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Supplementary Material for

In-Situ Catalytic Membrane Technology for Antifouling and Sustainable Landfill Leachate Management

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Section S1: Diagram of the experimental flow



Fig.S1 Diagram of the experimental flow

Section S2: MnO2 particles preparation and characterization

(1) Scheme I: Preparation using KMnO₄ and concentrated HCl

First, a precursor solution was prepared by adding 1.25 mmol of KMnO₄ and 0.5 mL of concentrated HCl to 22.5 mL of deionized water (DI). This mixture was stirred using a magnetic stirrer for 15 minutes. The precursor solution was then transferred to a 50 mL PTFE-lined autoclave and maintained at 140°C in a convection oven for 12 hours. After the hydrothermal reaction, the reactor was allowed to cool naturally to room temperature. The resulting black precipitate was repeatedly centrifuged and washed with deionized water at least six times. The prepared samples were dried at 70°C overnight, followed by calcination at 400°C for 2 hours in a muffle furnace at a heating rate of 2°C/min. The resulting manganese dioxide particles had a size of 2262 nm.

(2) Scheme II: Preparation using KMnO₄ and H₂O₂

506 g of KMnO₄ was weighed into a beaker containing 80 mL of DI water, and the mixture was stirred with a magnetic stirrer for 5 minutes to fully dissolve the KMnO₄. Then, 4 mL of 3 wt% H₂O₂ was added to the beaker while stirring. 1.6 mL of concentrated HCl was then added dropwise over 10 minutes while continuously stirring. After mixing, the solution was stirred for an additional 5 minutes and then transferred to a hydrothermal reactor and sealed. The reactor was maintained at 160°C in a convection oven for 12 hours. After the hydrothermal reaction, the reactor was cooled to

room temperature, and the resulting black reactants were washed five times with DI water and finally dried at 60°C for 4 hours. The resulting manganese dioxide particles had a size of 1397 nm.

(3) Scheme III: Preparation using KMnO₄ and HNO₃

7 g of KMnO₄ and 5 mL of HNO₃ (8.36 mol/L) were mixed with DI water and transferred to an 80 mL PTFE-lined autoclave. The autoclave was sealed and heated in a convection oven at 120°C for 20 hours, then allowed to cool naturally to room temperature. The resulting black-brown slurry was washed multiple times with DI water and anhydrous ethanol to remove soluble impurities and dried at 120°C for 4 hours. The dried powder was then washed repeatedly with DI water until the pH of the washing water reached 7, followed by drying. The resulting manganese dioxide particles had a size of 548.6 nm.



Fig. S2 Characterization of MnO₂ particle fabrication with different preparation schemes: (a) average particle size, and (b-d) SEM diagram of MnO₂ particles. (b)-(d) refer to the plan 1-3, respectively.



Section S3: Membrane surface modification with FDTS

Fig. S3 (a) The WCA and (b) the pure water flux of membrane prepared by different FDTS ratio

Section S4: Fluorescence region integration (FRI) method

The FRI method has been successfully applied to the analysis of three-dimensional fluorescence spectra from various water bodies [1]. This method involves dividing the Excitation-Emission Matrix (EEM) figure into several regions using horizontal and vertical boundary lines to study the integration of fluorescence intensity in water quality spectra. In this article, the graph is divided into five regions, with typical representative substances listed in Table S1.

Partition	Range	Typical representative substances		
Ι	$200 \text{ nm} \le \text{Ex} \le 250 \text{ nm}$, $280 \text{ nm} \le \text{Em} \le 330 \text{ nm}$	Aromatic protein I		
II	$200 \text{ nm} \le \text{Ex} \le 250 \text{ nm}$, $330 \text{ nm} \le \text{Em} \le 380 \text{ nm}$	Aromatic protein II		
III	$200 \text{ nm} \le \text{Ex} \le 250 \text{ nm}, 380 \text{ nm} \le \text{Em} \le 550 \text{ nm}$	Fulvic acid like		
IV	250 nm < Ex < 370 nm, 280 nm < Em < 350 nm	Soluble microbial by-product like		
V	$250 \text{ nm} \le \text{Ex} \le 450 \text{ nm}$, $380 \text{ nm} \le \text{Em} \le 550 \text{ nm}$	Humic acid like		

Table S1 Typical representative substances in fluorescent region





Fig. S4 Flux decline rate, flux recovery rate and IFR of M-PVDF and PVDF in cycle experiment

Section S6: Characterization of bubble generation

In this study, bubble generation was confirmed through light scattering tests using a green laser. As demonstrated in Fig. S4, an optical path indicative of the Tyndall effect is observed in the H₂O₂-MnO₂ system within the cleaning solution (0.006 wt% H₂O₂). The Tyndall effect dictates that a distinct optical path is evident in liquids containing ultrafine bubbles, whereas liquids lacking these bubbles exhibit no significant change in optical path. This observation indicates that the H₂O₂-MnO₂ system in the cleaning solution is capable of generating ultrafine bubbles, and conversely, that ultrafine bubbles are not produced in the absence of MnO₂.



Fig. S5 Light scattering test of H₂O₂ cleaned solution with green laser indicator in (a) M-PVDF and (b) PVDF membrane cleaning

To further analyze and quantify the fundamental characteristics of the bubbles, their sizes were measured during the cleaning process using different mass fractions of H_2O_2 (Fig. S5). Bubbles smaller than 10 µm are classified as micro- and nanobubbles (MNBs). The results clearly demonstrate that all bubbles generated by the H_2O_2 cleaning solution are smaller than 10 µm, confirming the production of MNBs during the cleaning process.



Fig. S6 Particle size distribution of MNBs produced by different concentrations of H₂O₂

Section S7: Concentration experiment removal rate of various indicators

Long-term concentration experiments were conducted using waste leachate with a concentration factor (CF) of 5 and a total recovery of 80%. Since the total water production from this concentration experiment was identical to that of the cycle experiment, the feed solution concentrations after a CF greater than two were higher than those in the cycle experiment. The rejection performance from this concentration experiment is summarized in Table S5. A comparison of Table S5 with Table 3 reveals a decrease in the retention rates for ammonia nitrogen and total organic carbon (TOC) in the concentration experiment. Specifically, the rejection rate for ammonia nitrogen declined from approximately 88% in the cyclic experiments to 80%. This reduced performance may be attributed to

the increasing concentration of contaminants at the membrane surface, which can affect separation efficiency.

Table S2 Removal rate of various foulants in landfill leachate treatment by M-PVDF in concentration experiments (CF=5).

Pollutant	NH4 ⁺ -N	TOC	Phosphate	COD	K	Na	Ca	Mg
Removal	80.80	97.71	99.97	99.99	99.96	99.98	99.98	99.98
rate								

References:

[1] W. Chen, P. Westerhoff, J.A. Leenheer, K. Booksh, Fluorescence Excitation–Emission Matrix Regional Integration to Quantify Spectra for Dissolved Organic Matter, ENVIRON. SCI. TECHNOL., 37 (2003) 5701-5710.