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Fouling removal in ceramic ultrafiltration membrane via catalyst modification with Fenton-like backwash

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ABSTRACT

Fouling remains a critical challenge for ceramic ultrafiltration membranes, limiting their long-term performance for water treatment. Fenton-like reactions have been widely used for fouling removal due to the formation of strong radicals. Integrating these reactions into backwash offers a promising strategy for fouling control. However, it has been unclear how Fenton-like backwash is influenced by operational parameters and fouling structures. Here we reveal the key factors influencing Fenton-like backwash by systematically studying its performance under varying conditions, such as backwash pressure (0.3–1 bar), duration (18–36 min), fouling structure (caused by 1–5 mM Ca) and the long-term operation, to provide an effective and practical cleaning. $CuFe_2O_4$ was grown on ceramic ultrafiltration membranes due to its stability and high catalytic efficiency in activating Fenton-like reactions. We found that Fenton-like backwash achieved the highest cleaning efficacy of approximately 70 % over three cycles at a low backwash pressure of 0.3 bar, while hydraulic backwash remained ineffective under all conditions. Backwash pressure, rather than duration, was identified as the dominant factor governing the Fenton-like cleaning, due to its impact on the residence time of Fenton-like agents (H_2O_2). The presence of a high Ca concentration (3 and 5 mM) altered the fouling behaviour, and reduced the cleaning efficacy of Fenton-like backwash. This reduction was attributed to the formation of rigid alginate clusters that were resistant to Fenton-like reactions. The contribution of •OH to the enhanced Fenton-like backwash was confirmed by the quenching experiments. Furthermore, the $CuFe_2O_4$-coated membranes exhibited stable flux recovery (83 %–94 %) in the long-term treatment of a concentrated alginate (800 mg/L), showed low or negligible leaching in hash environments (30 mM H_2O_2, 0.1 % NaClO or 10 mM NaOH), and maintained comparable performance after 96 h aging by 30 mM H_2O_2. This study clarifies the factors governing Fenton-like backwash, and demonstrates that a robust and effective strategy for fouling removal can be achieved by coupling this cleaning method with catalytic ceramic membranes.

1. Introduction

Ceramic ultrafiltration (UF) membranes have been regarded as a promising technology in the treatment of various complex polluted waters, due to their high thermal stability, low carbon footprint, and resistance to chemicals [1]. However, membrane fouling can account for 11 %–24 % of the operational expenses in treatment plants [2]. In addition, more than 60 % of flux decline is caused by the fouling formed on the ceramic membrane, as reported by Zhang et al. [3]. Among the different natural organic matter (NOM) fractions, polysaccharides—particularly alginate—have been identified as major contributors to irreversible membrane fouling. Compared to other organic foulants such as humic acids and proteins, alginate forms a dense and sticky gel layer that is more resistant to conventional cleaning techniques [4]. The situation is further deteriorated by the presence of divalent cations such as calcium (Ca), which can interact with alginate to alter its physicochemical properties. These interactions lead to aggregation, crosslinking, and compaction of the fouling layer, thereby reducing membrane permeability and increasing cleaning difficulty [5, 6]. As such, effective removal of alginate-Ca-induced fouling remains a bottleneck in the operation of ceramic UF membranes.

Hydraulic backwash is commonly employed to remove loose foulants

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from the membrane surface, but its efficacy against compacted alginate-Ca fouling is limited. Reported cleaning recoveries range from as low as 23 % for ceramic membranes to below 1 % for polymeric ones [7,8]. This low efficacy results from the hydraulically irreversible nature of alginate fouling layer, which adheres strongly to the membrane surface and resists physical cleaning. To address this, various fouling mitigation techniques have been explored, including enhancing membrane hydrophilicity, chemical cleaning with sodium hydroxide (NaOH), hydrochloric acid (HCl), or sodium hypochlorite (NaClO), and integration with advanced oxidation processes (AOPs) [5,9,11]. However, hydrophilic modifications can deteriorate fouling when adhesive forces dominate over surface properties [10]. Chemical cleaning with NaOH and HCl yields modest efficacies of 31 % and 45 %, respectively, while NaClO, despite its oxidative potential, poses environmental challenges due to its harsh nature and the need for post-treatment of cleaning wastewater [12]. AOPs, which generate reactive radicals for foulant degradation, offer a promising alternative. For instance, ozone-based cleaning in place outperforms NaClO and NaOH due to the radical-induced degradation, but its practical application is limited by low efficacy and high energy demands [5]. These limitations underscore the need for alternative, sustainable, and cost-effective cleaning strategies.

Fenton-like reaction, one type of AOPs, has been regarded as a potential solution for the removal of persistent fouling. In these reactions, hydroxyl radicals (•OH) can be induced from hydrogen peroxide (H_2O_2) in the presence of catalysts such as $CuFe_2O_4$ which exhibits a higher activity and stability over other spinel ferrites in radical generation [13]. Importantly, H_2O_2 decomposes into water and oxygen, making it an environmentally-friendly oxidant. Previous studies have integrated Fenton-like reactions into forward flush using catalytic ceramic membranes, and demonstrated enhanced fouling removal [14]. However, these methods require continuous dosing of H_2O_2 during a long-time flush process, leading to increased costs and concerns over oxidant consumption and residuals. An alternative and less-explored approach is to couple Fenton-like reactions with backwash. In hydraulic backwash, operational parameters such as backwash pressure and duration have been widely studied to physically loosen the cake layer [15]. When coupled with Fenton-like reactions during backwash, the cleaning performance can be influenced by both hydraulic force and the oxidation process. A higher backwash pressure can enhance drag force and promote partial fouling detachment, creating pathways for radical transport, which may improve radical-based cleaning. However, it can also increase flux, reducing H_2O_2 residence time and limiting radical formation, thus hindering fouling degradation. Similarly, while extended backwash duration may increase the total contact time of H_2O_2, its actual influence on the efficacy of Fenton-like backwash remains unclear. At present, it is not well understood how backwash pressure or duration interact with the Fenton-like reaction to influence the overall cleaning performance, and which mechanism plays the dominant role under different conditions. Furthermore, the effect of Ca ions on Fenton-like backwash remains unstudied, although Ca is known to alter fouling structure [6], increase flux decline [16], and reduce the efficacy of hydraulic backwash and Fenton-like forward flush [14,15]. The presence of Ca can form cake layer, which can limit the transport of H_2O_2. Notably, the interaction between Ca and alginate can result in distinct structures, such as the egg-box structures or rigid, cross-linking alginate-Ca clusters. These distinct structures may influence how the fouling attaches to the membrane and how •OH radicals diffuse into the fouling layer, thereby affecting the overall efficacy of Fenton-like backwash. These knowledge gaps highlight the need for a systematic investigation of how operational parameters and Ca-induced fouling structures affect Fenton-like backwash. A better understanding, therefore, is crucial to improve its cleaning performance and practical applicability.

This work aims to gain a comprehensive understanding of the effect of backwash duration, backwash pressure, and the presence of Ca on the performance of Fenton-like backwash for catalytic UF membranes fouled by alginate, thereby providing a practical and cost-effective cleaning strategy. $CuFe_2O_4$ was deposited as a stable and efficient catalyst to generate radicals from H_2O_2. The operational parameters of backwash pressure and duration were studied to reveal their roles in Fenton-like backwash. Additionally, we explored the effect of Ca on fouling structures, and its subsequent effect on cleaning performance. Finally, this study evaluated the cleaning performance for fouling caused by high-concentration alginate and the leaching of the catalytic UF membrane when exposed to H_2O_2, NaClO, and NaOH.

2. Materials and methods

2.1. Ceramic (un)coated UF membranes

Ceramic UF membranes with a selective layer of Al_2O_3, and a nominal pore size of 100 nm, were obtained from CoorsTek (the Netherlands). The tubular membranes had a single channel, an internal diameter of 7 mm, an outer diameter of 10 mm, and a length of 100 mm. The edges of the membranes (10 mm for each side) were sealed by two-component epoxy adhesives (Araldite AW 5047-1 and Hardener HW 5067-1, from VIBA, the Netherlands) to avoid potential leaking from the two edges of the membrane during filtration.

The precursor solution of the catalyst $CuFe_2O_4$ was prepared by dissolving copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$, from Merck, Germany), ferric nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$, from Sigma-Aldrich), and citric acid (from Sigma-Aldrich) with a molar ratio of 1:2:3.6, respectively. The mixed solution was stirred at 80 °C for 1 h. Then, 50 mL of precursor solution was filtered through the pristine UF membrane via a dead-end setup under a pressure of 0.1 bar to ensure that the membrane surface and body had sufficient contact time with the precursor solution. Afterward, the wet membrane was dried at 100 °C for 10 min. The coating and drying processes were repeated three times. Afterward, the membranes, covered with catalyst precursors, were calcined at 400 °C for 2 h, and then washed with demineralized water. This water was produced at WaterLab, TU Delft (conductivity <0.1 μs cm^{-1}, water filtered by a reverse osmosis filter, a candle filter, and a resin vessel).

2.2. Crossflow setup

A constant pressure crossflow setup (Fig. 1) was designed and constructed for the fouling and cleaning experiments. A balance (KERN, Germany) was used to measure the permeate flux with a time interval of 30 s. To capture the initial sharp drop in flux, which typically occurs within the first few min of filtration, the balance and pressure sensors (ESI, UK) were initiated before activating the pump (AxFlow, the Netherlands). Before the backwash process, the tube system was flushed with clean water. Subsequently, the orientation of the membrane module was reversed for backwash.

2.3. Performance tests

2.3.1. Effect of backwash intensities and Ca concentration over three cycles

Before fouling tests, the pure water flux was tested to ensure that the membranes were clean. An extended description of the preparation of the alginate solution is given in Text S1. 50 mg/L alginate solution, containing $CaCl_2$ (1, 3, and 5 mM), was filtered over the membranes at 0.3 bar and a crossflow velocity of 0.65 m/s (Re = 4531) until a steady flux was reached. The membranes were cleaned via backwashing with demineralized water or 30 mM H_2O_2 (pH 2.5) using varying times (6, 18, 36 min) and pressures (0.3, 0.5, 1 bar). A 1-min forward flush at a crossflow velocity of 1.1 m/s (Re = 7552) was followed to remove loose foulants. During the forward flush process, the tube connected to the permeate side of the membrane module was closed to prevent a permeate flow. Temperature was monitored for permeability

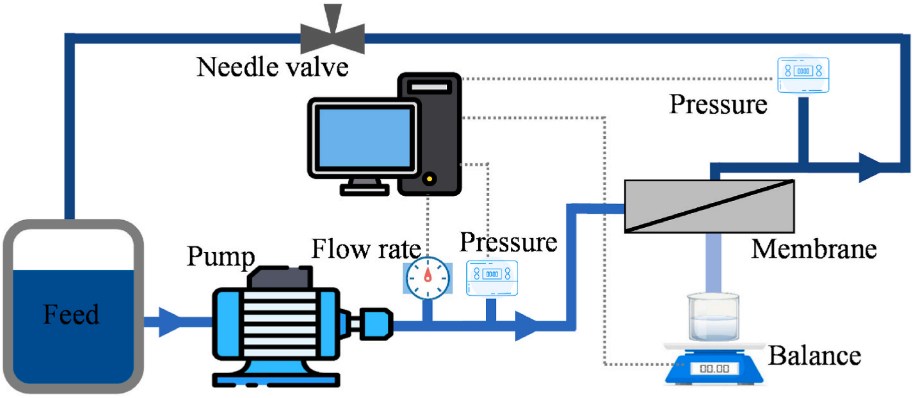

Fig. 1. The constant pressure setup for the fouling operation.

adjustments (Eq. S(1)). The (un)coated membranes cleaned with demineralized water served as blank experiments. The fouling and cleaning processes were conducted during three cycles.

2.3.2. *Radical quenching experiments*

Tert-butyl alcohol (TBA) was used to quench •OH radicals during Fenton-like backwash, in order to assess the role of •OH in fouling removal. The fouling process was conducted at 0.3 bar for 75 min by using a solution containing 50 mg/L alginate and 3 mM Ca. Then the fouled $CuFe_2O_4$ membranes were backwashed with demineralized water, 30 mM H_2O_2 and 300 mM TBA (at pH = 2.5), or 30 mM H_2O_2 (at pH = 2.5), at 0.5 bar for 36 min. Afterward, 1-min forward flush by demineralized water was applied. The pure water flux was measured before and after cleaning to determine flux recovery to assess the effect of radicals on fouling removal.

In addition to flux recovery tests, methylene blue degradation experiments were conducted to verify the oxidative activity of the coated membranes in a simplified system and to further confirm the involvement of •OH radicals. In these tests, the coated membranes were immersed in the prepared 50 mL solution containing 10 mg/L methylene blue and 30 mM H_2O_2 (pH 2.5), or 30 mM H_2O_2 with 300 mM TBA (pH 2.5).

2.3.3. *Effect of the concentrated alginate*

Single-cycle fouling and cleaning of the (un)coated membranes. In this experiment, the demineralized water flux of the clean (un)coated membrane was measured at 0.3 bar. Subsequently, a concentrated alginate solution (800 mg/L) containing $CaCl_2$ (3 mM), NaCl (1 mM), and $NaHCO_3$ (1 mM), was filtered through the pristine or coated membrane at 0.3 bar and a crossflow velocity of 0.65 m/s to simulate a municipal sewage filtration experiment of approximately 1.7 days [17]. Then the demineralized water flux was re-measured at 0.3 bar. The cleaning process involved a backwash using either demineralized water or the H_2O_2 solution (30 mM, pH 2.5) at 0.5 bar for 18 min, followed by a 1-min forward flush with demineralized water at a crossflow velocity of 1.1 m/s. After cleaning, the demineralized water flux was measured again at 0.3 bar. The pristine membranes, backwashed with demineralized water and the H_2O_2 solution, were used as blank experiments.

Long-term (seven-cycle) fouling and cleaning of the coated membrane. In the seven-cycle fouling and cleaning experiment, the $CuFe_2O_4$-coated membrane were fouled by 800 mg/L alginate with 3 mM $CaCl_2$, 1 mM NaCl, and 1 mM $NaHCO_3$ at 0.3 bar, 0.65 m/s crossflow velocity. The membrane was then cleaned by a 6-min backwash with a H_2O_2 solution (30 mM, pH = 2.5) at 0.5 bar, followed by a 1-min forward flush with demineralized water.

2.3.4. *Stability of the $CuFe_2O_4$ membrane*

The H_2O_2 solution (30 mM, pH = 2.5) and two other common cleaning agents (0.1 % NaClO, and 10 mM NaOH) were chosen for leaching tests of Cu and Fe. The leaching test was carried out by immersing the used $CuFe_2O_4$ membrane in a 500 mL H_2O_2 solution (pH = 2.5), 0.1 % NaClO, and 10 mM NaOH, respectively, for 8 h. Then the Cu and Fe leaching were measured by inductively coupled plasma-mass-spectrometry (ICP-MS, Plasma Quant MS, Analytik Jena AG, Germany). Additionally, we compared the cleaning performance of the aged catalytic membrane (after immersion in H_2O_2 for 96 h) with that of the newly coated membrane. The structures of the new and aged catalytic membranes were also analyzed by X-ray diffraction (XRD).

2.4. *Characterization*

The top and cross-sections of the (un)coated membranes were examined by scanning electron microscopy (SEM, Hitachi S-3400 II, Japan) equipped with energy dispersive spectroscopy (EDS). The D8 discover diffractometer (Bruker, USA) with Cu Kα radiation at 50 kV and 1000 μA was employed for the X-ray diffraction (XRD) pattern of the membranes under a scan step size of 0.04° and a step time of 2 s. We measured the alginate's size distribution using a particle size analyzer (Bluewave, Microtrac, USA).

2.5. *Performance analysis*

Multi-cycle fouling and cleaning. Flux was determined through the filtration of the alginate solution. Calculations of cleaning efficacy and resistances were based on the work of Lee et al. [18] and Zsirai et al. [19].

$$Cleaning\ efficacy = \frac{J_c - J_f}{J_0 - J_f} \tag{1}$$

$$R = R_m + R_t = R_m + R_r + R_{ir} = \frac{\Delta P}{\mu\, J_f} \tag{2}$$

$$R_m = \frac{\Delta P}{\mu\, J_0} \tag{3}$$

$$R_{ir} = \frac{\Delta P}{\mu\, J_c} - \frac{\Delta P}{\mu\, J_0} \tag{4}$$

$$R_r = \frac{\Delta P}{\mu\, J_f} - \frac{\Delta P}{\mu\, J_c} \tag{5}$$

where J_0 (in m/s) is the initial flux in the first fouling cycle, J_f (in m/s) is the final, steady flux at the end of the fouling (e.g., Cycle N), J_c (in m/s) is the initial flux in the subsequent fouling cycle (e.g., Cycle N+1), R (in m^{-1}) is the total resistance, R_t (in m^{-1}) is the total fouling resistance, R_m (in m^{-1}) is the membrane resistance, R_r (in m^{-1}) is the reversible resistance, R_{ir} (in m^{-1}) is the irreversible resistance, ΔP (in Pa) is the transmembrane pressure, and μ (in Pa s) is the dynamic viscosity of the permeate-side solution, depending on temperature.

To evaluate the fouling potential of the feed water, we used the unified membrane fouling index (*UMFI*), because it is independent from traditional fouling models (e.g., pore blocking and cake filtration) [20–22] in the multicycle test. The *UMFI* (in $m^2\ L^{-1}$) is defined as the slope of the linear equation of Eq. (6), where J_s' is the normalized specific permeate flux (J/J_0) and V_s (in $L\ m^{-2}$) is the unit permeate volume. *UMFI* can be expressed as $UMFI_t$ for each fouling curve, representing the total fouling index, while $UMFI_c$, being the chemically irreversible fouling index, can be obtained by using a two-point method based on the $1/J_s'$ values of the first and the last cycle.

$$\frac{1}{J_s'} = 1 + (UMFI) \times V_s \tag{6}$$

Single-cycle fouling and cleaning. Backwash performance was evaluated by flux recovery (Eq. (7)), based on the water flux measured before fouling (J_{w0}, in m/s) and after cleaning (J_{wc}, in m/s).

$$\text{Flux recovery} = \frac{J_{wc}}{J_{wo}} \tag{7}$$

The residence time of the H_2O_2 solution. As given in Eq. (8), the residence time (in s) of the H_2O_2 solution passing the membrane was calculated by the flux (J, in m/s), porosity (ϕ), and the thickness of the selective layer of the membrane (L, in m).

$$\text{Residence time} = \frac{L\,\phi}{J} \tag{8}$$

3. Results and discussions

3.1. Membrane characterization before and after modification

Fig. 2a and b show that the $CuFe_2O_4$ coating had a minimal influence on the overall morphology of the membrane, since no considerable structural difference was observed before and after the coating. This negligible effect of $CuFe_2O_4$ on ceramic membrane has also been found in a previous study [23]. Additionally, a uniform distribution of $CuFe_2O_4$ on the surface of the membrane was observed from the SEM-EDS elemental mapping analysis of the top-view $CuFe_2O_4$ coated membrane (Fig. 2c). SEM-EDS line scanning verified that $CuFe_2O_4$ was grown on the entire selective layer of the membrane (Fig. 2d). The XRD of the coated membrane (Fig. S1) shows that the characteristic peaks at 2θ of 18.4, 30.2, 35.6, 37.2, 43.0, 57.1, and 62.7, corresponded to the (111), (220), (311), (222), (400), (511), and (440) lattice planes of $CuFe_2O_4$, respectively [23–25]. Besides, Fig. S2 shows that the permeability of the ceramic UF membrane only declined from 362 to 346 $L\ m^{-2}\ h^{-1}$ after coating, while a larger permeability drop (from 470 to 196 $L\ m^{-2}\ h^{-1}$) was observed in polymeric UF membranes after $CuFe_2O_4$ coating [26].

3.2. Effect of backwash duration

In the experiments where the fouled coated membranes were backwashed with demineralized water for 6, 18, and 36 min over three cycles, their R_{ir} (1.1×10^{10}–$1.9 \times 10^{10}\ m^{-1}$) and R_{ir} ratio (85 %–96 %) remained at a high level (Fig. 3a–d). An extended duration of the hydraulic backwash did not exhibit a positive effect on the cleaning. For example, in the third cycle, cleaning efficacies of only 1.6 % and 1.0 % were found for a backwash duration of 6 min and 36 min, respectively. Moreover, in the single fouling and cleaning test (Fig. S3), the flux recovery was only 45 % after a 36-min hydraulic backwash. The extension of cleaning duration cannot improve the cleaning performance in the absence of chemical reactions, as reported by Ang et al. [27]. This is likely due to the inherent limitations of physical cleaning methods in removing strongly adhered alginate foulants.

With 6–36 min Fenton-like backwash, the R_{ir} of the $CuFe_2O_4$ membranes consistently remained at a low level, ranging from 1.7×10^9 to $7.6 \times 10^9\ m^{-1}$, one order of magnitude lower than that of the hydraulic

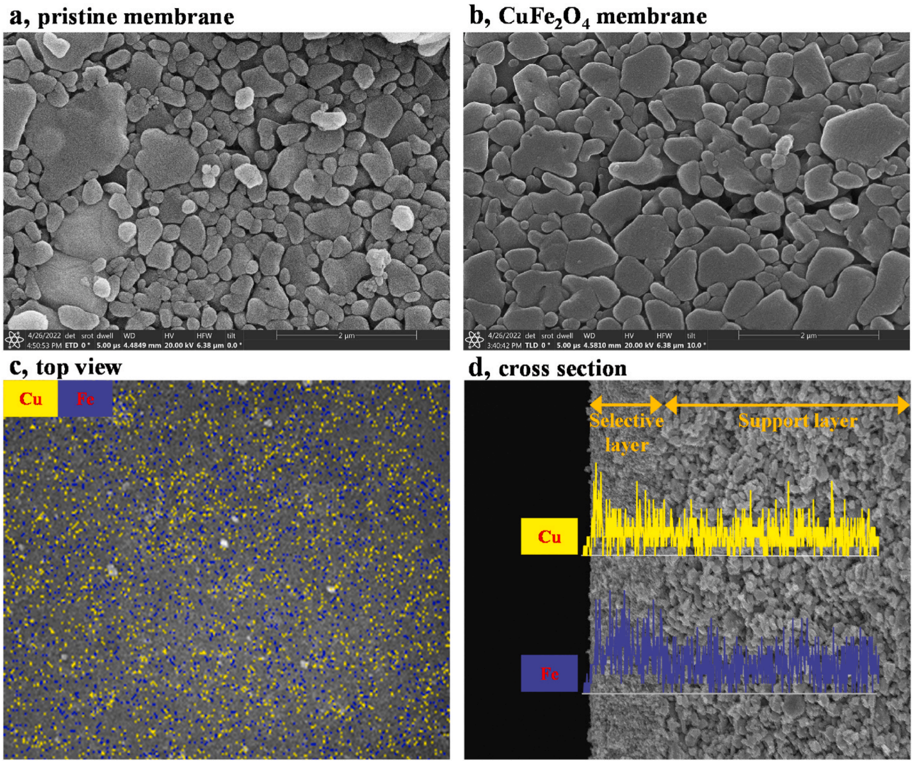

Fig. 2. Top SEM view of (a) the pristine and (b) the $CuFe_2O_4$ membranes. SEM-EDS images of (c) top-view mapping and (d) cross-section line scanning of the $CuFe_2O_4$ membranes.

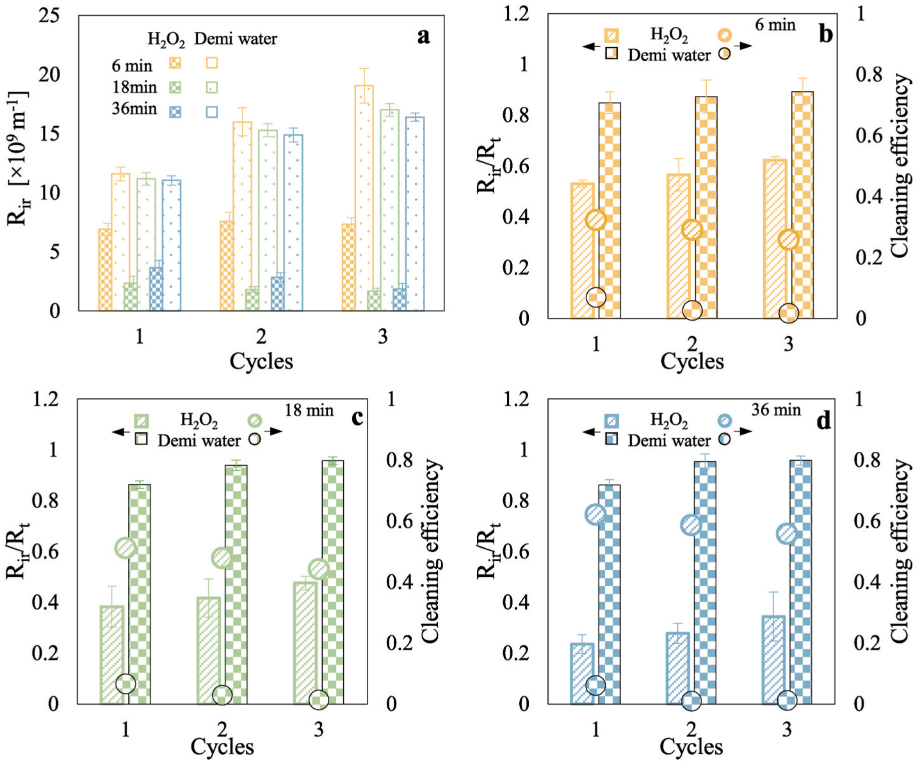

Fig. 3. (a) R_{ir}, (b–c) R_{ir} ratio and cleaning efficacy of the coated membrane with H_2O_2 backwash or the pristine membrane with hydraulic backwash, conducted at 0.3 bar with 50 mg/L alginate solution for 45 min each fouling cycle, then backwashed at 0.5 bar with demineralized water or 30 mM H_2O_2 (pH = 2.5) for 6, 18 and 36 min, respectively, and rinsed by 1-min forward flush with demineralized water.

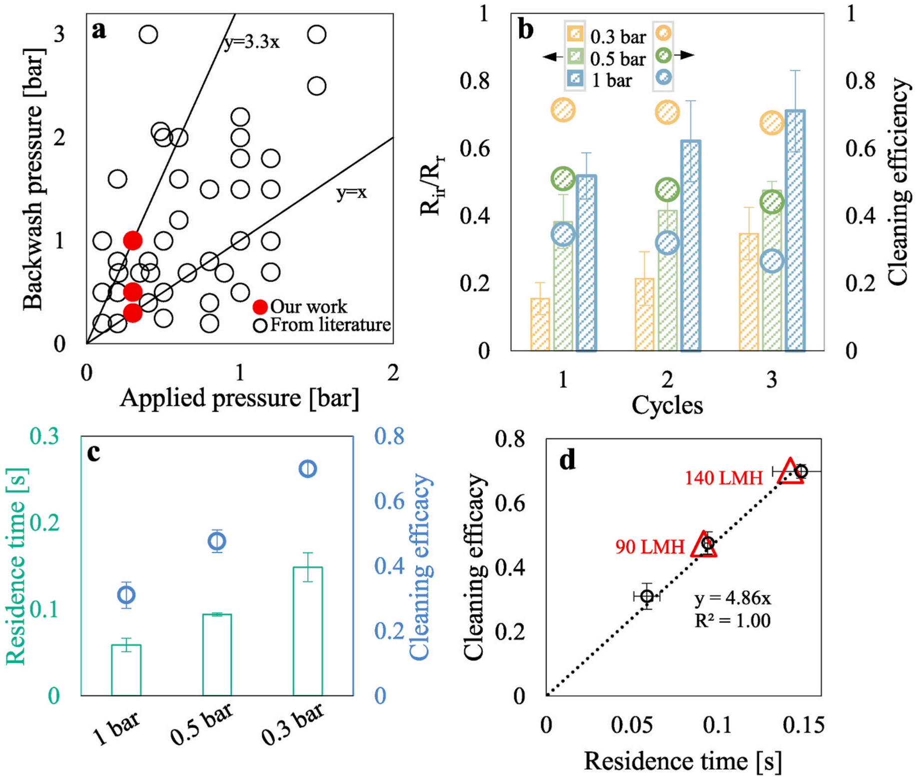

Fig. 4. (a) Applied (filtration) and backwash pressures used in previous studies and in this work (red dots) [15,29–38,38–43], (b) fouling resistance ratios and cleaning efficacies of the coated membranes over three cycles, and (c, d) the residence time and cleaning efficacies. The coated membranes fouled by 50 mg/L alginate were backwashed for 18 min with 30 mM H_2O_2, under various backwash pressures, followed by 1 min forward flush, while the constant flux backwash was carried out at a flux of 90 and 140 L m^{-2} h^{-1}. The residence time in constant pressure backwash was calculated by using the average flux during the backwash. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

backwash counterpart (Fig. 3a). In addition, the R_{ir} values in the Fenton-like backwash test were maintained at a low level over three cycles. The marginally higher R_{ir}, found in 36-min case compared to 18-min case, can be caused by the experimental variations. To eliminate this effect and allow for more consistent comparison, the normalized R_{ir}/R_t was used to evaluate the contribution of irreversible fouling. It is observed that the R_{ir}/R_t of $CuFe_2O_4$ membranes decreased with increasing Fenton-like backwash duration, indicating that a longer backwash can effectively reduce the relative contribution of irreversible fouling. Moreover, when the duration of the H_2O_2 backwash was extended from 6 to 36 min, the cleaning efficacy improved from 32 % to 62 %, much higher than the efficacy (1 %–7 %) achieved in hydraulic backwash (Fig. 3b–d). The prolonged H_2O_2 backwash increased contact time between H_2O_2 and catalytic sites, which, accordingly, generated more •OH radicals to degrade alginate fouling for the improved cleaning [14].

3.3. Effect of backwash pressure

Fig. 4 shows the effect of backwash pressure on cleaning efficacy over three cycles. The selected backwash pressures of 0.3, 0.5, and 1 bar were based on the correlation between applied filtration pressures and backwash pressures (Fig. 4a), where most employed backwash pressures are higher than the applied filtration pressures.

The low cleaning efficacy (1 %–14 %) and high R_{ir} ratio (81 %–96 %) were found at 1 bar hydraulic backwash over three cycles (Fig. S4). These suggest that most alginate fouling, formed on the membrane surface or in the pores, could not be flushed off by hydraulic backwash, even at a high backwash pressure. In addition, the demineralized water flux measured after hydraulic backwash, was even lower than the final flux measured at the end of the fouling cycle, as found in the single-cycle fouling and cleaning test (Fig. S5).

Fig. 4b shows that the highest cleaning efficacy (68 %–71 %) was achieved at 0.3 bar with Fenton-like backwash over three cycles. Usually, backwash at a higher pressure is assumed to enhance the cleaning by providing an intensified drag force to loosen and remove the cake fouling [8,28]. Therefore, a higher backwash pressure was widely used in previous studies, as shown in Fig. 4a. However, in the H_2O_2 backwash of the fouled $CuFe_2O_4$ membrane, higher backwash pressures resulted in a lower cleaning efficacy, along with a higher R_{ir} ratio and a higher R_{ir} (Fig. 4b and S6). As the backwash pressure increased from 0.3 to 1 bar, the residence time—calculated based on Eq. (8), and Fig. S7—decreased considerably from 0.15 to 0.06 s (Fig. 4c), due to the increased backwash flux. The reduced residence time, therefore, limited the transport of H_2O_2 towards the catalytic sites to form the $^{\bullet}OH$ radicals, and constrained the diffusion distance of the radicals. The linear relation (Fig. 4d) indicates that residence time, rather than the total backwash time (Fig. S8), dominated the backwash performance. The prominent effect of residence time on cleaning was further confirmed by experiments conducted at a constant backwash flux of 90 and 140 L m^{-2} h^{-1}, corresponding to residence times of 0.14 and 0.09 s, respectively (Fig. 4d).

3.4. Effect of calcium on cleaning performance

The presence of Ca will influence the fouling behaviour, which perhaps, in turn, will affect the Fenton-like backwash. Therefore, various Ca concentrations (1, 3, and 5 mM) were employed to evaluate the backwash performance with demineralized water or H_2O_2.

Fig. 5a shows that the total resistance caused by 1 mM Ca (3.1×10^9–3.3×10^{10} m^{-1}) was an order of magnitude higher than the range observed for both 3 and 5 mM Ca (3.5×10^9–7.2×10^9 m^{-1}). The higher fouling resistance, found in 1 mM Ca case, probably resulted from pore clogging. As reported in previous studies, a small dosage of Ca results in the formation of small alginate colloids [15,28]. These small-sized alginate particles contribute to pore blocking, which leads to a low flux and a high fouling resistance [15,44]. However, higher Ca concentrations promote alginate aggregation into more rigid clusters, resulting in the generation of a cake layer fouling with a relatively high porosity [6,44]. Fig. S9 shows that the size of the alginate indeed increased with an increased concentration of Ca. The highest cleaning efficacy (of 63 %) was achieved in 1 mM Ca case (Fig. 5b). Although fouling resistance was similar for 3 mM and 5 mM Ca, the Fenton-like backwash achieved a higher cleaning efficacy at 3 mM (51 %) than at 5 mM (36 %). Similarly, 9 mM Ca exhibited comparable resistance but a further decreased cleaning efficacy (Fig. S10). However, for the fouled catalytic membranes, the hydraulic backwash resulted in low cleaning efficacies (1 %–11 %, Fig. S11a), and high R_{ir} values (5.1×10^9–3.0×10^{10} m^{-1}, Fig. S11b), under all Ca conditions.

Fig. 6 shows the proposed mechanisms for cleaning the $CuFe_2O_4$ membranes fouled with a calcium-rich alginate solution. Demineralized water backwash promotes the reorganization of the alginate-Ca structures and flushes away only part of the Ca ions. However, the alginate can still interact with the residual Ca ions, which can then bind to the membrane surface again. In addition, low Ca concentrations lead to the formation of smaller alginate particles, which are more prone to pore blocking in the subsequent filtration cycle. This explains why hydraulic backwash gave a low cleaning efficacy in our experiments.

In contrast, during Fenton-like backwash, the stretchy egg-box alginate-Ca fouling (in less Ca case) is reorganized by the physical flush. This reorganization creates more space for H_2O_2 to transfer to $CuFe_2O_4$ areas, facilitating the formation of the strongly oxidizing $^{\bullet}OH$ radicals [45]. Ca then can be released due to the partial degradation of the alginate structures, which further loosens the fouling and facilitates the transfer of H_2O_2 to break down the fouling. However, as reported by

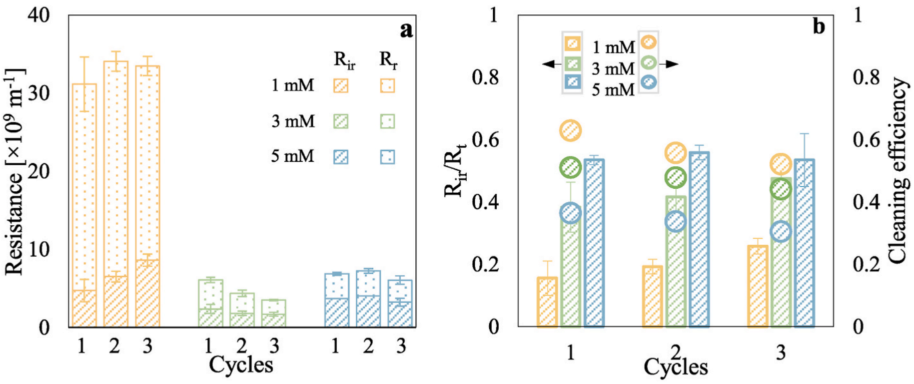

Fig. 5. (a) Fouling resistance, (b) R_{ir} ratio and cleaning efficacy of the coated membranes. The fouling was conducted at a pressure of 0.3 bar with 50 mg/L alginate solution with varying concentrations of Ca. The fouled membrane was cleaned by backwashing at 0.5 bar with 30 mM H_2O_2 (pH = 2.5) for 18 min, followed by 1 min forward flush.

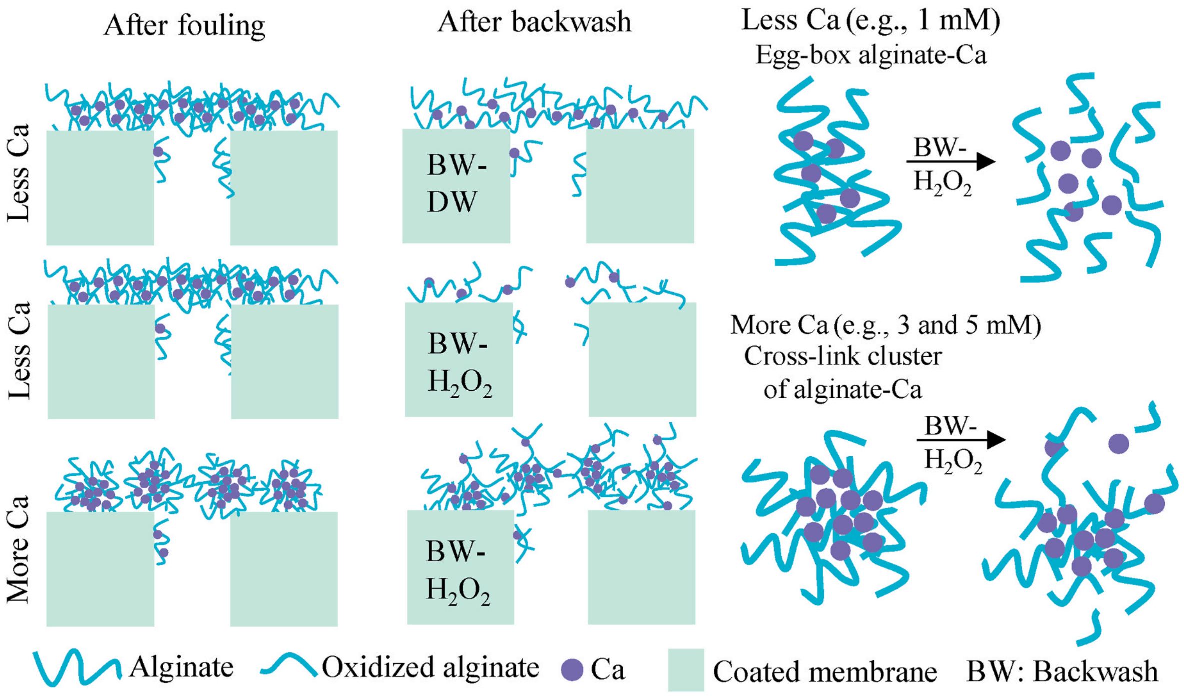

Fig. 6. Schematic illustration of the structure of alginate with Ca and the proposed mechanism of backwash with demineralized water (DW) and the H_2O_2 solution for the cleaning of the fouled $CuFe_2O_4$ membranes.

Zhang et al. [6], at higher Ca concentrations, fouling is prone to cake formation by the cross-linking alginate-Ca clusters, where the ions are trapped in the inner structure of alginate clusters. These clusters are rigid and compact because they strongly interact with Ca ions. This makes it more difficult for the physical flush to disperse the rigid structures of alginate-Ca during the backwash, thereby limiting the diffusion of H_2O_2 to the catalytic sites [5,46]. Besides, even if such complex rigid clusters are partially destroyed by the radials, the alginate fragments would be captured by and again bound to the Ca ions which are released from the inner fouling structure. These fragments would then reattach to the cleaning membrane surface or the residual fouling. Effective cleaning has been found to depend on the enhanced mass transfer of cleaning agents (towards fouling) and the fouling (towards the bulk), as well as the destruction of the intermolecular fouling interaction [27].

3.5. Performance of (un)coated membranes fouled by concentrated alginate

The pristine and coated membranes were backwashed with either demineralized water or an H_2O_2 solution after fouling with 800 mg/L alginate with 3 mM Ca, followed by a 1-min forward flush. In addition, the demineralized water flux was determined before and after the fouling process as well as after the cleaning, as shown in Fig. 7a. Flux recoveries and (ir)reversible resistances are given in Fig. 7b, where the permeability recovery was determined by the flux of demineralized water before fouling and after cleaning (Eq. (7)).

Flux curves show that both the pristine and coated membranes experienced a rapid flux decline during the initial phase of fouling. This phenomenon can be attributed to the rapid adsorption of alginate, leading to pore blocking and thus to a permeance decrease [47]. Subsequently, the flux exhibited a gradual decline, probably due to the formation of alginate-Ca gel layer and cake compression [15].

In all experiments, the demineralized water flux measured after fouling was comparable to the final, steady flux in the fouling test, suggesting that fouling could not be removed without cleaning. When an 18-min backwash with demineralized water was employed on the fouled pristine membrane, a flux recovery of 43 % was found. An 18-min H_2O_2 backwash achieved a slightly higher flux recovery of 53 %. An additional 18-min H_2O_2 backwash only increased the recovery from 53 % to 58 %. The modest improvement of backwash with H_2O_2 compared to the backwash with demineralized water likely resulted from the limited oxidation potential ($E^\circ H_2O_2/H_2O = 1.763$ V), due to the self-decomposition of H_2O_2 [14]. An earlier study has also reported that the limited reaction between the cleaning agent and alginate-Ca leads to ineffective cleaning [27].

The highest flux recovery (80 %) was achieved in the combination of the $CuFe_2O_4$ membranes and an 18-min H_2O_2 backwash, which is probably due to the highly reactive radicals of $^\bullet OH$ ($E^0 = 2.73V$) activated by $CuFe_2O_4$. This performance surpasses most existing cleaning strategies in alginate removal (Fig. 7c). It highlights the prominent influence of the Fenton-like backwash on the destruction of persistent alginate-Ca fouling, compared to the cleaning methods such as forward flush, hydraulic backwash, and chemical cleaning.

The evolution of the fouling resistances is shown in Fig. 7b. The high resistances, caused by alginate fouling, have also been revealed in previous studies [16,48]. The total fouling resistances were in the same order of magnitude (2.4×10^{10}–3.1×10^{10} m^{-1}) for the three experiments: the pristine membranes backwashed with demineralized water, the pristine membranes backwashed with an H_2O_2 solution, and the coated membrane backwashed with an H_2O_2 solution. However, their irreversible resistances differed. Because of Fenton-like reactions, the R_{ir} of the $CuFe_2O_4$ membrane with H_2O_2 backwash was reduced to 2.6×10^9 m^{-1}, five times lower than with the pristine membrane with hydraulic backwash (1.3×10^{10} m^{-1}).

3.6. Long-term performance of the $CuFe_2O_4$ membrane fouled by concentrated alginate

To evaluate the long-term performance of Fenton-like backwash on the $CuFe_2O_4$ membrane, the fouling experiments were conducted using a concentrated alginate (800 mg/L) with 3 mM Ca over seven cycles. Fig. 8a shows that the normalized flux was restored to 89 %–94 % in the first three cycles, and then stabilized at 83 %–87 % over the rest of the

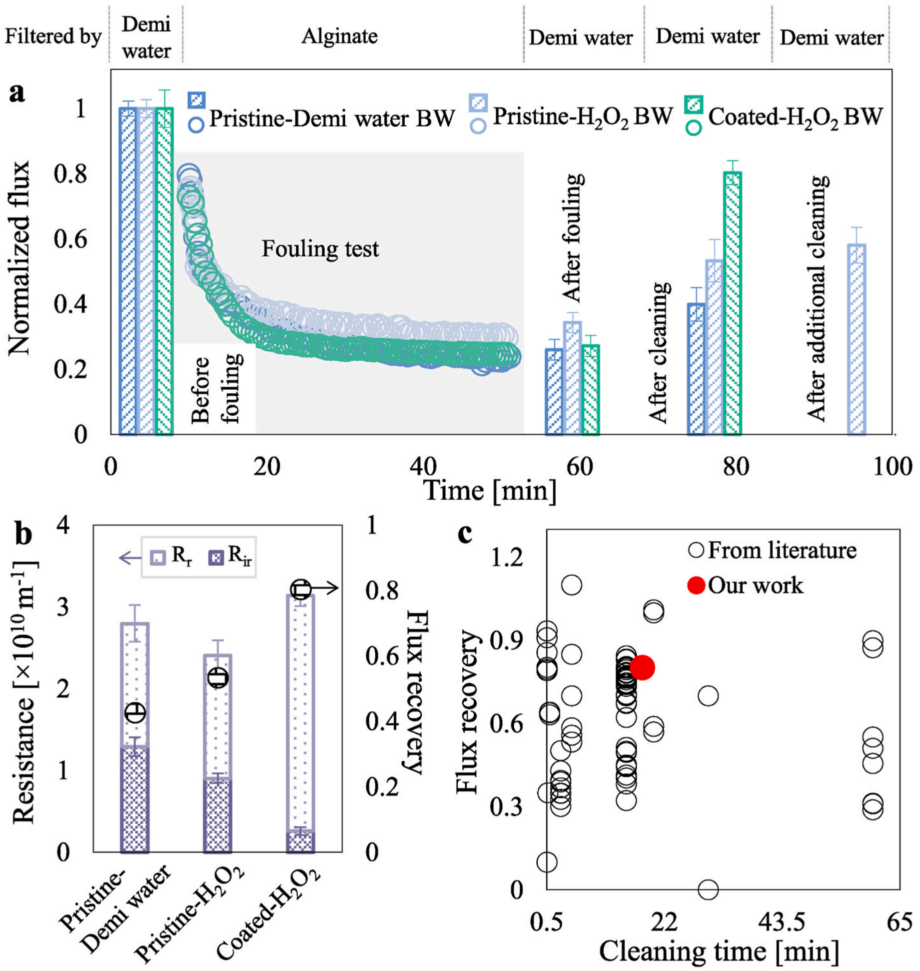

Fig. 7. (a) Normalized flux declines during fouling, and normalized demineralized water flux measured before the alginate adding, at the end of fouling, after cleaning and additional backwash procedure. (b) The resistances and flux recoveries for different systems. The fouling tests were conducted by 40 min filtration of 800 mg/L alginate solution with 3 mM Ca at 0.3 bar. Cleaning was done by backwashing with 30 mM H_2O_2 or demineralized water at 0.5 bar for 18 min, followed by a 1-min forward flush. The additional cleaning of the pristine membrane was performed by an H_2O_2 backwash for 18 min. (c) Performance comparison in removal of alginate fouling from the fouled membranes [14,17,18,27,49–55].

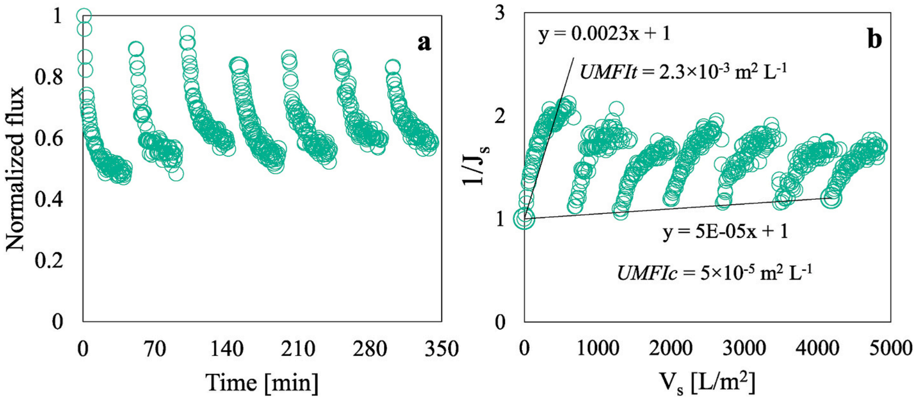

Fig. 8. (a) Long-term fouling and cleaning experiment conducted by filtration of 800 mg/L alginate with 3 mM Ca and backwash with 30 mM H_2O_2 under 0.5 bar for seven cycles. (b) Assessment of total fouling index ($UMFI_t$) and chemically irreversible fouling index ($UMFI_c$) in the long-term running.

four cycles. Since *UMFI* is independent of the traditional fouling models, it can be used in the prediction of anti-fouling performance, regardless of whether pore blocking or cake filtration occurs [22]. As depicted in Fig. 8b, $UMFI_t$ was 2.3×10^{-3} m^2 L^{-1}, higher than 1.13×10^{-3} m^2 L^{-1} in the ceramic UF membrane found by Alresheedi et al. [5]. Their fouling experiments used an approximately 31 mg/L alginate with 0.75 mM Ca, which was much lower than our test using 800 mg/L alginate with 3 mM Ca. This possibly led to the higher $UMFI_t$ found in our experiment. However, our observed $UMFI_c$ only accounted for 2.2 % of $UMFI_t$, much lower than 20 % and 30 % found in 10 mM NaOH and 14 mM NaClO backwash, respectively, found in the study by Alresheedi et al. [5]. The low $UMFI_c$ observed in our seven-cycle experiment indicates that the

Fenton-like backwash effectively removed alginate fouling that was resistant to hydraulic, NaOH, and NaClO cleaning, even when treating such a concentrated alginate feedwater.

3.7. Radical quenching

The •OH radical scavenger of TBA was used to assess the role of •OH in the $CuFe_2O_4$-coated membranes with H_2O_2. TBA was first introduced in the H_2O_2 backwash solution to inhibit •OH activity and assess its impact on fouling removal by the $CuFe_2O_4$ membrane (Fig. 9a). Cleaning performance was evaluated through flux recovery, based on the pure water fluxes before and after fouling. It shows that the presence of TBA in H_2O_2 backwash reduced the flux recovery from 80 % to 54 %, which was only slightly higher than the pristine membrane with demineralized water backwash (45 %). This suggests that •OH radicals play a key role in fouling removal during Fenton-like backwash by the $CuFe_2O_4$ membranes with H_2O_2.

The generation of •OH radicals was further confirmed using methylene blue as a model pollutant. As shown in Fig. 9b, 55 % of methylene blue was degraded by the $CuFe_2O_4$ membrane with H_2O_2. In contrast, the degradation was considerably inhibited due to the presence of TBA, confirming that •OH radicals were primarily responsible for the degradation process.

3.8. Leaching of the catalytic membrane

NaClO and NaOH are widely used in the cleaning of the fouled membranes to restore flux [5]. Hence, H_2O_2, NaClO, and NaOH were employed to examine the leaching of Cu and Fe. Besides, the performance of the newly coated membrane in alginate removal was compared to that of the aged catalytic membranes.

The $CuFe_2O_4$ membranes were examined by a prolonged leaching test, where the used membranes were immersed in 500 mL 30 mM H_2O_2 at a pH of 2.5, 0.1 % NaClO, or 10 mM NaOH, for 8 h. The leaching rate of Cu eventually stabilized, reaching a final value of 0.08 mg/L per hour in the H_2O_2 test during the last hour (Fig. 10a and S12a). Previous studies show H_2O_2 alone has negligible effects on Cu and Fe leaching, but higher Cu leaching occurs with acids such as HCl [56,57]. Hence, the leaching of Cu in H_2O_2 was probably caused by HCl addition for pH adjustment. Negligible Cu and Fe leaching was found in NaClO and NaOH (Fig. 10a, Fig. S12b and S12c). The XRD test (Fig. S13) confirmed the coated membrane retained its spinel structure after aging in H_2O_2 for 96 h. A study has reported that a 2-h treatment with oxidizing agents can remove unstable catalysts from the modified ceramic UF membranes, resulting in low leaching but maintaining high catalytic capacity [10]. After 96-h aging, the catalytic membrane was tested in a single-cycle fouling and cleaning experiment. As shown in Fig. 10b, the aged membrane experienced a slightly higher flux drop but acquired a similar flux recovery (around 78 %) compared to the newly coated membrane.

3.9. Comparison of Fenton-like cleaning during filtration and backwash

Direct injection of oxidant agents in feedwater is a broadly used method to mitigate the formation of fouling upon membranes [23]. Hence, 30 mM H_2O_2 was added to the alginate solution with an adjusted pH of 2.5 for the continuous oxidation of alginate during filtration process. The fouled catalytic membranes were then backwashed with demineralized water at 0.5 bar for 18 min, followed by a forward flush to remove the loosened alginate. We compared the cleaning performance and H_2O_2 consumption between the two application methods: the H_2O_2-in-feed method and the H_2O_2 backwash method.

Fig. S14a shows that the flux of the H_2O_2-in-feed method faced a sharper flux drop in the early phase, followed by an increase which can be attributed to the continuous Fenton-like oxidation of alginate fouling during the filtration. However, the H_2O_2-in-feed method exhibited a lower flux recovery (71 %) than the H_2O_2-backwash method (81 %). The total organic carbon (TOC) tests showed that the H_2O_2-in-feed method had a lower TOC rejection (50 %) than the H_2O_2-backwash method (79 %) (Fig. S14b). This is because the continuous Fenton-like reactions break alginate into small fragments during filtration, which are more likely to pass through the membrane. Furthermore, the H_2O_2-in-feed method consumed more H_2O_2 (7.35 kg) than the H_2O_2-backwash method (0.05 kg) during a 24-h running (Fig. S14c).

Although Fenton-like cleaning has been integrated into filtration or into forward flush to mitigate membrane fouling, these methods often suffer from high chemical consumption, which considerably raises environmental concerns related to residual oxidants, and increases operational costs (e.g., the high chemical consumption). Besides, the low TOC rejection may lead to secondary contamination. In contrast, the integration of H_2O_2 into the backwash phase provides a more efficient use of oxidants while maintaining high pollutant rejection and effective backwash performance. Therefore, the application of H_2O_2 in backwash represents a more practical and cost-effective strategy for the long-term operation of catalytic UF systems in treating alginate fouling. However, for full-scale applications, the proposed Fenton-like backwash process requires further optimization. For example, a low-pressure Fenton-like backwash can be combined with a high-pressure hydraulic backwash to first degrade the fouling and then flush away the detached fouling. This combined approach may achieve effective fouling removal while further reducing chemical consumption. Nevertheless, the evaluation and validation of such a hybrid cleaning strategy fall beyond the scope of the present study and should be addressed in future research.

4. Conclusion

To tackle fouling in ceramic UF membrane applications, we proposed

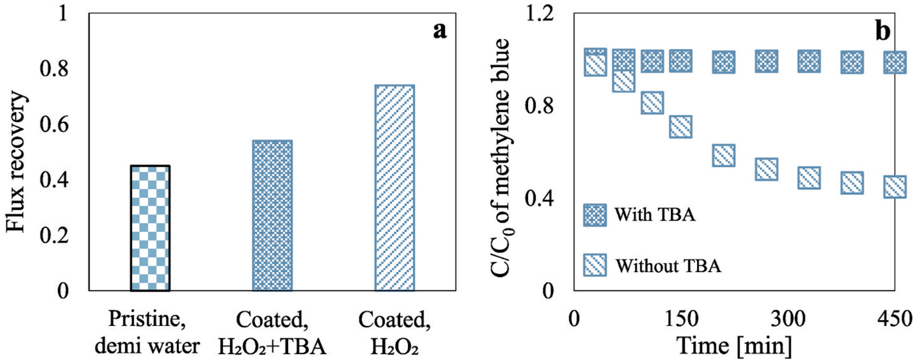

Fig. 9. Radical quenching experiments. (a) Flux recoveries in treating alginate water by the pristine membrane backwashed with demineralized water, the coated membrane backwashed with H_2O_2 and TBA, and the coated membrane backwashed with H_2O_2. (b) C/C_0 of methylene blue conducted by the coated membranes with H_2O_2 or H_2O_2 and TBA. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

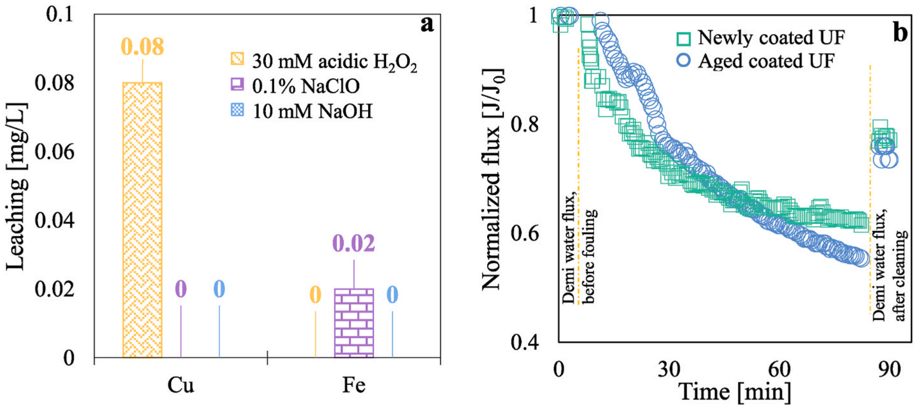

Fig. 10. (a) Leaching of Cu and Fe ions per hour during last-hour leaching test. (b) Performance comparison of newly and aged (after immersion in 30 mM H_2O_2 solution at pH of 2.5 for 96 h) catalytic membranes.

a practical and efficient cleaning strategy by coupling Fenton-like reactions with backwash. This study reveals how backwash pressure, duration, and calcium concentration influence the efficacy of Fenton-like backwash in the $CuFe_2O_4$-coated membranes fouled by alginate. The long-term performance of the coupled systems and leaching of the $CuFe_2O_4$ membranes were also examined in this work. The main conclusions can be described as follows:

(1) Backwash with demineralized water on both pristine and coated ceramic UF membranes was ineffective for removing alginate-Ca fouling, with cleaning efficacy remaining low (1 %–14 %), even when the duration (6–36 min) and pressure (0.3–1 bar) were increased.
(2) The backwash efficacy was considerably enhanced in the presence of Fenton-like reactions, achieving 71 % cleaning efficacy at a backwash pressure of 0.3 bar.
(3) The improved Fenton-like cleaning was dominated by reducing backwash pressure, rather than extending backwash duration. This improvement was attributed to the increased residence time of H_2O_2, facilitating the radical formation.
(4) Ca ions altered the fouling structure and impacted cleaning performance. At high concentrations, the rigid, and compacted alginate-Ca clusters restricted the backwash to loosen the fouling, limiting H_2O_2 and radical transport. Moreover, the broken alginate chains were captured and bound with the excess Ca ions released from the internal clusters, hindering fouling detachment.
(5) Fenton-like backwash effectively cleaned the catalytic membranes which was fouled by a concentrated alginate solution (800 mg/L), restoring 83 %–94 % of the initial flux over seven cycles.
(6) Cu leaching in 30 mM H_2O_2 gradually ceased to 0.08 mg/L. Negligible leaching of Cu and Fe ions occurred in 0.1 % NaClO and 10 mM NaOH. Flux recovery of the aged coated membranes backwashed with H_2O_2 was comparable to that of the newly coated membranes.

CRediT authorship contribution statement

Shuo Zhang: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Keyang Wang:** Methodology, Investigation, Conceptualization. **Luuk C. Rietveld:** Writing – review & editing, Supervision. **Sebastiaan G.J. Heijman:** Writing – review & editing, Supervision, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2025.124411.

Data availability

Data will be made available on request.

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