtration, the fouled membranes were air-dried at ambient temperature and stored in Petri dishes for subsequent ToF-SIMS analysis.

2.4. Sampling and analysis

2.4.1. Water quality analysis

DOC was measured using a TOC analyzer (TOC-VCPH, Shimadzu, Japan). DO was measured using a multiparameter water quality meter (HQ40d, Hach, USA). The concentration of NH_4^+ -N was determined using Nessler's reagent method. UV_{254} absorbance was measured with a UV-Vis spectrophotometer (U-3010, Hitachi, Japan). The concentrations of F^- , Cl^- , and SO_4^{2-} were analyzed by ion chromatography (INTEGRION, Thermo Fisher Scientific, USA). The concentrations of K^+ , Ca^{2+} , and Mg^{2+} were measured using ICP-OES (5110VDV, Agilent, USA). EEM fluorescence spectra were obtained using a fluorescence spectrophotometer (F-4600, Hitachi, Japan) to assess the transformation of DOM during filtration. EEM settings included excitation wavelengths of 200-450 nm and emission wavelengths of 250-550 nm, with a scanning speed of 12,000 nm/min. The zeta potential of selected water samples was analyzed using a zeta potential analyzer (Nano ZS90, Malvern Instruments, UK) to evaluate changes in colloid surface charge properties. To analyze the chemical composition of DOM, water samples were filtered through 0.22 μm membranes (MF-Millipore, mixed cellulose esters, hydrophilic, plain), acidified, and processed by solid-phase extraction (SPE) using Bond Elut PPL cartridges (1 g, 6 mL, Agilent Technologies, USA). Detailed SPE procedures are provided in [Text S1](#).

Organics were eluted using methanol ($\geq 99.9\%$, ANPEL, China), concentrated, and analyzed by high-resolution FT-ICR-MS in both positive and negative ion modes over a mass range of m/z 100-800. Molecular formula assignment and Van Krevelen diagram classification were employed to distinguish between compound classes. The identified compounds were assigned to seven classes,

including (1) lipids ($1.5 \leq \text{H/C} \leq 2$, $0 \leq \text{O/C} \leq 0.3$), (2) proteins ($1.5 \leq \text{H/C} \leq 2.2$, $0.3 \leq \text{O/C} \leq 0.67$), (3) carbohydrates ($1.5 \leq \text{H/C} \leq 2.4$, $0.67 \leq \text{O/C} \leq 1.2$), (4) unsaturated hydrocarbons ($0.7 \leq \text{H/C} \leq 1.5$, $0 \leq \text{O/C} \leq 0.1$), (5) lignin/carboxylic-rich alicyclic molecules (CRAM)-like ($0.7 \leq \text{H/C} \leq 1.5$, $0.1 \leq \text{O/C} \leq 0.67$), (6) tannins ($0.5 \leq \text{H/C} \leq 1.5$, $0.67 \leq \text{O/C} \leq 1.2$), and (7) condensed aromatic structures (CAS) ($0.2 \leq \text{H/C} \leq 0.7$, $0 \leq \text{O/C} \leq 0.67$).

2.4.2. Membrane surface characterization

The hydrophilic/hydrophobic properties of the UF membrane were evaluated by measuring contact angles before and after fouling. Dried membrane samples were tested at room temperature using 2 μL droplets of ultrapure water. Contact angle measurements were performed using a contact angle goniometer (OCA 15EC, Dataphysics Instruments GmbH, Germany). Each membrane was measured five times, and the average contact angle was reported. Membrane surface morphology was characterized using SEM (SU-8020, Hitachi, Japan). Samples were dried at 40°C for 2 hours prior to imaging to prevent moisture-related artifacts. The composition of contaminants in the fouling layer was determined using FTIR (Nicolet iN10MX, Thermo Fisher Scientific, USA).

2.4.3. ToF-SIMS depth profiling

To analyze the spatial distribution of foulants within the membrane fouling layer, ToF-SIMS (ToF-SIMS V, ION-TOF GmbH, Germany) was performed on dried, fouled membrane samples. The membranes were cut into 10 mm $\times$ 10 mm pieces and mounted with the fouled surface facing upward. Depth profiling was carried out using an argon cluster ion beam for sputtering and a Bi_3^+ ion beam for detection. A 500 $\mu\text{m} \times 500 \mu\text{m}$ area was sputtered, and secondary ion signals were collected from the central 100 $\mu\text{m} \times 100 \mu\text{m}$ region. Charge compensation was applied during measurement. The relative intensities of characteristic ions were normalized and plotted over sputtering time to reveal the depth distribution of foulants. Three-dimensional reconstructions of the fouling layer were generated based on the depth profiling data.

2.4.4. qPCR and Shotgun Metagenomic Sequencing

Genomic DNA was isolated from intracellular samples using the FastDNA® SPIN Kit for Soil (MP Biomedicals, Cleveland, OH, USA) following the manufacturer's specifications. Resultant DNA

extracts were cryopreserved at -80°C prior to downstream analysis. Total bacterial and archaeal abundance in the inlet_{-sand}, 50 cm_{-sand}, and 100 cm_{-sand} DNA extracts was quantified using SYBR Green qPCR, with primer sequences and thermal cycling protocols detailed in our prior work (Zhao et al., 2025). Metagenomic library construction and Illumina sequencing were conducted by the Beijing Genomics Institute (Shenzhen, China). Subsequent bioinformatic processing was performed, including raw data filtration, *de novo* assembly of quality-controlled reads, gene abundance quantification, and functional annotation with associated databases, as detailed in Text S2.

3. Results and discussion

3.1 Mitigation of UF membrane fouling by aerobic RBF

The long-term simulation of RBF aerobic zone was assessed by analyzing DO dynamics, DOC removal, and microbial abundance. Influent DO concentration averaged 6.1 ± 3.4 mg/L, declining significantly to 3.4 ± 1.2 mg/L in the effluent (Fig. 1a). This consistent DO consumption ($\sim 45\%$) while maintaining effluent DO above 2 mg/L unequivocally indicates sustained aerobic microbial respiration within the sand column. Concurrently, influent DOC concentration (4.8 ± 1.7 mg/L) was reduced to 3.7 ± 1.2 mg/L in the effluent (Fig. 1b), demonstrating DOC removal of $\sim 23\%$. This removal is likely attributed to microbial degradation of the biodegradable fraction of DOC (assimilable organic carbon, AOC) through aerobic respiration, a well-documented core mechanism in RBF systems (Li et al., 2025; Regnery et al., 2015; von Rohr et al., 2014). Moreover, qPCR analysis revealed that bacterial abundance (1.42×10^6 to 2.74×10^7 copies/ μL) in the simulated RBF was significantly higher than that of archaea (1.97×10^5 to 1.79×10^6 copies/ μL) (Fig. 1c). Microbial abundance for both domains was highest at the inlet_{-sand} and decreased at the 50 cm_{-sand} and 100 cm_{-sand}. The presence of active aerobic microbes in the simulated RBF is supported by sufficient DO (>2 mg/L), effective DOC removal, and qPCR-based profiling of the microbial community.

We further evaluated the impact of the RBF aerobic zone as a pretreatment on UF performance. The initial absolute membrane flux remained relatively consistent across different UF experiments, averaging 255.13 ± 8.59 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. Direct UF of river water in batch mode resulted in severe flux

decline, with final relative flux (J_t/J_0) ratios consistently falling below 0.5 within 2 hours (Fig. 1d). In contrast, coupling RBF pretreatment with UF dramatically improved membrane performance. The final J_t/J_0 ratio increased from 0.44 in direct UF to 0.78 in the RBF-UF system (Fig. 1d), representing a substantial (approximately 77%) reduction in the extent of flux decline. This finding aligns with the previous study which have reported that RBF (aerobic-anaerobic-anoxic) is an effective pretreatment method for alleviating UF membrane fouling (Haas et al., 2019; Zhai et al., 2022). To elucidate the mechanism by which aerobic RBF alleviates UF flux decline, we subsequently investigated the impact of RBF on the fouling behavior of UF membranes. Specifically, we analyzed changes in water quality during the RBF process, with a particular focus on NOM, and examined the microbial community structure and function within the RBF system.

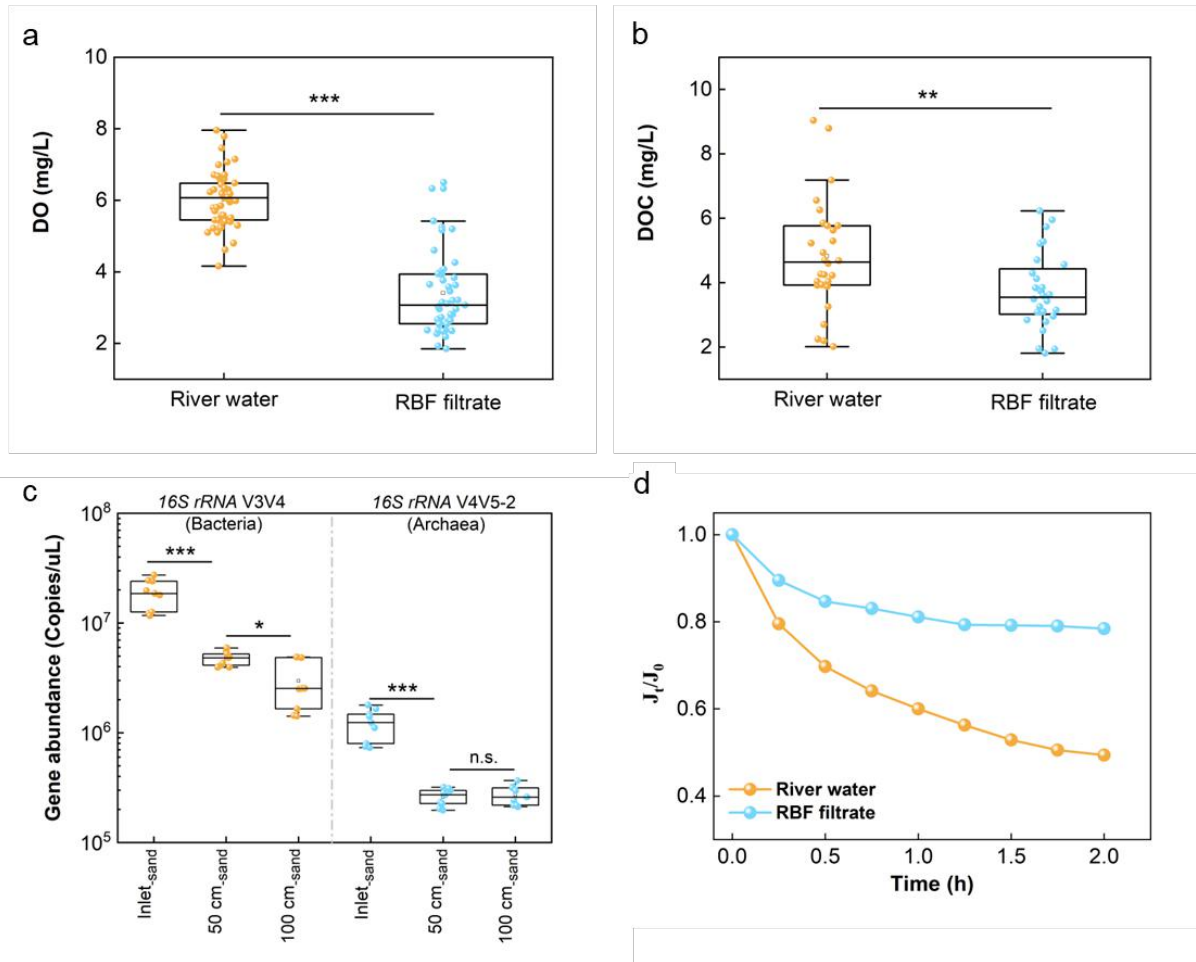


Fig. 1. The concentration of (a) dissolved oxygen (DO) and (b) dissolved organic carbon (DOC) in the river water and riverbank filtration (RBF) filtrate. (c) the abundance of bacteria and archaea in the column. (d) Normalized flux decline (J_t/J_0) during ultrafiltration (UF) of river water and RBF filtrate. Statistical analysis was performed using the Wilcoxon rank-sum test, * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$.

3.2. Impacts of RBF pretreatment on UF membrane fouling behavior

To investigate the fouling characteristics of UF membranes, a combination of SEM, water contact angle measurements, ToF-SIMS, and FTIR was employed on both pristine and fouled membranes. The pristine UF membrane exhibited a smooth and uniform porous surface (Fig. S1a), however, the UF treatment of river water led to severe fouling with the membrane surface completely obscured by a thick, dense, and continuous foulant layer (Fig. S1b). Nevertheless, pretreatment via RBF prior to UF reduced foulant accumulation, leaving the membrane surface partially visible beneath a thinner, discontinuous layer (Fig. S1c). This morphological change indicates that RBF pretreatment mitigates fouling severity. The less compact and discontinuous structure of the foulant layer is consistent with the enhanced operational sustainability observed in the RBF-UF process.

Water contact angle measurements further supported these observations (Fig. S1d-f). Direct UF of river water caused a marked increase in the membrane's contact angle, indicating decreased hydrophilicity due to adsorbed organic foulants. In contrast, the contact angle after UF of RBF-treated water remained near-pristine. The preserved hydrophilicity after RBF pretreatment is crucial, as hydrophilic surfaces generally exhibit lower foulant adhesion propensity (Zhou et al., 2023). This explains the reduced fouling severity observed by SEM and suggests RBF helps maintain the membrane's inherent anti-fouling properties by limiting hydrophobic organic deposition. ToF-SIMS 3D analysis (Fig. 2a, b) revealed homogeneous spatial distributions of key NOM components, including humic substances, proteins, and polysaccharides, within the UF membrane cake layers from both feed water sources. This compositional profile aligns with our earlier findings that the stronger the cake layer uniformity, the stronger the water channel connectivity and the lower degree of membrane fouling (Wu et al., 2021). The observed uniformity likely stems from Ca^{2+} (River water, 63.8 mg/L; RBF filtrate, 61.9 mg/L) present in both water sources, which facilitate aggregation of heterogeneous organic compounds through cation bridging (Li et al., 2011; Wu et al., 2023). This mechanism promotes co-deposition and consistent fouling layer structure. When comparing data obtained after direct UF of river water with those after RBF pretreatment, it is also obvious that the sputter time required to reach the membrane surface (increase of $\text{C}_3\text{H}_2\text{F}_4^+$ signal intensity as marker for the membrane polymer PVDF) was much shorter for the fouled membrane after RBF pretreatment,

in line with a thinner and discontinuous fouling layer seen in SEM analyses. Notably, the uniformity of the fouling layer persists even after RBF pretreatment that significantly reduces overall foulant loading (SEM evidence). This indicates that while RBF effectively removes bulk foulants, it does not disrupt the deposition mechanism of residual calcium-complexed NOM fractions.

Complementary FTIR analysis ([Fig. 2c-e](#)) identified intensified peaks for organic functional groups (O-H, N-H, aliphatic C-H, C=O, C-N) on fouled membranes, correlating with fouling severity. The specific increase in protein-associated groups (N-H, C-N, C=O) and polysaccharide markers (C-O, O-H) confirms the major contribution of biopolymers to fouling ([Tominaga et al., 2022](#)). Critically, the correlation between FTIR spectral intensity and independent fouling indicators (SEM morphology / contact angle hysteresis) provides direct spectroscopic evidence that RBF pretreatment mitigates organic accumulation on membrane surfaces, suggesting that this reduction drives the enhanced UF performance.

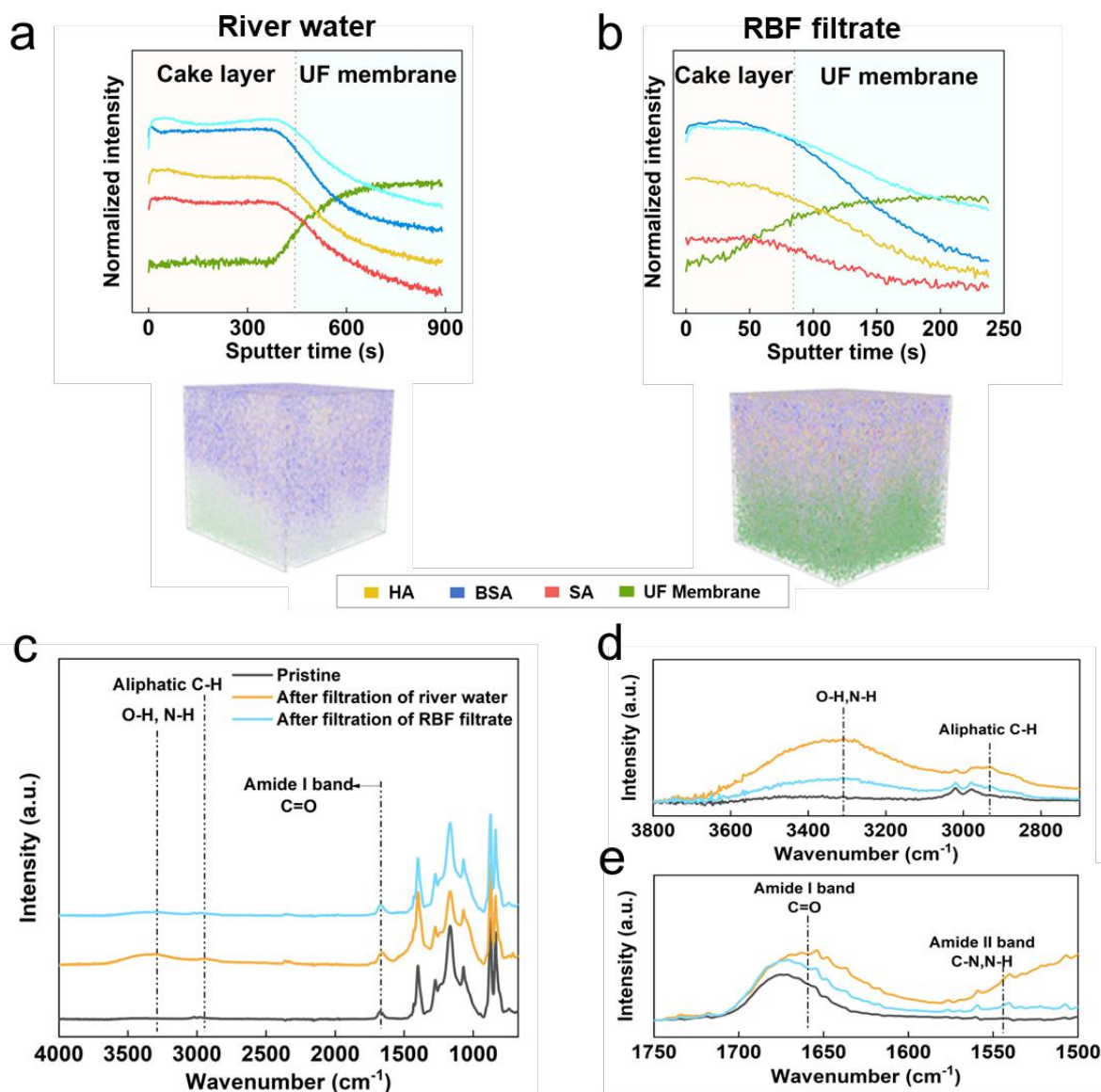


Fig. 2. ToF-SIMS depth profiles and corresponding 3D reconstructed images of the foulant (cake) layers on UF membranes after filtration of (a) river water and (b) RBF filtrate, showing the distribution of key components: humic acid (HA), bovine serum albumin (BSA), and sodium alginate (SA). (c-e) FTIR spectra of the pristine UF membrane compared to those fouled by river water and RBF filtrate.

3.3 Effects of aerobic RBF on water quality

To investigate the mechanism by which the RBF aerobic zone mitigates UF membrane fouling, its impact on key water quality parameters, including DOC, UV₂₅₄, cations, and zeta potential, was evaluated. During the RBF-UF experiment (~2 weeks after 16 months of microbial acclimation), the RBF aerobic zone reduced the river water DOC concentration from 4.4 mg/L to 2.7 mg/L (Fig. S2). Our findings support the view that the RBF aerobic zone serves as the primary region for DOC removal (von Rohr et al., 2014). DOC removed in the simulated RBF aerobic zone was likely

predominantly AOC (Zhai et al., 2022). When comparing treatment efficiencies, the combined RBF-UF process achieved a higher DOC removal efficiency ($84 \pm 1\%$) than either process alone (RBF: $37 \pm 1\%$; UF: $43 \pm 9\%$). This demonstrates that UF following RBF provides additional effective DOC removal. Since DOC is a major contributor to UF membrane fouling (Liu et al., 2022), the observed reduction in UF membrane fouling after RBF aerobic pretreatment can be largely attributed to DOC removal. Previous studies have shown that RBF can reduce UV_{254} (Bertelkamp et al., 2014; Liu et al., 2016). Similarly, in this study, the simulated RBF aerobic zone decreased UV_{254} from 0.075 to 0.060 (Fig. S2), which could also help mitigate UF membrane fouling (Zhao and Zhou, 2024). Future studies incorporating a broader set of parameters, such as UV_{254} and zeta potential, alongside DOC, during UF, RBF-UF, would provide a more comprehensive evaluation of the RBF-UF process.

In natural RBF systems, redox processes typically follow the sequence $O_2 \rightarrow NO_3^- \rightarrow Mn \rightarrow Fe \rightarrow SO_4^{2-}$ (Bertelkamp et al., 2016; Zuo et al., 2022). Under anoxic-anaerobic conditions, RBF poses a risk of Mn and Fe release (Paufler et al., 2018), and elevated metal concentrations can aggravate UF membrane fouling (Haas et al., 2019). In this study, the simulated RBF had no significant effect on NO_3^- concentrations ($P > 0.05$, data not shown) and did not increase Mn or Fe levels (Fig. S3a, b). These findings support the effectiveness of the sand-column setup in mimicking aerobic RBF and suggest that aerobic RBF can mitigate Mn and Fe release issues typical of conventional systems. Additionally, the filtration through the RBF aerobic zone showed no significant ($P > 0.05$) effect on the concentrations of Ca^{2+} , K^+ , Na^+ , and Mg^{2+} (Fig. S3c-f). However, permeation through the RBF aerobic zone raised Zn^{2+} concentration to 0.07-0.17 mg/L (Fig. S3g). While Zn^{2+} may influence fouling, its net effect on UF membrane performance remains an unresolved issue that requires further investigation.

Zeta potential measurements indicated a shift in the net surface charge of colloidal/carbonaceous material from -4.1 mV in river water to -2.8 mV after RBF treatment (Fig. S2). Theoretically, the reduction in negative charge could weaken electrostatic repulsion with the typically negative UF membrane, potentially promoting adsorption and fouling (Abd-Razak et al., 2021). However, given that the observed change falls near the measurement uncertainty (Fig. S2), its practical influence is likely limited. Instead, the mitigation of UF membrane fouling is primarily

attributed to the substantial decreases in DOC and UV₂₅₄, consistent with reported mechanisms where RBF reduces fouling via the removal of DOM (Wang et al., 2024).

3.4 Evolution of DOM composition and characteristics during aerobic RBF: insights from 3D-EEM and FT-ICR MS

To further explore the mechanism by which the aerobic zone of RBF mitigates UF membrane fouling, we analyzed the impact of the aerobic zone on the composition of DOM using 3D EEM fluorescence spectroscopy and FT-ICR MS. River water showed strong fluorescence intensities in regions IV (soluble microbial by-products, SMPs) and V (humic acid-like substances) (Fig. 3a), indicating that the primary organic compounds in the river water were SMPs and humic acid-like substances. In contrast, the fluorescence intensities of regions IV (SMPs) and V (humic acid-like substances) were markedly reduced in the RBF effluent (Fig. 3b-d), suggesting that the RBF aerobic zone plays a role in removing these compounds. This finding aligns with previous studies that have demonstrated the ability of RBF to remove DOM and humic acid-like substances (Abdelrady et al., 2018). Since SMPs, which are often rich in proteins and polysaccharides, and humic acids are well-known contributors to membrane fouling—promoting pore blocking, cake layer formation, and hydrophobic interactions (Yang et al., 2021; Zhou and Meng, 2015), the results from 3D EEM fluorescence spectroscopy suggest that the aerobic zone of RBF may mitigate UF membrane fouling by removing or transforming these problematic compounds.

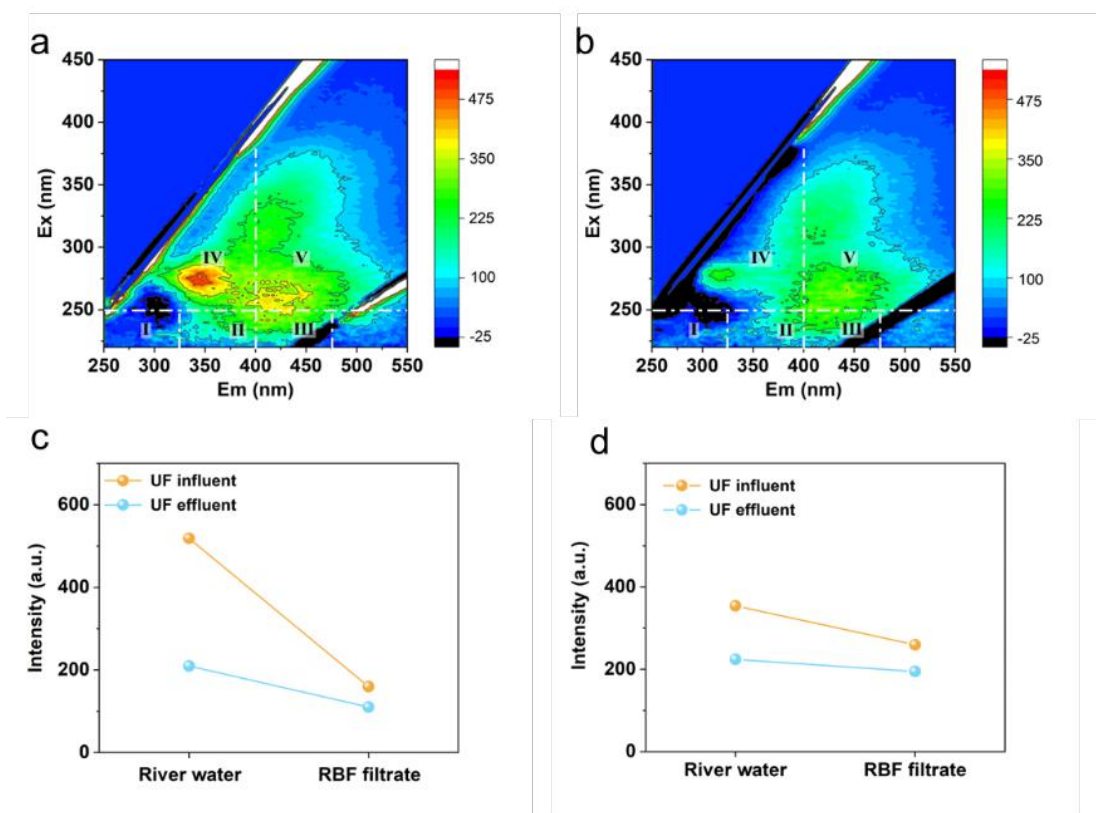


Fig. 3. 3D fluorescence spectra of (a) river water and (b) RBF filtrate. Changes in 3D-EEM fluorescence intensity for (c) soluble microbial by-products (SMPs) and (d) humic acid-like substances in river water, RBF filtrate, and UF effluent. The regions are categorized as follows: Region I: aromatic proteins; Region II: aromatic proteins II; Region III: fulvic acid-like substances; Region IV: SMPs; Region V: humic acid-like substances.

FT-ICR MS analysis detected 6403-6561 DOM molecular formulas in the water samples using both ionization modes (Table S3). The river water contained more molecular species (6561) than the RBF filtrate (6403). Four major compound classes were identified: CHO, CHON, CHOS, and CHONS. CHO compounds were predominant (42.10%-42.23%), followed by CHON (38.44%-38.63%), CHOS (11.68%-11.81%), and CHONS (7.51%-7.57%). This distribution pattern is consistent with that observed in natural water bodies such as lakes (Guo et al., 2025; Wang et al., 2025). The number of molecules within each class (i.e., CHO, CHON, CHOS, and CHONS) was consistently higher in the river water than in the RBF filtrate (Table S3). This observation demonstrates that permeation through the simulated RBF aerobic zone reduced the overall number of DOM molecules. The average molecular weight of DOM was nearly identical in river water (478 Da) and RBF filtrate (476 Da) (Table S3). This suggests that permeation through RBF primarily reduced the number of DOM molecules rather than altering their average size.

AI_{mod} analysis classified DOM into three structural groups: non-aromatic (AI_{mod} ≤ 0.5), aromatic (0.5 < AI_{mod} < 0.67), and condensed polycyclic aromatics (AI_{mod} ≥ 0.67) (Roebuck et al., 2025). Non-aromatics predominated in both river water and RBF filtrate (Fig. 4a, b). Notably, the RBF filtrate showed a marked decrease in the number of non-aromatic and condensed polycyclic aromatics compared to river water (Fig. 4a, b). DOM was further classified into lipids, proteins, carbohydrates, CRAM-like, tannins, and CAS based on O/C and H/C ratios (Fig. 4c). The quantities of lipids, carbohydrates, and tannins in the RBF filtrate was comparable to or higher than those in the river water (Table S3, Fig. 4c, d). Notably, the quantities of proteins, CRAM-like, and CAS compounds decreased after RBF treatment (Fig. 4c, d). The decrease in protein-like compounds is attributable to biodegradation. The CRAM-like class includes lignin-derived structures and CRAM. Lignin, slowly biodegradable hydrophobic compounds, was likely removed through a combination of adsorption and fungally mediated degradation (Kuan and Tien, 1993; Salamon and Goda, 2019). CRAM-like molecules and CAS compounds are typically recalcitrant to biodegradation (Liu et al., 2023). Therefore, their reduction during RBF is likely due primarily to adsorption processes. Notably, the simulated RBF system maintained its adsorption capacity for refractory compounds such as CAS even after 16 months of continuous operation. Although adsorption capacity limits would theoretically be expected, the sustained removal efficiency may be explained by mechanisms such as desorption or degradation of adsorbed substances. It is also plausible that accumulated materials in the sand column contribute to continued adsorption by providing additional surfaces or sites. Further research is necessary to elucidate the mechanisms underlying the long-term adsorption behavior in RBF systems. In addition, the persistent adsorption of organics like CAS may contribute to long-term matrix clogging, a plausible mechanism that warrants further investigation. While FT-ICR MS revealed a reduction in the number of CAS molecules, changes in their absolute concentration remain unclear. Future studies should quantify these organics to better understand the impact of RBF on DOM.

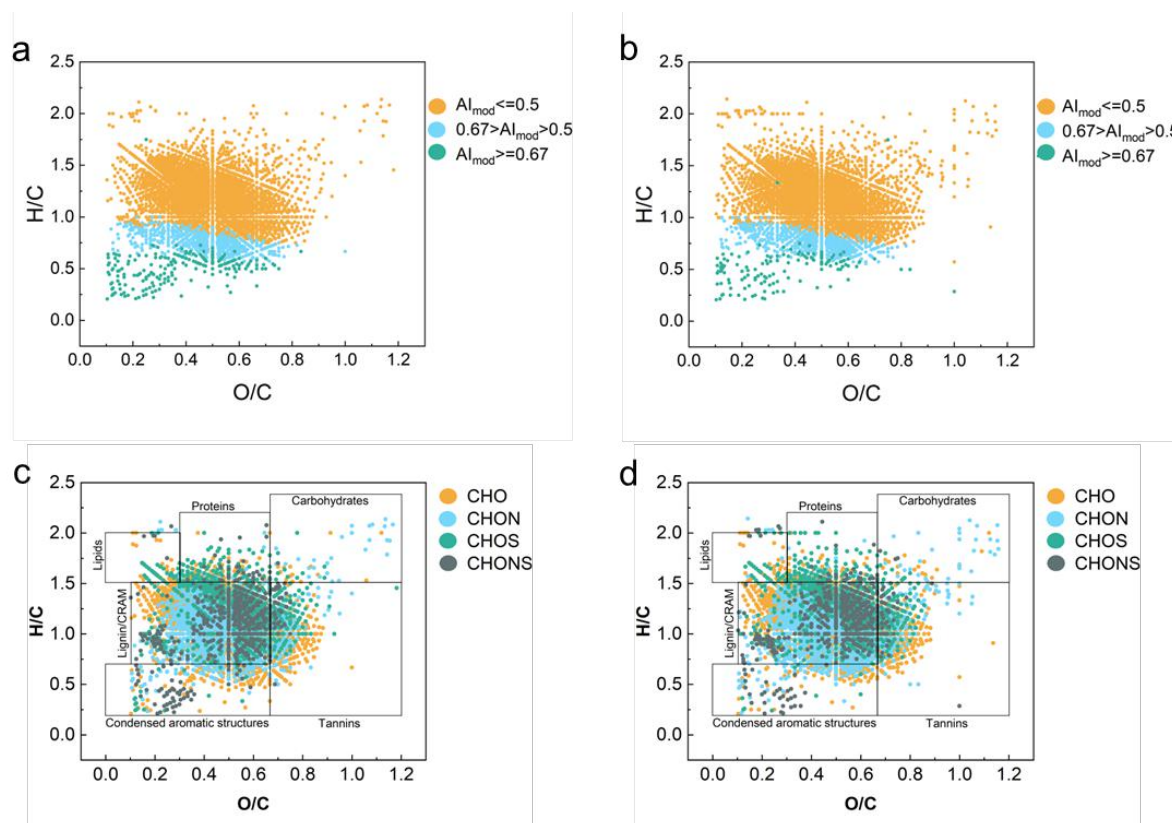


Fig. 4. Almod-classified Van Krevelen diagrams for (a) river water and (b) RBF filtrate. Compounds are categorized based on Aromaticity Index (AI): non-aromatic ($AI \leq 0.5$), aromatic ($0.5 < AI < 0.67$), and condensed polycyclic aromatics ($AI \geq 0.67$). Van Krevelen diagrams from the mass spectra of (c) river water and (d) RBF filtrate. Boxes overlain on the plots indicate major biomolecular compound classes: lipids, proteins, carbohydrates, unsaturated hydrocarbons, lignin/carboxylic-rich alicyclic molecules (CRAM)-like, tannins, and condensed aromatic structures.

Analysis of precursors (compounds unique to river water) and products (compounds unique to RBF filtrate) identified 1240 precursors and 1082 products (Fig. 5a), indicating extensive transformation and generation of organic matter within the simulated aerobic RBF zone. Notably, proteins were present in both precursor (127) and product (73) pools (Fig. 5b), demonstrating simultaneous protein degradation and generation. Protein degradation likely resulted from microbial activity, while their generation may stem from endogenous protein release during microbial lysis. In addition, both the precursors and products contained CRAM (carboxyl-rich alicyclic molecules) (Fig. 5b). The presence of CRAM in the products may be attributed to either microbial synthesis of CRAM molecules or the transformation of other organic compounds into CRAM (Bayer et al., 2019; Liu et al., 2023). The number of proteins, CRAM-like, and CAS compounds was higher among precursors than products (Fig. 5c, d), indicating a net decrease due to removal exceeding generation. Further analysis revealed 29 potential reactions associated with protein transformation. Among these,

oxidation of methyl groups to carboxylic acids and oxidation of amine groups to nitro compounds were the most frequent (Table S4).

3D-EEM fluorescence spectroscopy indicated that the aerobic zone of the RBF effectively reduced the relative fluorescence intensity of humic acid-like substances and SMPs (e.g., proteins). Complementary FT-ICR MS analysis confirms a decrease in the number of proteins, CRAM-like, and CAS molecules. This reduction is likely attributed to a combination of adsorption and biodegradation processes occurring within the aerobic zone. Notably, although new protein, CRAM-like, and CAS compounds may be generated during treatment, their overall molecular abundance decreases. These findings suggest that the aerobic zone of the RBF contributes to UF membrane fouling mitigation primarily by transforming and reducing the abundance of key fouling-related compounds. Future comparative analysis of DOM in UF, RBF-UF, and RBF effluents would further elucidate NOM fate in integrated systems and provide deeper mechanistic insights into fouling control.

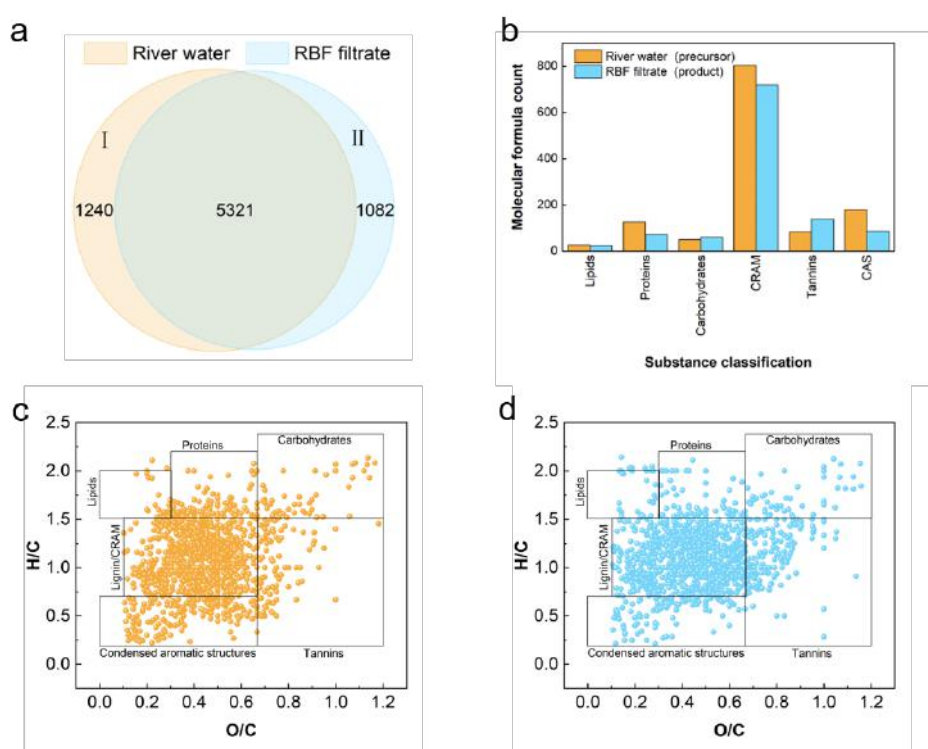


Fig. 5. (a) Venn diagram of molecular formulas identified in river water and RBF filtrate. Area I: precursors; Area II: products. (b) Molecular counts by organic compound class for precursors and products. (c) Van Krevelen diagram of precursor molecules. (d) Van Krevelen diagram of product molecules.

3.5 Microbial community structure and metabolic potential in RBF

To elucidate the microbial mechanisms by which RBF transforms DOM (specifically protein and lignin) and thereby mitigates UF membrane fouling, we conducted a metagenomic analysis of the RBF sand microbiome at the inlet (inlet_{-sand}), middle (50 cm_{-sand}), and outlet (100 cm_{-sand}) depths. Microbial community richness and evenness, assessed via alpha diversity indices, were consistently high across the RBF profile (Table S5). Genus-level Shannon indices ranged from 7.96 to 8.09, exceeding those reported in a recent RBF simulation study (Wang et al., 2024). The higher genus-level Shannon indices (7.96-8.09) observed in this study are likely attributable to the extended pre-cultivation period (16 months versus <4 months (Wang et al., 2024)). Other factors, such as water quality (e.g., DOM) and media properties (e.g., organic carbon content), may also influence Shannon indices. Further dedicated investigations are needed to elucidate the specific causes of these differences. High Chao1 values (1471-1499) indicated considerable species richness, while high Simpson indices (0.9849-0.9898) suggested a balanced and even population distribution within this simulated aerobic ecosystem. Principal Coordinates Analysis (PCoA) revealed distinct clustering, indicating differences in genus-level community composition between the inlet_{-sand} and samples from 50 cm_{-sand} and 100 cm_{-sand} (Fig. S4a). Venn diagram analysis (Fig. S4b) highlighted this shift, with 70 genera unique to the inlet_{-sand} compared to only 11 and 15 unique genera at 50 cm_{-sand} and 100 cm_{-sand}, respectively. Crucially, 1262 genera were shared across all depths, indicating a core microbiome despite spatial variations in relative abundance.

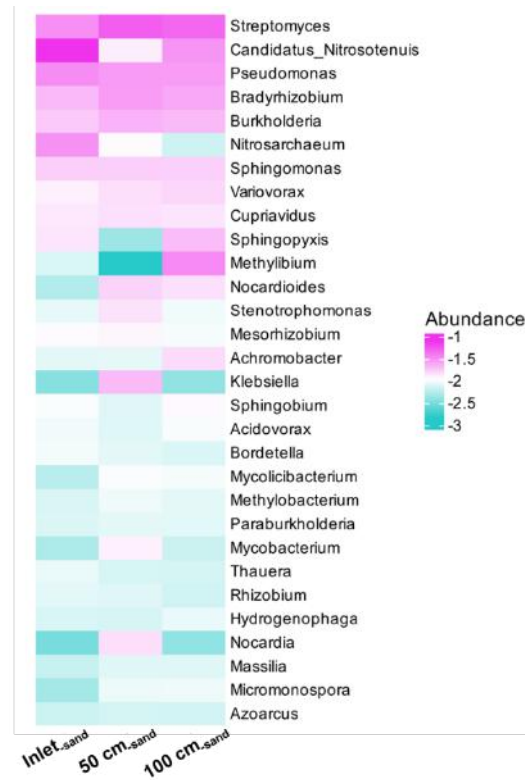


Fig. 6. Relative abundance of the top 30 microbial genera identified in sand samples from the inlet_{sand}, middle (50 cm_{sand}), and outlet (100 cm_{sand}) of the simulated RBF system.

Taxonomic profiling identified the top 10 most abundant genera (Fig. 6): *Streptomyces*, *Candidatus Nitrosotenuis*, *Pseudomonas*, *Bradyrhizobium*, *Burkholderia*, *Nitrosarchaeum*, *Sphingomonas*, *Variovorax*, *Cupriavidus*, and *Sphingopyxis*. Functionally, *Streptomyces* and *Pseudomonas* are well-documented producers of potent extracellular proteases, underpinning significant proteolytic capabilities (Ercan et al., 2006; Griffith and Fletcher, 1991). *Streptomyces* degrades lignin via extracellular enzymes like laccases and dye-decolorizing peroxidases (DyP), which cleave aromatic rings through radical reactions (Majumdar et al., 2014; Riyadi et al., 2020). Similarly, *Pseudomonas* employs laccases, peroxidases, and the β -aryl ether cleavage pathway to depolymerize lignin into small aromatic compounds (e.g., vanillin) (Li et al., 2025). *Burkholderia* and *Sphingomonas* also exhibit lignin-degrading potential: *Burkholderia* utilizes β -aryl ether cleavage and 4,5-PDOG pathways, while *Sphingomonas* employs intracellular multi-copper oxidase and membrane-bound enzyme systems, preferentially targeting syringyl lignin units (Li et al., 2025). Collectively, these functional insights suggest that *Streptomyces*, *Pseudomonas*, *Burkholderia*, and *Sphingomonas* may help mitigate membrane fouling through the degradation of protein- and lignin-based foulant precursors within the RBF environment.

While the sand column simulating the RBF system underwent 16 months of pre-cultivation, our findings do not fully reflect the behavior of a coupled RBF aerobic zone and UF under real field conditions. Future studies should therefore conduct long-term field experiments to rigorously validate the feasibility of this approach. Although theoretically capable of increasing water yield, the potential for RBF clogging necessitates optimizing the balance between aquifer self-purification capacity and pumping rates (Hu et al., 2022). Furthermore, given the critical role of anoxic zones in removing certain specific contaminants that are not addressed in this work (e.g., NO_3^- -N) (Bai et al., 2019), future research should prioritize leveraging these zones to enhance pollutant removal, mitigate membrane fouling, and address secondary issues like ion release (e.g., Fe, Mn) and groundwater consumption. This study advances the understanding of aerobic RBF's role in mitigating UF membrane fouling using a PVDF system. The mechanistic insights obtained offer valuable references for other UF membranes such as polyethersulfone. However, given that global PFAS regulations (Wang et al., 2024) are driving a shift from PVDF membranes, future research on RBF-UF mechanisms and applications should prioritize the use of non-PVDF alternatives.

Regarding the practical significance and feasibility of coupling aerobic RBF with UF, several full-scale systems have been reported to operate under predominantly aerobic conditions. For instance, at RBF sites in Switzerland, groundwater filtrate remained aerobic with DO concentrations of 5.7-10.2 mg/L even at extraction wells situated more than 10 meters from the riverbank (Hollender et al., 2018), suggesting the potential technical feasibility of this approach under suitable field conditions. However, maintaining aerobic conditions in a full-scale setting is influenced by multiple factors, such as the well-river distance, pumping rate, temperature, and microbial activity in the subsurface. Therefore, to advance toward reliable implementation of the combined aerobic RBF-UF process, future work should focus on clarifying the relationships between these operational/hydrogeological factors and the resulting redox zonation, which could support the development of robust strategies for sustaining aerobic conditions.

4. Conclusion

This study investigated the impact of a simulated aerobic RBF zone on UF performance. The

aerobic RBF reduced UF membrane fouling by ~77%, attributed to diminished organic accumulation on membrane surfaces, evidenced by thinner discontinuous foulant layers and maintained hydrophilicity. Consistent with this mechanism, RBF pretreatment lowered DOC and UV₂₅₄, confirming that organic reduction critically mitigates fouling. Further analysis revealed decreased contents of humic acid-like substances and soluble microbial products (e.g., proteins) during the simulated RBF process. At the molecular level, fouling alleviation correlated with reduced quantities of proteins, CRAM-like, and CAS compounds after RBF pretreatment. Within the RBF system, the decline in persistent NOM (e.g., CAS compounds) appears attributable to adsorption. In contrast, the reduction in more labile organics such as proteins and lignins is likely associated with biodegradation by indigenous microbes, including genera such as *Streptomyces* and *Pseudomonas*. This work offers new molecular-level insights into NOM transformation during aerobic RBF, demonstrating the potential of this pretreatment to mitigate membrane fouling and improve UF performance.

Acknowledgements

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Supplementary Information

Integration of Aerobic Riverbank Filtration and Ultrafiltration for Advanced Water Treatment and Membrane Ageing Reduction

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Text S1. Detailed SPE procedures

The filtered water sample was acidified to pH 2.0 with 1 mol/L HCl. A PPL cartridge was conditioned on an SPE system with 12 mL methanol followed by 12 mL of 0.01 mol/L HCl. The sample was then loaded at approximately 5 mL/min. The sample volume was determined based on the DOC concentration, accounting for 50% loss during extraction to achieve a final concentration of approximately 100 mg C/L. After loading, the cartridge was rinsed with 18 mL of 0.01 mol/L HCl to remove salts, dried under nitrogen, and eluted with 12 mL methanol. The eluate was evaporated to dryness under nitrogen and stored at -20°C . Prior to FT-ICR-MS analysis, the sample was reconstituted in 1 mL of a 1:1 (v/v) methanol:water solution or pure methanol.

Text S2. The pruning of the raw data, de novo assembly of high-quality reads, quantification of gene abundance, annotation of gene function, and related databases.

All the acquired raw data were pruned by SOAPnuke v.1.5.2 ([Chen et al., 2018](#)). The pruned reads were mapped to the host genome employing SOAP2 software to distinguish and eliminate host originated reads (only for samples of host origin) ([Li et al., 2009](#)). The MEGAHIT software was utilized to de novo assemble the high-quality reads ([Li et al., 2015](#)). Assembled contigs with length less than 300 bp were retained for subsequent analysis. The prediction of genes over contigs were accomplished by MetaGeneMark ([Zhu et al., 2010](#)). The resulting genes were de-redundant using CD-HIT software ([Fu et al., 2012](#)). The relative abundance of each gene was quantified using Salmon software ([Patro et al., 2017](#)). Non-redundant genes were aligned to CARD, KEGG and EggNOG databases using DIAMOND to complete gene function annotation with an E value cutoff of 10^{-5} ([Buchfink et al., 2015](#)).

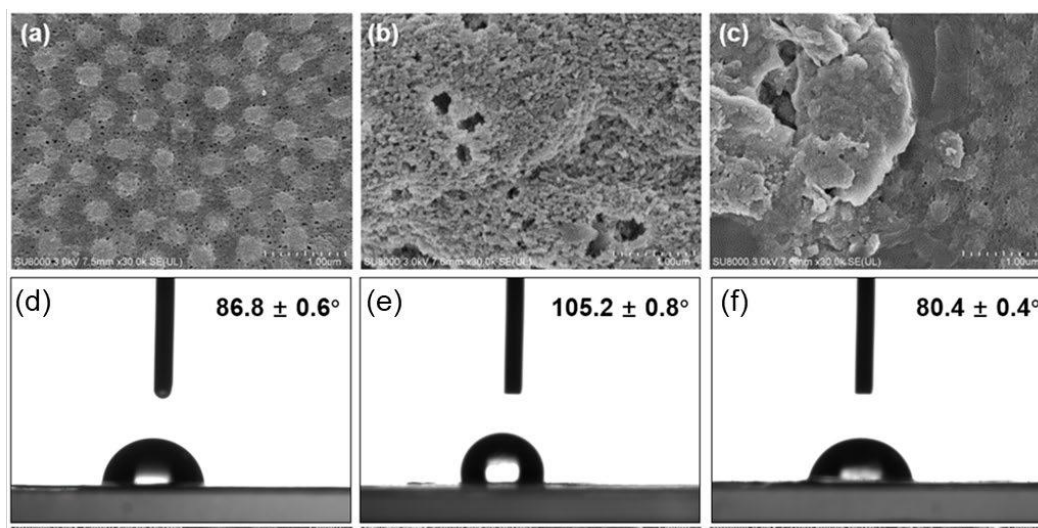


Fig. S1. SEM images of UF membranes: (a) Pristine, (b) After filtration of river water, and (c) After filtration of RBF filtrate. Water contact angles on the surface of UF membranes: (d) Pristine, (e) After filtration of river water, and (f) After filtration of RBF filtrate.

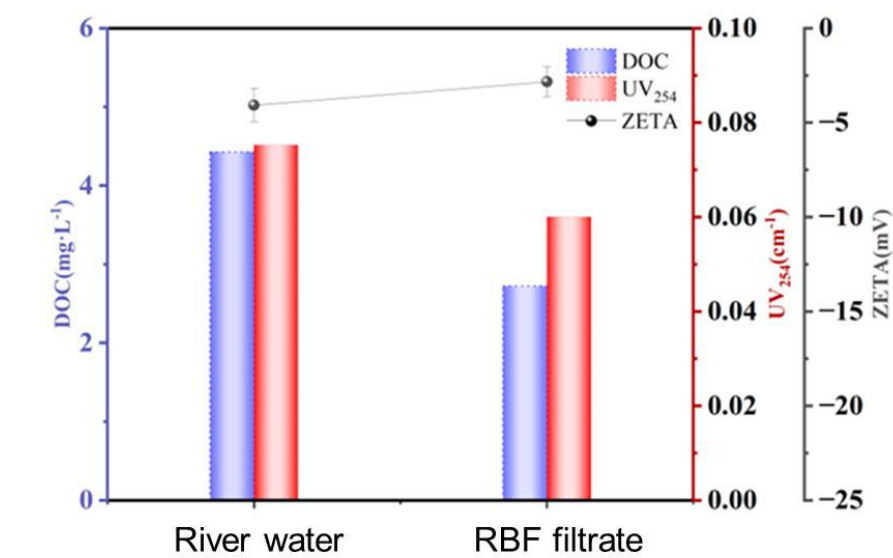


Fig. S2. Changes in DOC, UV₂₅₄ absorbance, and zeta potential between river water and RBF filtrate.

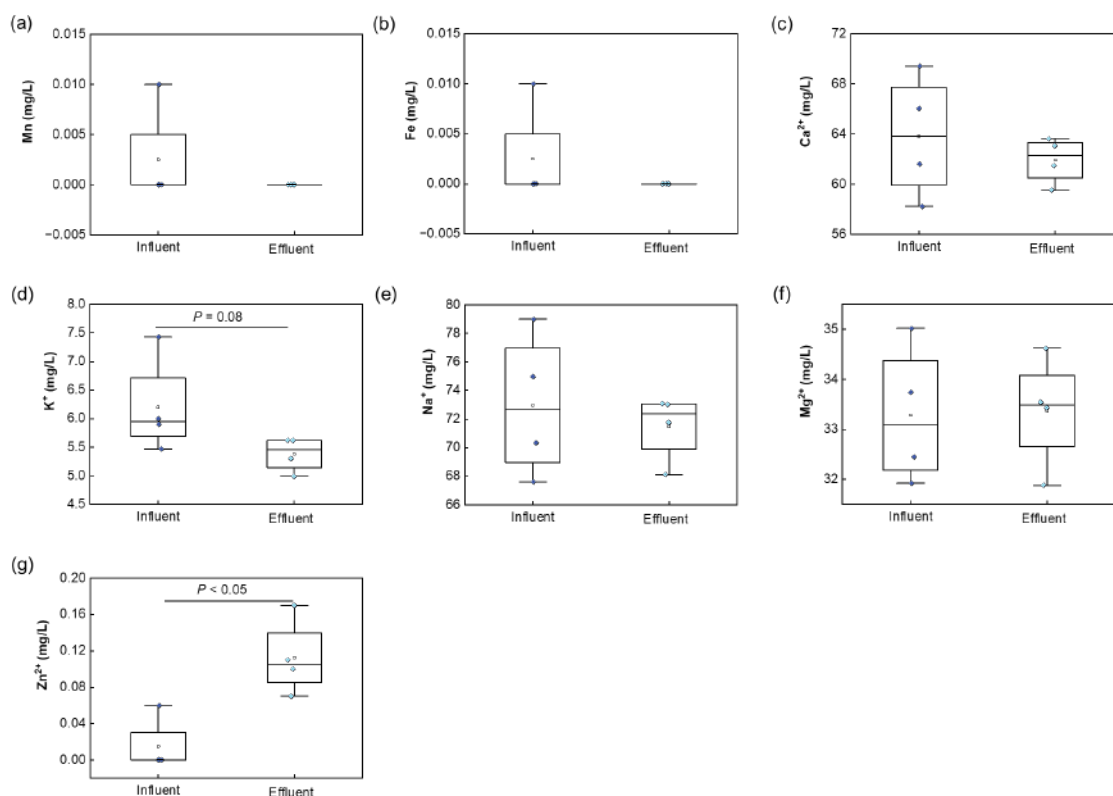


Fig. S3. Concentrations of cations in river water (influent) and RBF filtrate (effluent). (a) Mn, (b) Fe, (c) Ca^{2+} , (d) K^+ , (e) Na^+ , (f) Mg^{2+} , (g) Zn^{2+} . Statistical analysis was performed using the Wilcoxon rank-sum test.

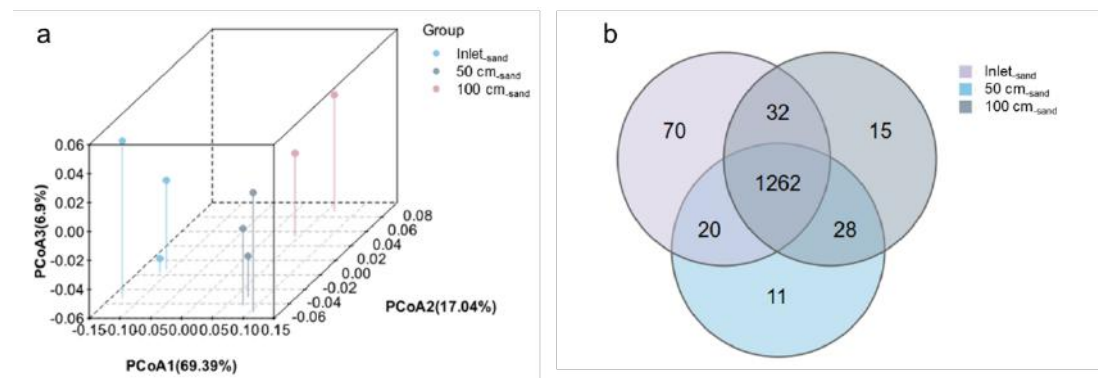


Fig. S4. (a) 3D PCoA plot showing β -diversity of microbial communities at the genus level based on Bray-Curtis distance. (b) Venn diagram showing the overlap of microbial genera among inlet_{sand}, 50 cm_{sand}, and 100 cm_{sand}.

Table S1. Recent advances (last ten years) in RBF-membrane system integration: process configurations, redox conditions, target contaminants, fouling mitigation mechanisms and analytical approaches.

Year of study	Process Configuration	Redox Condition of RBF	Fe and Mn in RBF filtrate	Target contaminants	Analytical methods for the effects and mechanisms of RBF on membrane fouling			Reference
					Fouling reduction efficiency	Analytical parameters	Analytical techniques	
2018	RBF-NF	Aerobic-anoxic-anaerobic*	~1.8 mg/L Fe, ~0.5 mg/L Mn	DOC, Fe, Mn, OMPs, etc.	-	TMP	-	(Jhrig et al., 2018)
2019	RBF-UF	Aerobic-anoxic-anaerobic*	< 0.02 mg/L Fe, 0.17~0.43 mg/L Mn	Turbidity, ATP, DOC, etc.	> 90%	TMP	-	(Haas et al., 2019)
2022	RBF-RO	Aerobic-anoxic-anaerobic	-	Turbidity, pathogens, viruses, DOC, OMPs, etc.	-	-	-	(Zhai et al., 2022)
2024	RBF-UF	Short-distance RBF; redox condition not reported.	-	Turbidity, total nitrogen, ammonia nitrogen, and total organic carbon, etc.	~70%	TMP, membrane flux	SEM, FT-IR, EEM, <i>16S/18S rRNA</i> gene sequencing	(Wang et al., 2024)

2025	RBF-NF	Short-distance RBF; redox condition not reported.	-	Turbidity, NOM, OMPs, AOC, TP, etc.	~70%	TMP	EEM, <i>16S/18S</i> <i>rRNA</i> gene sequencing	(Li et al., 2025)
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Notes: *: Possibly present, uncertain; Normalized transmembrane pressure (TMP). RBF, Riverbank filtration. Membrane Processes: NF - Nanofiltration; UF - Ultrafiltration; RO - Reverse Osmosis. Water Quality Parameters & Pollutants: DOC - Dissolved Organic Carbon; AOC - Assimilable Organic Carbon; ATP - Adenosine Triphosphate; OMPs - Organic Micropollutants; TP - Total Phosphorus. Analytical Techniques: SEM - Scanning Electron Microscopy; FT-IR - Fourier Transform Infrared Spectroscopy; EEM - Excitation-Emission Matrix (3D fluorescence spectroscopy).

Table S2. Physicochemical properties of natural riverbank sand.

Parameters	Units	Results
Grain size distribution	< 8 μm	0.28 ± 0.02
	8~63 μm	0.44 ± 0.05
	63~2000 μm	99.28 ± 0.05
pH	d ₅₀	1.02 ± 0.20
	-	8.05 ± 0.06
Soil organic matter content	mg/kg	234.71 ± 40.31
Nitrate	mg/kg	4.41 ± 0.29
Total nitrogen	mg/kg	33.34 ± 17.79

Table S3. The molecular composition of small molecule DOM (m/z 100–800) in river water and RBF filtrate.

Samples	River Water	RBF filtrate
DOM	6561	6403
CHO	2771	2696
CHON	2522	2474
CHOS	775	748
CHONS	493	485
Lipids	109	107
Proteins	476	422
Carbohydrates	70	78
Lignin/carboxylic-rich alicyclic molecules (CRAM)-like	5148	5064
Tannins	549	603
Condensed aromatic structures (CAS)	348	256
Average molecular weight	478	476

Note: The categories of compounds were identified into seven classes, including (1) lipids ($1.5 \leq H/C \leq 2$, $0 \leq O/C \leq 0.3$), (2) proteins ($1.5 \leq H/C \leq 2.2$, $0.3 \leq O/C \leq 0.67$), (3) carbohydrates ($1.5 \leq H/C \leq 2.4$, $0.67 \leq O/C \leq 1.2$), (4) unsaturated hydrocarbons ($0.7 \leq H/C \leq 1.5$, $0 \leq O/C \leq 0.1$), (5) lignin/carboxylic-rich alicyclic molecules (CRAM)-like ($0.7 \leq H/C \leq 1.5$, $0.1 \leq O/C \leq 0.67$), (6) tannins ($0.5 \leq H/C \leq 1.5$, $0.67 \leq O/C \leq 1.2$), and (7) condensed aromatic structures (CAS) ($0.2 \leq H/C \leq 0.7$, $0 \leq O/C \leq 0.67$).

Table S4. Inferred protein reactions in simulated RBF based on molecular weight changes of precursors and products.

No.		Reactions	Molecular formula change	Quantity
1		Demethylation	-CH ₂	7
2		Dealkylation	-C ₂ H ₂	5
3	Dealkyl group	Di-demethy or Deethylation	-C ₂ H ₄	4
4		Dealkylation	-C ₂ H ₆	7
5		Decyclopropyl	-C ₃ H ₄	3
6		Deisopropyl	-C ₃ H ₆	6
7		Hydroxylation/N or S- oxidation	+O	4
8	Oxygen addition	Carbonylation/Methyl to aldehyde/Alcohol to carboxylic acid	+O-H ₂	6
9		Hydration	+H ₂ O	2
10		Methyl to carboxylic acid	+O ₂ -H ₂	14
11		Oxygen addition	+O ₂	5
12		Reductive displacement of carboxylic acid	-CO	3
13	Reaction of carboxylic	Decarboxylation	-CO ₂	2
14		Decarboxylation to carbonyl/Loss of aldehyde	-CH ₂ O	7
15		Loss of acetic acid	-C ₂ H ₂ O ₂	6
16			-C ₄ H ₂ O ₄	3
17		Loss of N atom	-N+3H	3
18			-NH	1
19	Reaction of amine	Oxydative displacement of amine	-NH ₂ +OH	1
20			-NH ₂ +CH ₃	2
21		Nitration of the amine group	-NH ₂ +NO ₂	14
22		Cleavage of triazine	-2N-CO	1
23	Reaction of surfer		-SO	3
24			-SO ₂	3
25		Desulfonation	-SO ₃	1
26		Dehydrogenation	-H ₂	5
27	Other reactions	Dehydration	-H ₂ O	5
28		Loss of oxygen	-O ₂	2
29		Deacetylation	-C ₂ H ₂ O	4

Table S5. Alpha diversity index of microbial communities at the genus level.

Sample position	Shannon		Simpson		Chao1	
	avg.	SD	avg.	SD	avg.	SD
Inlet _{-sand}	7.9656	0.1610	0.9849	0.0040	1471	21.5
50 cm _{-sand}	8.0905	0.1035	0.9898	0.0009	1469	14.4
100 cm _{-sand}	8.0223	0.0143	0.9894	0.0001	1499	6.4

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