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Biofouling control of reverse osmosis membrane using free ammonia as a cleaning agent

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A B S T R A C T

Reverse osmosis (RO) is an important and widely-used membrane separation process for water recycling. However, biofouling is extensively considered a major problem for RO membranes due to the biofilm formation on the membrane surfaces. This study proposed and demonstrated a novel and sustainable chemical cleaning approach using a free ammonia (FA) solution for the removal of biofouling on RO membranes. The feasibility of FA solution for biofouling removal was investigated through a series of lab-scale soak cleaning tests and cross-flow cleaning tests on four fouled RO membranes (M1-M4) collected from municipal wastewater recycling plants. In soak cleaning tests on M1, FA concentrations of 65–560 mg NH_3–N/L (pH = 8.9) can remove adenosine triphosphate (ATP) by 32–75 %, remove proteins by 18–47 % and remove polysaccharides by 31–74 %, which was up to 3.4 times of the removals by using NaOH solution under the same pH. FA solution of 310–560 mg NH_3–N/L (pH = 8.9) even showed higher removals than NaOH solution with a higher pH of 11. In the cross-flow cleaning tests on M2-M4, FA solution of 310–560 mg NH_3–N/L (pH = 8.9) removed the ATP by 82–100 %, removed proteins by 58–87 % and removed polysaccharides by 68–100 % in the fouling layers and increased the permeability by 8–16 %. Such cleaning effects in cross-flow tests were also positively correlated ($R > 0.9$, $p < 0.05$). Compared to the conventional anti-biofouling agent of NaOH solution (pH = 11), FA solution (310–560 mg NH_3–N/L) showed significantly better cleaning performance. A high FA concentration of 560 NH_3–N/L (pH = 8.9) could achieve comparable cleaning effect to 1 % EDTA solution (pH = 10). Additionally, increasing the frequency of cleaning or using a higher concentration of FA solution for biofouling removal will be more advantageous to prolong the membranes' lifespan. The findings provide a promising alternative to using FA as a cost-effective and environmentally friendly solution for cleaning biofouling on RO membranes.

1. Introduction

The global demand for freshwater is increasing at an unprecedented rate with the urbanization process, which highlights the need for effective and efficient water treatment technologies [1]. Currently, membrane-based technologies are considered one of the most promising technologies to produce high-quality effluent for water and wastewater treatment [2,3]. Among various membrane-based technologies, the reverse osmosis (RO) process is widely applied globally due to the high water quality, easy maintenance, low energy requirements, and simple installation [4].

In municipal wastewater recycling plants (MWRPs), biofouling stands out as a particularly challenging issue in membrane processes, due to the high levels of microbes and carbon sources in the feed water, while the contributions of inorganic foulants are limited [5,6]. Biofouling refers to the attachment, growth, and multiplication of bacteria on the membrane surface receiving the influent. These bacteria also bind to extracellular polymeric substances (EPS) (mainly proteins and polysaccharides) in the water, eventually leading to the formation of biofilm on the membrane [7,8]. The formation of biofilms reduces membrane flow rate and increases pressure loss across the membrane, which further increases energy consumption and brings contamination risks. The cost to address the biofouling of RO membranes is estimated to be around 20–30 % of operating expenditure for each plant applying the RO process [9]. Furthermore, biofouling also accelerates the biodegradation of polymers and other components composing the membrane and eventually shortens the lifespan of the RO membrane [7,8].

To control or mitigate biofouling on RO membrane, several strategies have been proposed and tested through physical, biological and chemical approaches. The biological control measures for biofouling are achieved by adding bactericides such as chlorine or chloramine to remove bacteria from the influent before it arrives at the RO membrane, limiting bacterial growth on the membrane surface [2,10,11]. However, as strong oxidants, chlorine and chloramine may degrade the active polyamide layer of the RO membrane, consequently raising the risk of membrane damage and associated maintenance expenses [12].

Common chemical cleaning is still considered the most effective way to mitigate the biofouling of RO membranes [13]. The combinations of

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alkaline and acid cleaning were reported to remove the organic matter and biofilm attached to the membrane and to restore the RO membrane processing capacity [13,14]. However, the common chemical cleaning not only increases the cost of operation but also leads to potential environmental pollution caused by the post-cleaning waste solution [13,14].

Free ammonia (FA, i.e., NH_3), a waste by-product from the sludge digestion process in MWRPs, has been revealed to have a strong biocidal effect, resulting in microbial inactivation and cell lysis [15,16]. The biocidal effect of FA has also been utilized to pretreat the sludge to enhance the sludge digestion performance in MWRPs [16,17]. FA directly exists in the digestion liquor from MWRPs, which can be obtained without additional purchasing expense [16]. In MWRPs, FA-containing digestion liquor is directly discharged into the microbiological treatment unit [16,20]. Thus, the residual FA solution from the membrane cleaning can be discharged directly into the microbiological treatment unit, minimizing the need and cost for the post-treatment membrane cleaning residuals. Thus, we propose that the FA solution can be used as an emerging chemical agent to control biofouling and restore the processing ability of the RO membrane.

This study aimed to explore the feasibility of FA as a new chemical cleaning agent for cleaning the biofouling of RO membranes. A series of laboratory-scale soak cleaning tests and cross-flow cleaning tests were conducted on RO membranes subjected to biofouling from MWRPs. The effects of FA on biofouling control were tested by evaluating the removals of adenosine triphosphate (ATP), proteins and polysaccharides levels on the membrane using FA solution. Compared with the effects of conventional alkaline cleaning (i.e., NaOH and EDTA), FA solution has a better performance on biofouling control, indicating its potential application in MWRPs.

2. Material and methods

2.1. Chemicals

A series of FA solutions were prepared using ammonium chloride (>99 %, Chem-supply, Australia). pH was maintained at 8.9 ± 0.1 using NaOH solution. The FA concentration was calculated based on the total ammonia nitrogen concentration, pH, and temperature as follows: FA concentration (as mg NH_3/L) = $S(NH_4^+\text{-N} + NH_3\text{–N}) \times 10^{pH}/(K_b/K_w+10^{pH})$ [18]. The $S(NH_4^+\text{–N} + NH_3\text{–N})$ is the total ammonia nitrogen concentration. The K_b/K_w equals to $e^{6,344/(273+T)}$ [18]. Two common chemical cleaning solutions, i.e., 1 % EDTA solution (pH = 10) and NaOH solution (pH = 11) were prepared by using EDTA (>99 %, Sigma-Aldrich, USA) and NaOH (>98 %, Sigma-Aldrich, USA).

2.2. Reverse osmosis modules and fouling characterization

Four fouled RO modules (M1-M4) subjected to biofouling were collected from three full-scale water recycling plants in Australia. The influent of the MWRPs, which are primarily domestic wastewater, undergo tertiary treatment before being processed by the RO membrane, with a daily recycling water treatment capacity of 2.2–39.2 ML/day. All four RO modules are commercial thin-film composite polyamide membranes and sourced from the first third of the respective membrane modules in the MWRP. All RO membranes have been used in full-scale MWRPs for 4–12 months and have undergone 1 to 6 chemical cleaning, including alkaline and acidic cleaning. This enables the capture of diverse fouling conditions of the membranes (e.g., moderate to severe). M1 was used for the soak cleaning (section 2.3.1), while M2-M4 were used for cross-flow cleaning (section 2.3.2).

Membrane autopsies were conducted on the four fouled membranes to characterize the fouling layer. The chemical components of the fouling layers were characterized by the loss of ignition (LOI), polysaccharide, and protein content. LOI is the ratio of the inorganic fraction to the organic fraction of the fouled layer, which could help to determine if the contamination is biofouling [2]. Protein and polysaccharide are the predominant components of EPS, which are abundant in biofouling layers [7,8]. Thus the polysaccharides and proteins concentrations were measured to reflect the EPS level and biofilm content in the biofouling layers. The ATP levels were used to reflect the active level of microbes in the fouling layers [2].

2.3. Lab-scale cleaning trials

2.3.1. Soak cleaning

Soak tests served as pre-tests to identify the ideal range of FA concentrations for cleaning biofouling on the RO membrane surfaces. Membrane coupons (36 cm^2 with 6 cm × 6 cm) were cut from the M1 RO module using a sterilized scissor. Each coupon with fouling layers was completely soaked in a beaker containing 300 mL of cleaning solution for 24 h at room temperature (25 ± 1 °C). Two kinds of NaOH cleaning solution with pH of 8.9 and 11.0 were employed, while DI water was used as a control. Five FA concentration gradients (65, 185, 310, 435 and 560 mg NH_3–N/L, pH = 8.9) were used in the soak cleaning. The concentration of FA differs among various anaerobic digestion systems, ranging from approximately 50 mg/L to several hundred or even a thousand mg/L [19]. Based on our previous observations [20], this study selected a FA range of 65–560 mg/L, which can be directly obtained from the digestion liquor in local MWRP [15]. The beakers were placed on an orbital shaker (Ratek large orbital shaker, Australia) and agitated at 120 rpm. For each cleaning solution, the experiments were triplicate. The levels of ATP, polysaccharides, and proteins on the membrane surface were measured before and after soak cleaning tests.

2.3.2. Cross-flow cleaning tests

Cross-flow cleaning is the protocol that actually used in the membrane cleaning process in MWRPs [2]. In this study, cross-flow cleaning tests were conducted to simulate the real cleaning conditions in MWRPs using M2-M4 membrane modules. Membrane coupons (90 cm^2 of membrane-active surface) along with respective feed spacers were cut from membrane modules using a sterilized scissor and placed in the cleaning cells. Cleaning cells were designed to simulate the configuration of the RO filtration system and were operated with cross-flow cleaning tests. Five kinds of cleaning solution were used for the cross-flow cleaning, including three FA concentrations of 370, 435, and 560 mg NH_3–N/L (pH = 8.9) and two kinds of conventional cleaning solution, NaOH (pH = 11.0) and 1 % EDTA W/V% (pH = 10.0). These FA concentrations were selected based on the soak cleaning results. DI Water was used as a control (Table 1).

For each membrane coupon, a certain type of cleaning solution was pumped (Cole Parmer, Masterflex L/S economy drive pump, Germany) through the cleaning cell for 24 h according with a cross-flow velocity of 0.1 m/s. This cross-flow velocity was selected based on the actual operating conditions of the MWRPs. Each cleaning test was conducted with coupons from the same membrane in triplicates.

The cleaning process in each test lasted for approximately 24 h and 15 min including the following three stages:

·DI water rinse (2 h) to remove biomass at the external layer of biofilm;

Table 1
List of cleaning conditions for the cross-flow cleaning tests.

Cell	Cleaning Type	Cleaning Condition
A	Water (Control)	DI water
B	Free ammonia	370 mg NH_3–N/L, pH = 8.9
C	Free ammonia	435 mg NH_3–N/L, pH = 8.9
D	Free ammonia	560 mg NH_3–N/L, pH = 8.9
E	Alkaline (the benchmark)	NaOH, pH = 11.0
F	EDTA	1 % EDTA W/V%, pH = 10.0

· Recirculation of cleaning solution (22 h);
· DI water rinse (15 min) to remove the residual chemicals.

The ATP, polysaccharide, and protein levels on the membrane coupons before and after the cross-flow cleaning were measured to reflect the cleaning efficiency on biofouling layer removal.

2.3.3. Membrane performance recovery tests

The membrane performance recovery in terms of permeability was assessed in a separate lab-scale cross-flow filtration unit. Clean water permeability is commonly used to assess the recovery of the performance of RO membranes [12,21]. This part of the test was carried out on a laboratory-scale staggered flow filtration system. The system consisted of a 20 L tank, a Driven Diaphragm Pump (Scintex, Australia), a damper (to balance the flow and pressure in the system, China), and a filtration unit (CF042, Sterlitech, USA). During the operation of the system, the membrane under test was firstly installed in the filtration unit. Then the cleaning solutions were pumped from the tank into the filtration unit. Finally, the filtered solution (i.e., the permeable solution and the concentrated solution) was pumped back into the solution tank. The clean water permeability test was determined by running DI water through the system at a flow rate of 5 bar and 40 L/h for a continuous period of 1.5 h.

2.4. Analytical methods

The biofouling layer was collected by scraping a known surface area of the membrane (40 × 40 cm^2). Solids accumulated on membrane surfaces were dried in an oven at 105 °C overnight to measure the total solids (TS) level and then moved into a furnace at 500 °C for 4 h to measure the volatile solids (VS) level. The TS and VS concentrations were then calculated as follows:

$$\text{Total solids concentration}: \text{TS} = \frac{w2 - w1}{S}$$

$$\text{Volatile solids concentration}: \text{VS} = \frac{w2 - w3}{S}$$

where w1 (g) is the weight of the crucible, w2 (g) is the weight of the crucible and deposits after the oven, w3 (g) is the weight of the crucible and deposits after the furnace and S (cm^2) is the surface area of the membrane sample.

To measure the ATP, polysaccharide, and protein levels, the biofilm (biofouling layers) was removed from the membrane surface, a Braun Oral-B Vitality electrical toothbrush (Procter & Gamble, USA) was used and the removed items were suspended in 200 ml DI water. Total ATP was determined using the ATP Assay kit (Sigma-Aldrich, USA) according to the manufacturer's instructions. Protein and polysaccharide contents were measured using the QuantiPro™ BCA Assay Kit (Sigma-Aldrich, USA) and the Phenol–Sulphuric acid method, respectively [2]. All tests were carried out in triplicate.

Pairwise comparisons of groups with different cleaning agents (p value) were carried out by t-test via Origin and the significant level was set as 0.05. Correlations (R value) between FA concentrations and relevant parameters were evaluated through Pearson's correlation coefficient using Matlab software, where the R value closer to 1 represents a more positive linear correlation.

3. Results

3.1. The effects of FA solution on soak cleaning performance

3.1.1. Fouling layer characterization of M1

A series of bench-scale soak cleaning tests were conducted as pretests to verify the feasibility of using FA solutions to clean biofouling on the surface of RO membranes. The fouling layer was characterized based on membrane autopsies for M1. The TS content of the fouling layer contained 94.1 ± 0.2 % organics. The concentration of protein and polysaccharide (major compounds of EPS) in the fouling layer was 0.20 ± 0.02 g BSA/m^2 and 0.44 ± 0.10 g glucose/m^2, respectively. The ATP concentration in the fouling layer reached 0.39 ± 0.09 pg ATP/m^2, indicating the considerable active microbes in the fouling layer. The concentrations of proteins and polysaccharides and ATP levels in the fouling layer are comparable to other reported biofouling layers formed on RO membranes, confirming the presence of biofouling in the membranes used in this study [2].

3.1.2. ATP, proteins, and polysaccharides removals of M1

In the soak cleaning test, the removal efficiency for the fouling layer was evaluated by the reduction of ATP, proteins, and polysaccharides on the membrane surface. Only a small account of ATP was removed by the DI water (control, 4 % removal) and NaOH solution (pH = 8.9, 25 % removal) (Fig. 1). On the contrary, FA solution significantly enhanced the ATP removal ($p < 0.05$) compared to the NaOH solution under the same pH (8.9) and the DI water. FA solution of 65, 185, 310, 435 and 560 mg NH_3–N/L achieved ATP removals of 32 ± 7 %, 40 ± 1 %, 51 ± 3 %, 66 ± 2 % and 75 ± 4 %, respectively, which were 8–19 times higher than that of the control (4 %) and 0.28–2 times higher than that of the NaOH solution (pH = 8.9, 25 %). Additionally, the ATP removal through the soak cleaning was positively correlated with the FA concentration ($R > 0.9$, $p < 0.05$). This implies that FA rather than the alkali inactivated or killed the microbes in the fouling layer (biofilm).

Similar trends were also observed for proteins and polysaccharides on membrane surfaces. DI water hardly reduced the proteins and polysaccharides on the membrane. The NaOH solution (pH = 8.9) removed protein and polysaccharide by 14 ± 5 % and 23 ± 5 %, respectively (Fig. 2). The FA solution (65–560 mg NH_3–N/L) significantly enhanced the removal of protein and polysaccharide ($p < 0.05$). When the concentration of FA in the cleaning solution increased from 65 to 185, 310, 435 and 560 mg NH_3–N/L, the removal of protein increased from 19 ± 4 % to 18 ± 2 %, 25 ± 5 %, 39 ± 2 % and 47 ± 3 %, and the removal of polysaccharide increased from 31 ± 5 % to 46 ± 6 %, 55 ± 2 %, 60 ± 4 %, and 74 ± 8 % (Fig. 2), respectively. Such promotion effect was positively related to the FA concentration ($R > 0.9$, $p < 0.05$). The highest removal of protein and polysaccharide was achieved under 560 mg NH_3–N/L, which are 3.4 and 3.2 times the removals by using the NaOH solution under the same pH (8.9), respectively. This indicated that FA enhanced the EPS and biofilms removals of M1 and the

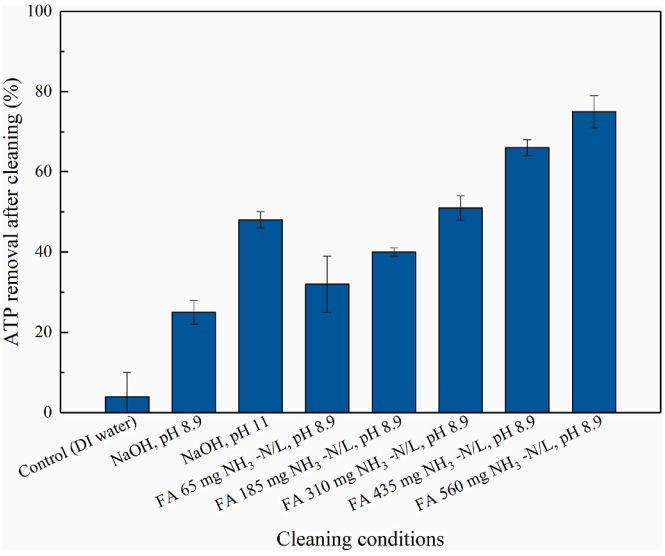

Fig. 1. ATP removals of the membranes M1 after 24 h soak cleaning tests. Error bars represent standard errors.

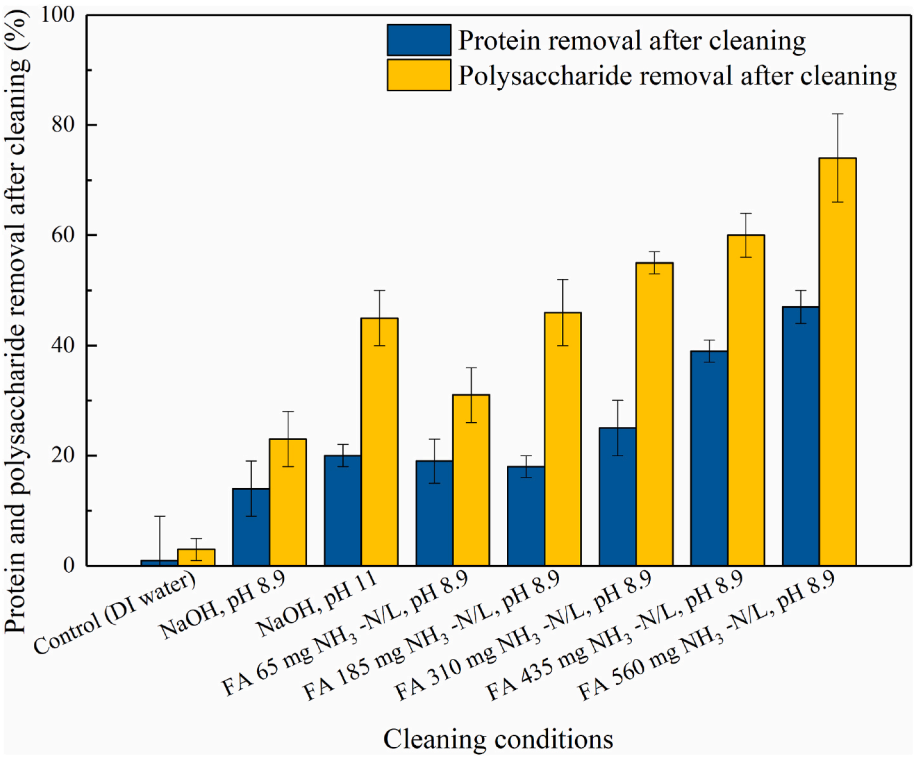

Fig. 2. Protein and polysaccharide removals of the membranes M1 after 24 h soak cleaning tests. Error bars represent standard errors.

effectiveness of protein and polysaccharide removals are attributed to the FA solutions instead of a high pH (8.9). In a word, the removals of ATP and EPS through FA solution imply that FA solution (65–560 mg NH_3–N/L) is effective in removing biofilms and biofouling from the membrane M1.

The effect of NaOH solutions at pH = 11.0, a common solution for cleaning biofouling, was also evaluated in soak cleaning tests. Through NaOH solution, ATP was reduced by 48 ± 2 %, while protein and polysaccharides were reduced by 20 ± 2 % and 45 ± 5 %, respectively (Figs. 1 and 2). The removals of ATP, protein and polysaccharides were significantly lower than the FA solution over 310 mg NH_3–N/L (Figs. 1 and 2), while slightly higher than that with the FA solution of 185 mg NH_3–N/L (pH = 8.9). This indicates that FA concentration over 310 mg NH_3–N/L is more effective for cleaning biofouling than conventional alkaline cleaning. Three concentrations of FA solution (i.e., 310, 435 and 560 mg NH_3–N/L) were then selected in the subsequent cross-flow cleaning experiments.

3.2. The effects of FA solution on the cross-flow cleaning performance

3.2.1. Fouling layer characterization of M2-M4

Three commercial RO membranes (i.e., M2-M4) were collected from MWRPs in Sydney for the cross-flow cleaning tests. The LOI results showed that the fouled layer of the M2-M4 membranes mainly consisted of organic contaminants (>89.4 % of TS level). The concentrations of ATP, protein, and polysaccharides are shown in Fig. 3. Among these three membranes, M2 had the highest ATP, protein and polysaccharide levels, which were 0.52 pg ATP/m^2, 0.43 g BSA/m^2, and 0.71 g glucose/m^2, respectively. The levels of ATP, protein and polysaccharide at M2 were almost 2.6 times of M3 and 6 times of M4. According to these results, M2 and M3 could be classified as heavily fouled and M4 as moderately fouled in this study.

3.2.2. ATP removal of M2-M4

Based on the results of the soak cleaning tests, three FA concentrations of 310, 435, and 560 mg NH_3–N/L (pH = 8.9) were selected for the cross-flow tests. In addition, the common chemical cleaning agents used for biofouling removal from RO membranes, i.e., NaOH solution (pH =

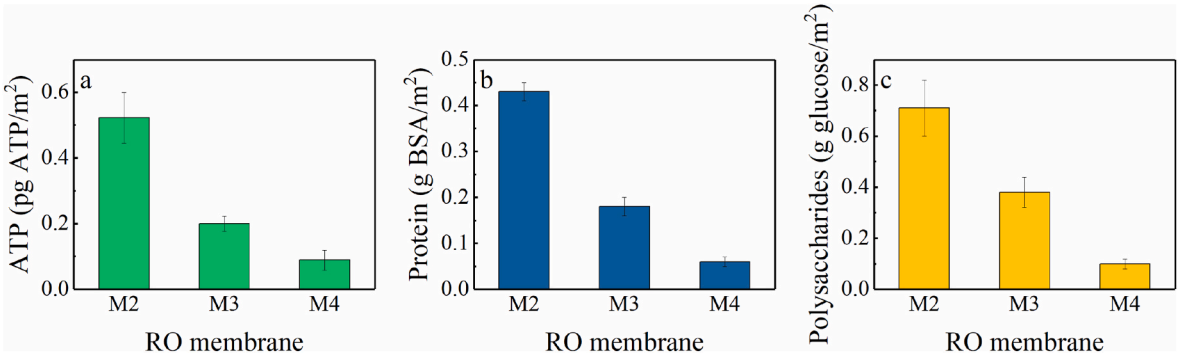

Fig. 3. Fouling layer characterization of M2-M4. Error bars represent standard errors.

11.0) and 1 % EDTA solution, were also tested for comparison.

FA solution significantly reduced the ATP levels in the fouling layers regardless of the severity of the fouling on the membranes ($p < 0.05$). For M2 and M3 with severe fouling conditions, the water rinse, and DI water cleaning removed only 31 ± 2 % and 35 ± 10 % of ATP in the fouling layers, respectively. However, FA solution of 310 mg NH_3–N/L significantly improved the ATP reduction level to 82 ± 4 %. The further increase of FA concentrations to 435 and 560 mg NH_3–N/L led to 97 ± 3 % and 98 ± 3 % reduction in the ATP level, respectively (Fig. 4). For the membrane M4 with the least fouling severity, the water rinse and DI water cleaning removed 66 ± 9 % and 87 ± 6 % of ATP in the fouling layer, respectively. However, the FA solution of 310 mg NH_3–N/L reduced 96 ± 2 % of the ATP level on the membrane surfaces and higher FA solution of 435 and 560 mg NH_3–N/L could even achieve complete ATP removal (100 % ± 2 % and 100 % ± 0 %, respectively). Consistent with the soak cleaning results, the ATP removal was positively correlated with the FA concentration ($R > 0.9$, $p < 0.05$). Additionally, FA was more effective on the ATP removals of moderately fouled membranes (M4, 96–100 %) than the heavily fouled membranes (M2-M3, 82–99 %). This result also suggests that an appropriate frequency of membrane cleaning can eliminate the formation of heavy fouling and therefore result in a greater recovery of membrane capacity according to the up to 100 % ATP removals of moderately fouled membranes.

The conventional NaOH (pH = 11.0) cleaning achieved the ATP removals by 72 ± 7 %, 86 ± 4 %, and 96 ± 1 % (Fig. 2) for M2, M3, and M4, respectively, which were all significantly lower than the ATP removals achieved by FA solution regardless of the FA concentrations ($p < 0.05$). The 1 % EDTA cleaning (pH = 11.0) achieved the ATP removal for M2, M3, and M4 by 99 ± 1 %, 99 ± 1 % and 100 % ± 0 %, respectively (Fig. 4), which were comparable to the results achieved by 560 mg NH_3–N/L FA solution ($p > 0.05$). This indicates that the effect of FA solution cleaning (310–560 mg NH_3–N/L, pH = 8.9) on ATP removals is more effective than the common alkaline cleaning and FA concentration of 560 mg NH_3–N/L showed a comparable performance to the 1 % EDTA solution.

3.2.3. Protein and polysaccharide removals of M2-M4

Three concentrations of FA solution, i.e., 310, 435, and 560 NH_3–N/L, were more effective in reducing proteins and polysaccharides in fouling layers of M2-M4 compared to pre-cleaning on M1 ($p < 0.05$). For M2 and M3, the water rinse and DI water removed 24–56 % of protein and 34–72 % of polysaccharides in the fouling layer, respectively (Figs. 5 and 6). FA cleaning solution of 310 mg NH_3–N/L increased the protein reduction levels of M2 and M3 to 58 ± 6 % and 64 ± 4 % and increased polysaccharides reduction levels to 68 ± 4 % and 83 ± 8 %, respectively (Figs. 4 and 5). The further increase of FA concentrations to 435 mg NH_3–N/L led to 65 ± 8 % and 86 ± 3 % reduction of protein, as well as 80 ± 3 % and 84 ± 6 % reduction of polysaccharides in the fouling layer of M2 and M3, respectively (Figs. 5 and 6). FA concentration of 560 mg NH_3–N/L led to 75 ± 5 % and 87 ± 3 % reduction of protein, as well as 91 ± 3 % and 95 ± 5 % reduction of polysaccharides in the fouling layer of M2 and M3, respectively.

For M4, the water rinse and DI water cleaning removed 46 ± 7 % and 70 ± 6 % of protein and 77 ± 9 % and 92 ± 6 % of polysaccharides in the fouling layer, respectively (Figs. 5 and 6). Using FA solutions at concentrations of 310, 435 and 560 mg NH_3–N/L reduced protein levels to 75 ± 6 %, 85 ± 8 % and 86 ± 5 %, respectively (Fig. 4). Meanwhile, FA solutions at all the concentrations completely removed the polysaccharides (100 % removal) on the membrane surfaces (Fig. 6).

For conventional NaOH cleaning (pH = 11.0), the protein removals for M2-M4 were 53 ± 7 %, 60 ± 2 %, and 80 ± 9 %, respectively, and the polysaccharide removals were 75 ± 5 %, 78 ± 4 %, and 96 ± 3 %, respectively (Figs. 5 and 6). These results were significantly lower than the protein and polysaccharide reduction achieved by FA solutions regardless of the FA concentration ($p < 0.05$). This is consistent with the experimental results for ATP, indicating that the selected concentrations of FA solution of 310, 435 and 560 mg NH_3–N/L had better cleaning efficiency in removing EPS than the NaOH solution at pH = 11.0 ($p < 0.05$). For 1 % EDTA cleaning (pH = 10.0), the protein removals achieved for M2, M3, and M4 were 80 ± 12 %, 89 ± 2 %, and 90 ± 2 %, and the polysaccharide removals were 89 ± 2 %, 96 ± 2 %, and 100 ± 0 % (Figs. 5 and 6), respectively. Similarly, the results achieved by EDTA are similar to the FA solution of 560 mg NH_3–N/L, which is consistent with

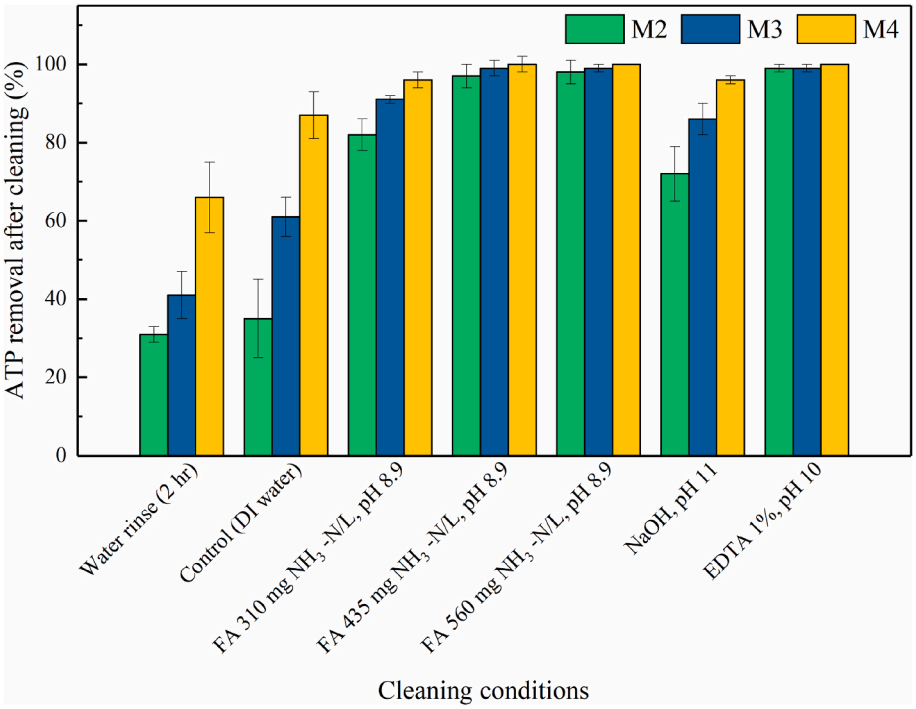

Fig. 4. ATP removals of the membranes M2-M4 after 24 h cross-flow conditions (cross-flow velocity 0.1 m/s). Error bars represent standard errors.

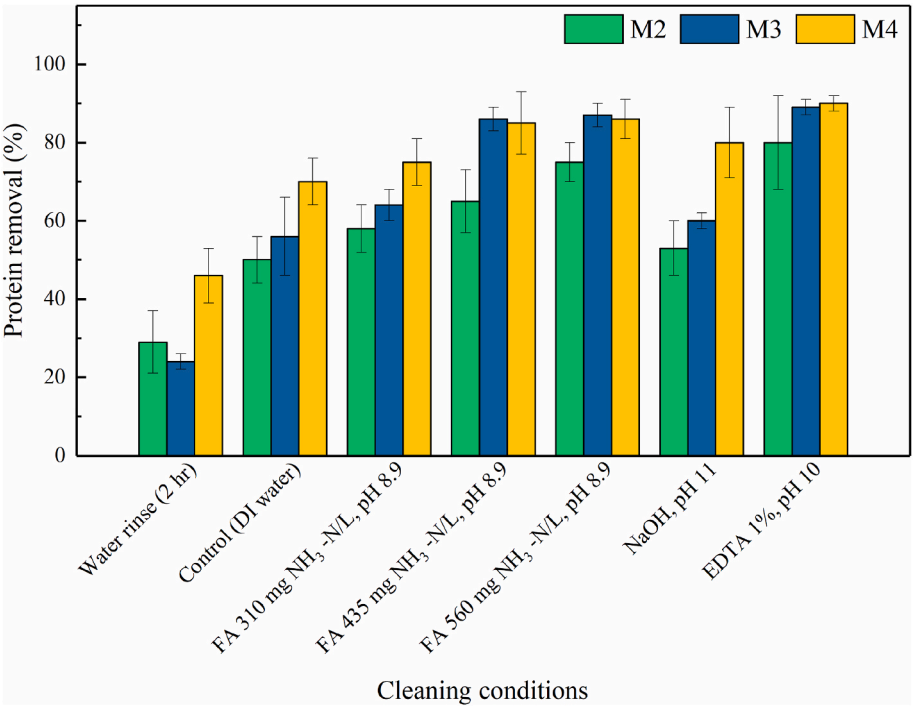

Fig. 5. Protein removals of the membranes M2-M4 after 24 h cross-flow conditions (cross-flow velocity 0.1 m/s). Error bars represent standard errors.

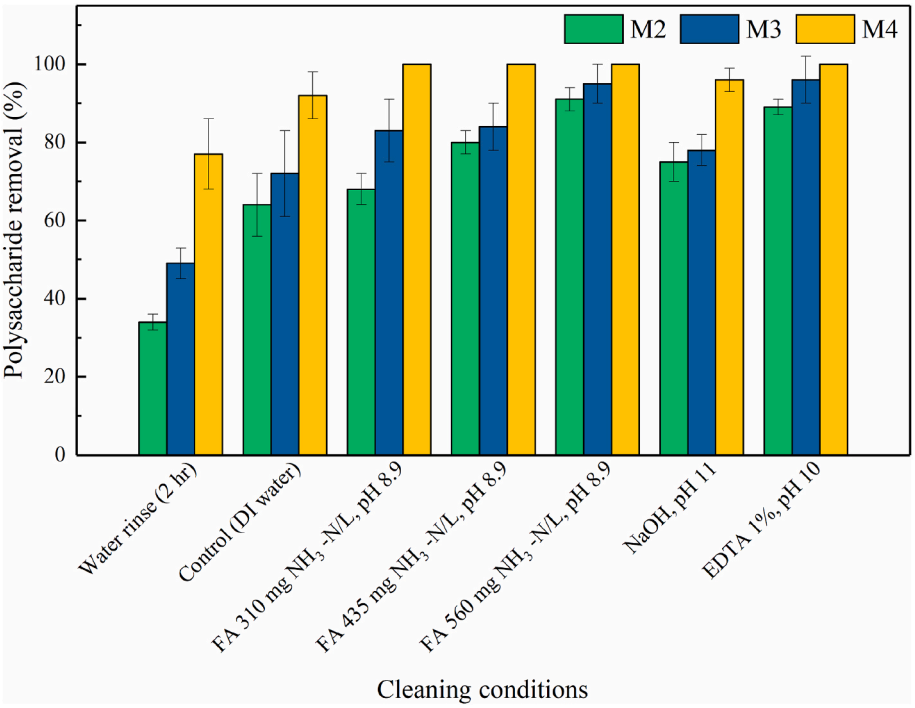

Fig. 6. Polysaccharide removals of the membranes M2-M4 after 24 h cross-flow conditions (cross-flow velocity 0.1 m/s). Error bars represent standard errors.

the result for ATP removals (Figs. 5 and 6). According to experimental results, an FA solution of 560 mg NH_3–N/L can work as a replacement for the traditional EDTA solution involving biofouling removal of RO membranes.

3.2.4. *Membranes performances recovery after cleaning*

The membrane recovery performance of the RO membrane after the cleaning, i.e., hydraulic performance, was measured and indicated by the relative permeability increase before and after cleaning (Fig. 7). FA solution of 310, 435 and 560 mg NH_3–N/L significantly increased the permeability by 8.0–16.0 % for M2-M4 ($p < 0.05$), which were higher than the results of the NaOH cleaning (increased by 5.8–9.5 %) (Fig. 7). Similarly, the permeability increased by the 1 % EDTA cleaning was similar to that of the FA solution at 560 mg NH_3–N/L (increased by 10.0–15.1 %). This is also consistent with the previous results for the removals of ATP, proteins, and polysaccharides. The permeability

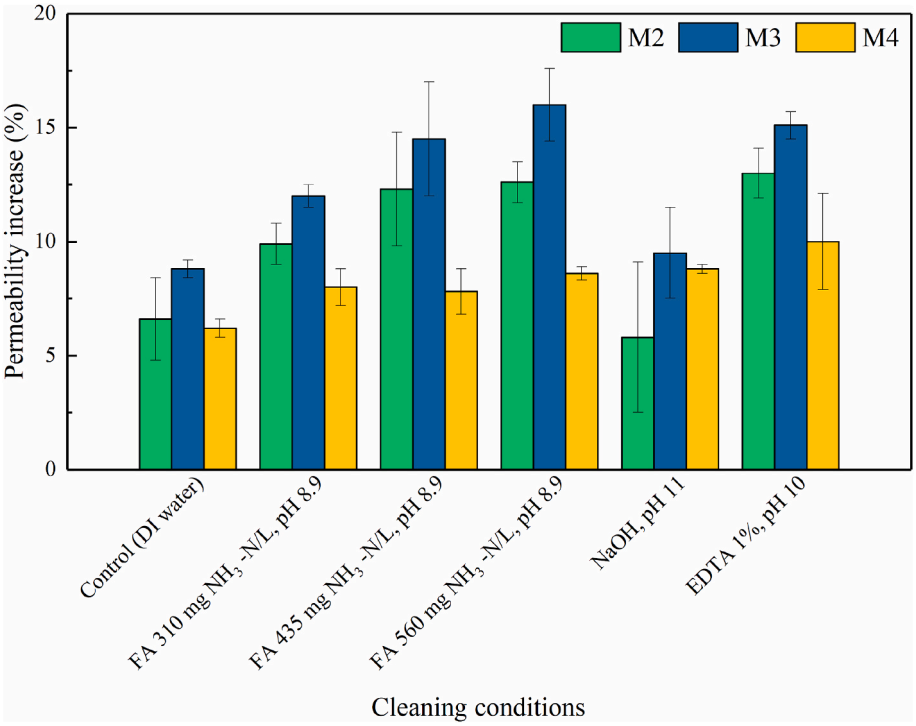

Fig. 7. Permeability increases of the membranes M2-M4 after 24 h cross-flow conditions (cross-flow velocity 0.1 m/s). Error bars represent standard errors.

increases via 310–560 mg NH_3–N/L demonstrated the recovery performance of the RO membrane had been well improved.

4. Discussion

This study for the first time demonstrates the use of FA as a novel cleaning agent to remove biofouling from RO membrane. Its effectiveness was investigated through a series of soak cleaning and cross-flow cleaning tests. In soak cleaning tests, the FA solution (65–560 mg NH_3–N/L, pH = 8.9) significantly contributed to the reduction of ATP, protein, and polysaccharide ($p < 0.05$) by up to 75 % on the fouling layers, which were by up to 3.4 times in comparison to the control and NaOH solution (pH = 8.9). This implies that FA rather than the alkali alone was the major contributor to the enhanced biofouling removal. In cross-flow cleaning tests, the removals of ATP protein, and polysaccharide ($p < 0.05$) on the fouling layers were 58–100 % by using FA solution (310–560 mg NH_3–N/L, pH = 8.9), which were significantly higher than the common NaOH cleaning (pH = 11.0) and comparable to that of 1 % EDTA cleaning when FA concentration was 560 mg NH_3–N/L (pH = 8.9). The permeability increases via FA solution (310–560 mg NH_3–N/L, pH = 8.9) were 8–16 %, which confirmed the performance recovery of the RO membranes. All of these implied that FA cleaning is a promising alternative to the current membrane cleaning solutions with significantly better or comparable performance.

The effect of FA cleaning on the biofouling control for RO membrane is likely due to the biocidal effect of FA on microbes and its ability to break down EPS [15]. Previous studies have shown that FA has a strong biocidal effect on active bacterial cells [15]. This is mainly due to its ability to diffuse through the cell membrane into the cytoplasm, which leads to changes in intracellular pH and an imbalance in the transmembrane proton gradient, ultimately leading to a loss of intracellular potassium, an increase in cellular energy requirements and eventual cell death [22]. Recent evidence also suggests that FA diffusing into the cell may directly lead to DNA damage, which in turn leads to cell death and that it is positively correlated with FA concentration [15,17]. This is supported by the significant reduction of ATP observed on the membrane surface after FA cleaning in both the soak cleaning and cross-flow cleaning tests and the positive correlation between such reduction effects and FA concentrations in our study. Furthermore, enhanced EPS destruction due to FA cleaning was observed in our study [16,20]. Previously, FA has been reported to destroy the EPS in sludge [15,16]. Such an effect is likely due to that FA, when killing cells, causes large amounts of enzymes in cells to be released into the environment, further accelerating the breakdown of EPS [25]. As EPS largely protects microbe from external aggressions and reduce survival stress in biofilms [23–25], the enhanced breakdown of EPS observed in this study supports the effeteness of FA in removing biofouling. However, the detailed mechanism of FA in breaking EPS in biofouling layers require future investigations. It has been reported that higher FA concentrations contributed to higher EPS degradation rates [15]. This is in accordance with the significant removal of EPS via FA solution and the positive correlation observed between the removal efficiency and FA concentrations in this study.

In addition, the effects of FA cleaning also depended on the extent of fouling on the membranes. For example, the FA solution of 310 mg NH_3–N/L removes 82–91 % of ATP from heavily fouled membranes (i.e., M2 and M3), but it removes over 96 % of ATP from moderately fouled membranes (i.e., M4) in cross-flow cleaning tests. This indicated that FA solution is more effective on moderately fouled membranes than on heavily fouled membranes. Therefore, we recommend that for ideal cleaning results, an appropriate increase in the frequency of membrane cleaning can effectively avoid serious biofouling. Previous studies also revealed that the removal efficiency for biofouling varies with the age and maturity of the biofilm [26]. A membrane with heavier fouling layers tends to have less biofilm removal through chemical cleaning using NaOH, EDTA, etc. [7,8]. This is consistent with our observations and this phenomenon is likely related to structural changes in the biofilm from mild to serious fouling. More serious fouling layers on the membrane are denser and more compact, which in turn prevents the penetration of cleaning agents into the fouled layer, thus reducing cleaning efficiency [2,27]. Therefore, a proper increased cleaning frequency and higher FA concentration are crucial for restoring the performance of RO membranes.

FA cleaning is a promising alternative to the current membrane

cleaning solutions with significantly better or comparable performance, in comparison to two traditional chemical cleaning methods (i.e., NaOH and EDTA), especially for the FA concentration of 560 mg NH_3–N/L, pH = 8.9. Nevertheless, compared with the conventional chemical cleaning approaches, FA is a by-product that can be directly obtained from the concentrated, centrifuged or filtered digestion liquor [16,20]. Thus, the use of FA as a membrane cleaning agent requires minimized chemical cost and can achieve a 'closed-loop' concept in MWRPs (Fig. 8). This approach not only allows the reuse of MWRP waste (i.e., anaerobic digestion liquor) and the mitigation of membrane contamination but also allows a significant reduction in cost for chemical cleaning agents, thus moving the plant from a 'linear economy' to a partial 'circular economy'. Furthermore, the production and transportation of conventional chemical agents (e.g., EDTA and NaOH) consume a lot of fossil energy. The use of FA as a cleaning agent undoubtedly reduces the environmental footprints of the RO membrane. However, it is worth noting that a small amount of alkali would be needed when the pH of the digestion liquor is less than the experimental conditions in this study (pH = 8.9) [16].

Previous studies claimed that a technology based on free nitrite acid (FNA) functions as a chemical cleaning agent to eliminate biofouling from membrane surfaces [2,28]. However, the FNA approach relies on the on-site generation of FNA via side-stream nitritation of anaerobic digestion liquid [29,30]. Unfortunately, side-stream nitritation reactors are rarely installed in MWRPs, limiting their application and requiring additional facilities and associated costs. In contrast, the FA solution proposed in this work can be extracted directly from the anaerobic digestor, which is more economical and easy-handling for the current MWRPs.

It should be emphasized that this is a proof-of-concept study demonstrating the feasibility of FA as a chemical cleaning agent for the removal of biofouling on RO membranes. A series of FA concentrations were tested and demonstrated in this study. However, the cleaning effect may also depend on other factors, such as cleaning protocols (e.g., flushing time, backwashing time, backwashing repeating frequency, etc.) [31]. Furthermore, previous studies also demonstrated that sequential cleaning solutions, involving acid for inorganic foulants, alkaline for organic foulants, and disinfectants for microbial fouling could achieve a better cleaning effect than a single solution [32]. Thus, it is highly recommended for future studies to explore the potential of adjusting the cleaning protocols and using FA in conjugation with other cleaning agents to achieve better cleaning effects. Also, although living cells, reflected by ATP levels in this study, are the major contributor, some dead cells might also play a role in the biofouling process [33]. In light of this, future studies are highly recommended to investigate the detailed contribution of FA on dead cells attached to the membrane/biofouling layers. Besides, the morphology change of biofouling layers can be beneficial for the in-depth understanding of the impact of FA cleaning, which shall be investigated in the future.

Moreover, ammonia (NH_3) has been considered a promising hydrogen carrier due to its high hydrogen content and ease of liquefaction under mild conditions [34]. However, the production and collection/separation of ammonia from anaerobic digestion systems are still challenging and energy/chemical-consuming, limiting its current application as a hydrogen carrier [35–37]. In the future, the application of ammonia from anaerobic digestion systems might become more versatile when the production/collection technology for ammonia from the anaerobic digestion process becomes more economically feasible. Finally, the examination of FA's impact on membrane durability holds paramount importance for the future application of this technology, making it a highly recommended area for further research.

5. Conclusions

In this study, we investigated the effects of FA on the removal of biofouling on RO membranes. A series of soak cleaning and cross-flow cleaning tests were performed using four fouled RO membranes (M1-M4) from full-scale MWRPs. The following conclusions can be drawn:

- In soak cleaning tests of M1, FA solution of 65–560 mg NH_3–N/L achieved ATP removal by 32–75 %, achieved protein removal by 18–47 %, and achieved polysaccharides removal by 31–74 % from membrane surfaces. The cleaning effects were positively correlated with the FA concentration ($R > 0.9$, $p < 0.05$).

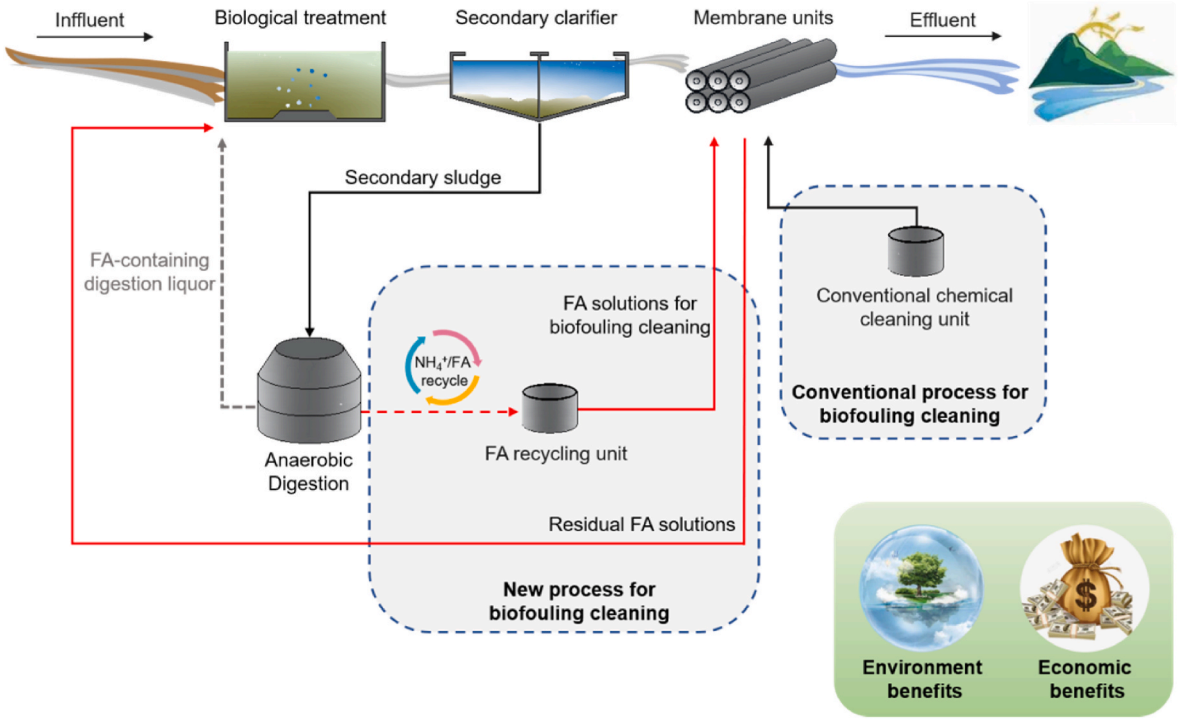

Fig. 8. A "closed-loop" concept in a MWRP based on the proposed FA cleaning method.

- In cross-flow cleaning tests of M2-M4, FA solution of 310–560 mg NH_3–N/L removed the ATP by 82–100 %, removed protein by 58–87 %, and removed polysaccharides by 68–100 % from membrane surfaces. FA solution also significantly increased the membrane permeability by 8–16 %. The cleaning effects were positively correlated with the FA concentrations ($R > 0.9$, $p < 0.05$). Additionally, a properly increased cleaning frequency and higher FA concentration are good strategies for biofouling control and recovering the performance of RO membranes.
- For both soak cleaning tests of M1 and cross-flow cleaning tests of M2-M4, the cleaning effects of FA solution (310–560 mg NH_3–N/L, pH = 8.9) were significantly higher than the conventional NaOH cleaning (pH = 11.0). However, only the FA solution of 560 mg NH_3–N/L (pH = 8.9) achieved comparable performance to the conventional EDTA cleaning.
- FA cleaning is a cost-effective method for biofouling removal RO applications with minimized environmental footprints.

CRediT authorship contribution statement

Zehao Zhang: Conceptualization, Data curation, Methodology, Resources, Writing – original draft. **Xuan Li:** Data curation, Supervision, Writing – review & editing. **Huan Liu:** Conceptualization, Formal analysis, Visualization. **Ting Zhou:** Investigation, Validation. **Zhenyao Wang:** Writing – review & editing. **Long D. Nghiem:** Resources, Writing – review & editing. **Qilin Wang:** Funding acquisition, Project administration, Supervision, Writing – review & editing.

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.

Data availability

No data was used for the research described in the article.

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References

[1] G. Gopi, G. Arthanareeswaran, A.F. Ismail, Perspective of renewable dalination by using membrane distillation, Chem. Eng. Res. Des. 144 (2019) 520–537.
[2] E. Filloux, J. Wang, M. Pidou, W. Gernjak, Z. Yuan, Biofouling and scaling control of reverse osmosis membrane using one-step cleaning-potential of acidified nitrite solution as an agent, J. Membr. Sci. 495 (2015) 276–283.
[3] A. Møllebjerg, R.L. Meye, Biofouling control in water filtration systems, in: Antibiofilm Strategies: Current and Future Applications to Prevent, Control and Eradicate Biofilms, Springer International Publishing, 2022, pp. 521–551.
[4] S.S. Shenvi, A.M. Isloor, A.F. Ismail, A review on RO membrane technology: developments and challenges, Desalination 368 (2015) 10–26.
[5] L. Zheng, C. Zhang, S. Kang, C. Li, D. Hou, S. Wu, J. Wang, Y. Wei, Insight into the microbial distribution and succession and biofouling mechanism in membrane distillation for desulfurization wastewater treatment, Chem. Eng. J. 428 (2022) 131097.
[6] T. Yu, L. Meng, Q.-B. Zhao, Y. Shi, H.Y. Hu, Y. Lu, Effects of chemical cleaning on RO membrane inorganic, organic and microbial foulant removal in a full-scale plant for municipal wastewater reclamation, Water Res. 113 (2017) 1–10.
[7] H.C. Flemming, Biofouling in water systems - cases, causes and countermeasures, Appl. Microbiol. Biotechnol. 59 (6) (2002) 629–640.
[8] R.A. Al-Juboori, T. Yusaf, Biofouling in RO system: mechanisms, monitoring and controlling, Desalination 302 (2012) 1–23.
[9] M. Jafari, M. Vanoppen, J.M.C. vanAgtmaal, E.R. Cornelissen, J.S. Vrouwenvelder, A. Verliefde, M.C.M. van Loosdrecht, C. Picioreanu, Cost of fouling in full-scale reverse osmosis and nanofiltration installations in The Netherlands, Desalination 500 (2021) 114865.
[10] M. Al-Abri, B. Al-Ghafri, T. Bora, S. Dobretsov, J. Dutta, S. Castelletto, L. Rosa, A. Boretti, Chlorination disadvantages and alternative routes for biofouling control in reverse osmosis desalination, NPJ Clean Water 2 (1) (2019) 2.
[11] S. Jamaly, N.N. Darwish, I. Ahmed, S.W. Hasan, A short review on reverse osmosis pretreatment technologies, Desalination 354 (2014) 30–38.
[12] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination-Development to date and future potential, J. Membr. Sci. 370 (1–2) (2011) 1–22.
[13] S. Jiang, Y. Li, B.P. Ladewig, A review of reverse osmosis membrane fouling and control strategies, Sci. Total Environ. 595 (2017) 567–583.
[14] A. Al-Amoudi, R.W. Lovitt, Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency, J. Membr. Sci. 303 (1–2) (2007) 4–28.
[15] Q. Wang, A roadmap for achieving energy-positive sewage treatment based on sludge treatment using free ammonia, ACS Sustain. Chem. Eng. 5 (11) (2017) 9630–9633.
[16] H. Liu, X. Li, Z. Zhang, L.D. Nghiem, L. Gao, Q. Wang, Q. Semi-continuous anaerobic digestion of secondary sludge with free ammonia pretreatment: focusing on volatile solids destruction, dewaterability, pathogen removal and its implications, Water Res. 202 (2021) 117481.
[17] Z. Zhang, X. Li, H. Liu, L. Gao, Q. Wang, Free ammonia pretreatment enhances the removal of antibiotic resistance genes in anaerobic sludge digestion, Chemosphere 279 (2021) 130910.
[18] A.C. Anthonisen, R.C. Loehr, T.B.S. Prakasam, E.G. Srinath, Inhibition of nitrification by ammonia and nitrous acid, J. Water Pollut. Control Fed. (1976) 835–852.
[19] A.M. Mustafa, X. Chen, H. Lin, K. Sheng, Effect of ammonia concentration on hythane (H2 and CH4) production in two-phase anaerobic digestion, Int. J. Hydrogen Energy 44 (2019) 27297–27310.
[20] W. Wei, X. Zhou, D. Wang, J. Sun, Q. Wang, Free ammonia pre-treatment of secondary sludge significantly increases anaerobic methane production, Water Res. 118 (2017) 12–19.
[21] D. Kim, S. Jung, J. Sohn, H. Kim, S. Lee, Biocide application for controlling biofouling of SWRO membranes - an overview, Desalination 238 (1–3) (2009) 43–52.
[22] K. Martinelle, L. Häggström, Mechanisms of ammonia and ammonium ion toxicity in animal cells: transport across cell membranes, J. Biotechnol. 30 (3) (1993) 339–350.
[23] Z. Wang, J. Ma, C.Y. Tang, K. Kimura, Q. Wang, X. Han, Membrane cleaning in membrane bioreactors: a review, J. Membr. Sci. 468 (2014) 276–307.
[24] H.C. Flemming, J. Wingender, U. Szewzyk, P. Steinberg, S.A. Rice, S. Kjelleberg, Biofilms: an emergent form of bacterial life, Nat. Rev. Microbiol. 14 (9) (2016) 563–575.
[25] C. Zhang, Y. Qin, Q. Xu, X. Liu, Y. Liu, B.J. Ni, Q. Yang, D. Wang, X. Li, Q. Wang, Free ammonia-based pretreatment promotes short-chain fatty acid production from waste activated sludge, ACS Sustain. Chem. Eng. 6 (7) (2018) 9120–9129.
[26] N.A. Weerasekara, K.H. Choo, C.H. Lee, Hybridization of physical cleaning and quorum quenching to minimize membrane biofouling and energy consumption in a membrane bioreactor, Water Res. 67 (2014) 1–10.
[27] W.S. Ang, A. Tiraferri, K.L. Chen, M. Elimelech, Fouling and cleaning of RO membranes fouled by mixtures of organic foulants simulating wastewater effluent, J. Membr. Sci. 376 (1–2) (2006) 196–206.
[28] N.H. Ab Hamid, L. Ye, D.K. Wang, S. Smart, E. Filloux, T. Lebouteiller, X. Zhang, Evaluating the membrane fouling formation and chemical cleaning strategy in forward osmosis membrane filtration treating domestic sewage, Environ. Sci. Water Res. Technol. 4 (12) (2018) 2092–2103.
[29] Q. Wang, L. Ye, G. Jiang, P.D. Jensen, D.J. Batstone, Z. Yuan, Free nitrous acid (FNA)-Based pretreatment enhances methane production from waste activated sludge, Environ. Sci. Technol. 47 (20) (2013) 11897–11904.
[30] Q. Wang, H. Duan, W. Wei, B.J. Ni, A. Laloo, Z. Yuan, Achieving stable mainstream nitrogen removal via the nitrite pathway by sludge treatment using free ammonia, Environ. Sci. Technol. 51 (17) (2017) 9800–9807.
[31] T. Yu, L. Meng, Q.B. Zhao, Y. Shi, H.Y. Hu, Y. Lu, Effects of chemical cleaning on RO membrane inorganic, organic and microbial foulant removal in a full-scale plant for municipal wastewater reclamation, Water Res. 113 (2017) 1–10.
[32] M.C. Hacıfazlıoğlu, İ. Parlar, T.Ö. Pek, N. Kabay, Evaluation of chemical cleaning to control fouling on nanofiltration and reverse osmosis membranes after desalination of MBR effluent, Desalination 466 (2019) 44–51.
[33] Y. Zhao, Y. Gu, B. Liu, Y. Yan, C. Shan, J. Guo, S. Zhang, C.D. Vecitis, G. Gao, Pulsed hydraulic-pressure-responsive self-cleaning membrane, Nature 608 (2022) 69–73.
[34] K.E. Lamb, M.D. Dolan, D.F. Kennedy, Ammonia for hydrogen storage; A review of catalytic ammonia decomposition and hydrogen separation and purification, Int. J. Hydrogen Energy 44 (2019) 3580–3593.
[35] S.A.A. Rawoof, P.S. Kumar, D.-V.N. Vo, S. Subramanian, Sequential production of hydrogen and methane by anaerobic digestion of organic wastes: a review, Environ. Chem. Lett. 19 (2021) 1043–1063.
[36] K. Chetty, S. Xie, Y. Song, T. McCarthy, U. Garbe, X. Li, G. Jiang, Self-healing bioconcrete based on non-axenic granules: a potential solution for concrete wastewater infrastructure, J. Water Process Eng. 42 (2021) 102139.
[37] Q. Wang, W. Wei, Y. Gong, Q. Yu, Q. Li, J. Sun, Z. Yuan, Technologies for reducing sludge production in wastewater treatment plants: state of the art, Sci. Total Environ. 587 (2017) 510–521.