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Cleaning and regeneration of irreversibly fouled and discarded reverse osmosis membranes: method and mechanism

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ABSTRACT

The regeneration and recycling of discarded membranes are of great importance for extending the membrane lifespan, and thus, they are crucial to achieve the economic feasibility of the industrial scale membrane process. In this research, an end-of-life reverse osmosis (RO) membrane was analyzed, and a cleaning protocol and mechanism were investigated. Several chemical agents were optimized, including acid (H_2SO_4), base (NaOH), metal-chelating agents (Na_2-EDTA), surfactants (SDS), oxidizing agents ($KMnO_4$), and their combinations. The results showed that good regeneration of the membrane can be achieved after the membrane was cleaned by a $KMnO_4$ + NaOH solution, followed by $NaHSO_3$. To achieve a high cleaning efficiency, the effects of oxidant concentration, cleaning time, and solution pH were studied. The optimum cleaning protocol was a 0.5% (w/v) $KMnO_4$ + 0.2% (w/v) NaOH solution, followed by $NaHSO_3$; and the optimum cleaning time was 60 min, allowing for a cleaning efficiency of 5.87. The experimental results showed that the cleaning procedure could be divided into three stages and that both the $KMnO_4$ concentration and pH can control the cleaning stage. Based on economic feasibility, controlling the solution pH with low $KMnO_4$ concentrations could lead to the transformation of membranes into target recycled membranes (such as reverse osmosis, nanofiltration, and ultrafiltration).

Keywords: Discarded reverse osmosis membrane; Potassium permanganate; Chemical cleaning; Membrane recycling

1. Introduction

Increasing global demand for potable water has raised the need for wastewater reclamation and reuse to address water shortages. Reclamation of textile wastewater is an available option to mitigate such water shortages. The textile industry is characterized by very high water consumption and high discharge of wastewater with high chemical oxygen demand (COD), strong color, high hardness, high salinity, and low biodegradability, leading to severe environmental pollution [1]. Due to these characteristics of textile wastewater, the contaminant concentrations of membrane bioreactors (MBRs) effluents are difficult to meet the environmentally permissible levels and should be followed by advanced treatments [2]. Thus, the reverse osmosis (RO) process has been applied widely in advanced wastewater treatment of MBRs effluents for indirect potable use over the past few decades [3]. However, membrane fouling results in increased membrane resistance, productivity decline, increased energy consumption, and shortened membrane lifespan [4]; thus, membrane fouling has been one of the largest limiting factors to the widespread application of RO process.

Membrane fouling can be divided into reversible and irreversible fouling according to the attachment strength of the foulants to the membrane surface [5]. Reversible fouling is caused by slight attachment of foulants, which can be easily removed by strong shear force or washing (physical cleaning) [6]. Irreversible fouling is caused by strongly attached foulants, such as cake, gel and biofilm,

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and pore blocking and plugging [7,8]. It is difficult to remove irreversible foulants by physical methods in most cases; hence, the use of a biological, enzymatic, or physicochemical cleaning is needed. RO membranes with severely irreversible foulants are reported to be reused, recycled, or abandoned as waste disposal after long-term operation. Scarce research has been reported in the literature regarding discarded RO membrane recycling. Alternative routes to the end-of-life RO membrane disposal are shown in Fig. 1. Studies have been performed that involved treatment of discarded RO membranes as RO membranes, nanofiltration (NF) membranes, and ultrafiltration (UF) membranes with a chemical cleaning process [9–11]. Pacheco et al. [10] introduced the transformation of end-of-life RO membranes into NF and UF membranes using a NaOCl solution applied over different exposure times. Silva et al. [9] investigated whether tannic acid was an efficient rejuvenating agent for recycling discarded polyamide membranes for RO processes. Some studies [11,12] investigated the transformation of discarded RO membranes into UF membranes. Among the chemical agents used in the experiment, $KMnO_4$ was identified as the most successful agent. Research efforts have been focused on transforming the discarded RO membranes into recycled membranes. However, it is necessary to investigate how to control the reaction conditions that transform discarded RO membranes into target recycled membranes.

The discarded RO membranes may be secondarily cleaned and recycled, thereby decreasing the treatment cost and realizing the effective utilization of resources. Hence, effective cleaning procedures and agents are required. Chemical cleaning agents are commonly used to dissolve and remove the majority of foulants deposited on membrane surfaces [13,14]. Foulants in the RO process have been reported to be of four major types: biofouling [15], organic fouling [16], inorganic scaling [17], and colloidal fouling [18]. Membrane cleaning has been widely used to remove foulants, and the cleaning process should be tailored to target membrane–foulant system. Typical chemicals used for membrane cleaning include acid solutions, alkaline solutions, metal-chelating agents, surfactants, and oxidizing agents [19–24]. Acid cleaning is an effective means to remove precipitated salts through hydrolysis and chelation [25]. Alkaline solutions remove organic and microbial foulants by hydrolysis and solubilization [26]. Metal-chelating agents effectively remove divalent cations [27], and surfactants can solubilize micro-molecules by forming micelles around them [19]. For more serious organic foulants, oxidizing agents are found to have higher instant cleaning rates and overall cleaning effectiveness [28]. Optimizing the use of cleaning agents and operating conditions is necessary to maximize the cost-efficiency of the process and minimize the amount of environmental pollution.

The objective of this study is to find types of effective chemical agents and the optimum conditions for cleaning the severely irreversible foulants deposited on RO membranes. The chemical cleaning agents such as sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), ethylene diamine tetra-acetate (Na_2-EDTA), sodium dodecyl sulfate (SDS), and potassium permanganate ($KMnO_4$) were selected as models for alkaline solutions, acid solutions, metal-chelating agents, surfactants, and oxidizing agents, respectively. In addition, the operating conditions for cleaning, such as agent concentration, solution pH, and operating time, were optimized. The results of this study are expected to provide useful information on the chemical cleaning procedures of discarded RO membranes fouled by severely irreversible foulants after the secondary treatment of textile wastewater.

2. Materials and methods

2.1. Membranes and water samples

2.1.1. RO membrane samples

The fouled RO membrane (TM720D-400, TBMC) had been used continuously for 6 years and then collected and cleaned for secondary recycled use in a dyeing wastewater recycling facility located at Tongxiang, Zhejiang Province, China.

The membrane is a thin film of composite polyamide cast on a thicker supporting layer of polysulfone. According to the manufacturer, the new membrane tolerates a pH range of 1 to 13, a maximum temperature of 45°C, and a chlorine tolerance lower than 0.1 mg/L; the average salt rejection is 99.8%.

2.1.2. Water samples

RO influent, RO permeates, and RO concentrates from the MBR-RO process were collected and loaded into amber

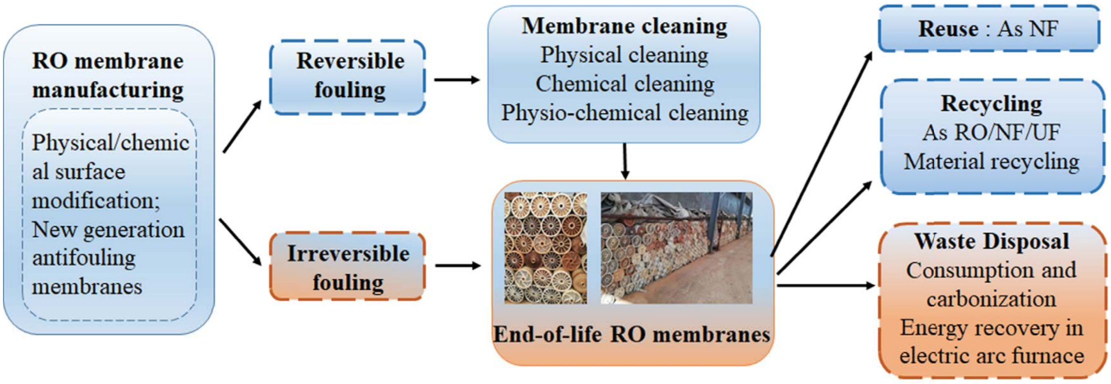

Fig. 1. Alternative routes to the end-of-life RO membranes disposal.

glass bottles. All water samples were kept in ice and delivered to the laboratory. The water samples were filtered through a 0.45-μm membrane (ANPLE Laboratory Technologies Shanghai Inc.) to minimize the effects of suspended particles and then stored at 4°C and analyzed within 48 h. The key properties of the water samples are shown in Table 1.

2.2. Bench-scale RO membrane system

A bench-scale cross-flow batch experimental setup was used to determine the membrane flux and salt rejection rates, as shown in Fig. 2. This system is equipped with a membrane cell, valves, pumps, pressure gauges, flow gauges, and two water tanks. The dimensions of the cell are 300 mm long, 110 mm wide, and 80 mm deep. The valves control the flow and the pressure. Two gear pumps (Weittpump, 701120, China) were used to feed the water sample into the membrane module. The transmembrane pressure (TMP) levels were monitored based on the pressure differences between the inlet and outlet pressure gauges (YB-131, China). Cross-flow filtrations were conducted under a constant pressure of 0.6 MPa.

Before and after cleaning, the water flux (J, L/m^2·h) of the membrane was measured by passing distilled water through the membrane. The flux through the cake and the membrane may be described by Darcy's law [27]:

$$J = \frac{\Delta P}{\mu \Sigma R} = \frac{1}{A} \times \frac{\Delta V}{\Delta t} \tag{1}$$

2.3. Cleaning agents

The chemical cleaning agents used were potassium permanganate ($KMnO_4$) as an oxidative agent, sodium hydroxide (NaOH) as an alkaline agent, sulfuric acid (H_2SO_4) as an acid agent, certified grade disodium ethylene diamine tetra-acetate (Na_2-EDTA) as a metal-chelating agent, and certified grade sodium dodecyl sulfate (SDS) as an anionic surfactant. All agents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification. The stock chemical solutions were prepared freshly by dissolving each chemical in deionized (DI) water. The oxidative solution is prepared in an alkaline environment before the cleaning process.

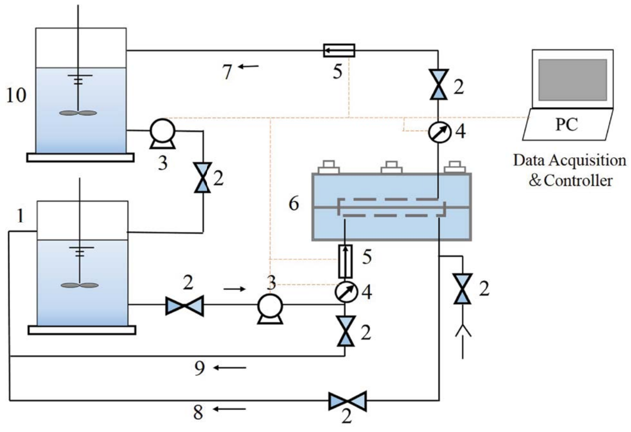

Fig. 2. Schematic of the reverse osmosis experimental setup.

2.4. Cleaning experiments

The cleaning experiments adopted immersion-type cleaning in liter beakers. The fouled membranes were immersed in solutions for a period of time at 45°C. At the end of the cleaning process, the membranes were rinsed with excess solution of aqueous sodium bisulfite ($NaHSO_3$) and DI water to flush out the chemical residue. Next, the flux of the membrane was tested at the condition of Section 2.2. The effects of the solution component, concentration, and cleaning time on the cleaning efficiency were investigated. The cleaning efficiency (η) is evaluated as follows [19,29,30]:

$$\eta = \frac{J_c}{J_f} \tag{2}$$

where J_c and J_f are the flux through a cleaned membrane and a fouled membrane (L/m^2·h), respectively.

2.5. Analysis methods

Turbidity was measured by a HACH DR3900 turbidity meter (USA). Conductivity was measured by an INESA DDSJ-308F conductivity meter (Shanghai Electronics Science Instrument Co. Ltd). Total organic carbon (TOC) and total nitrogen were measured by a Shimadzu TOC-5000A analyzer. pH was measured by an E-201-C pH meter (Shanghai Electronics Science Instrument Co. Ltd). COD was measured by a HACH DRB200 COD meter (USA). The surface morphologies of fouled RO membranes and cleaned RO membranes were observed using a scanning electron microscope (Phenom pro scanning electron microscopy (SEM), the Netherlands). All membranes were dried at 80°C and then coated with a conductive sputtered gold layer before analysis. Elemental microanalyses of the deposits on the RO membrane surfaces fouled by MBR effluents of textile wastewater were investigated by scanning electron microscopy-energy dispersive spectrometry (SEM-EDS). The concentrations of phosphorus, calcium, silica, iron, manganese, and aluminum were determined by inductively coupled plasma emission spectrometry (ICP-AES, Agilent). Fourier transform infrared spectroscopy (FTIR) (Thermo Scientific Nicolet iS5, USA) analysis was performed on cleaned membranes. The spectra were recorded in transmittance mode in the range of 400 to 4,000 cm^{-1}.

The excitation emission matrix (EEM) fluorescence spectroscopy of the water samples of RO influent, RO effluent, and RO concentration was analyzed using a fluorescence spectrophotometer (F-7000, Hitachi, Japan). For analysis, the excitation wavelengths ranged from 240 to 450 nm, with 5 nm increments, and the emission wavelength ranged from 280 to 550 nm, with 1 nm increment. The EEM of ultrapure water from a Milli-Q instrument (Millipore, USA) was used as a blank sample for limiting Raman scattering.

The surface roughness was characterized by an SPM-9500J3 atomic force microscope (AFM) (Shimadzu, Kyoto, Japan) in contact mode. The silicon probes (AN-CSC01, Appnano, USA) were coated with a 30-nm-thick aluminum layer. The membrane surface roughness was characterized by the root mean square (RMS), which is the deviation of the peaks and valleys from the mean plane [29].

3. Results and discussion

3.1. Fouled RO membrane deposits

To choose the appropriate cleaning agents and explore the cleaning mechanisms, elemental microanalyses of the deposits of the RO membrane surfaces fouled by MBRs effluents of textile wastewater were investigated by SEM-EDS, as shown in Fig. 3. The fouled RO membrane deposits are categorized into two types: inorganic deposits and organic deposits. The results showed that inorganic deposits on RO membranes comprised mainly of Ca, Fe, S, Si, Al, and Mg. Ca was the most abundant inorganic component, indicating that the formation of scaling on the fouled RO membrane was mainly composed of calcium carbonate and sulfates. The Fe content in the deposit was high, whereas it was low in the RO influent (as shown in Table 1), indicating that Fe could deposit on the RO membrane much more easily than other elements. Similar results were reported by Tang et al. [31]. Moreover, some ionic species were found to play important roles in the evolution of membrane fouling, and should not be disregarded, such as the co-presence of silica and organic matter that seems to have synergetic effects that cause severe membrane fouling in RO [4]. Calcium ions tend to promote intra- and intermolecular bridge formation and aggregation of organic matter [32].

The EEM spectra for dissolved organic matter (DOM) in the RO influent and effluent are presented in Fig. 4. The EEM spectrum was divided into five regions (Region I to Region V) based on the characteristics of each type of organic matters [33–35]. Regions I and II (Ex < 250 nm; Em < 380 nm)

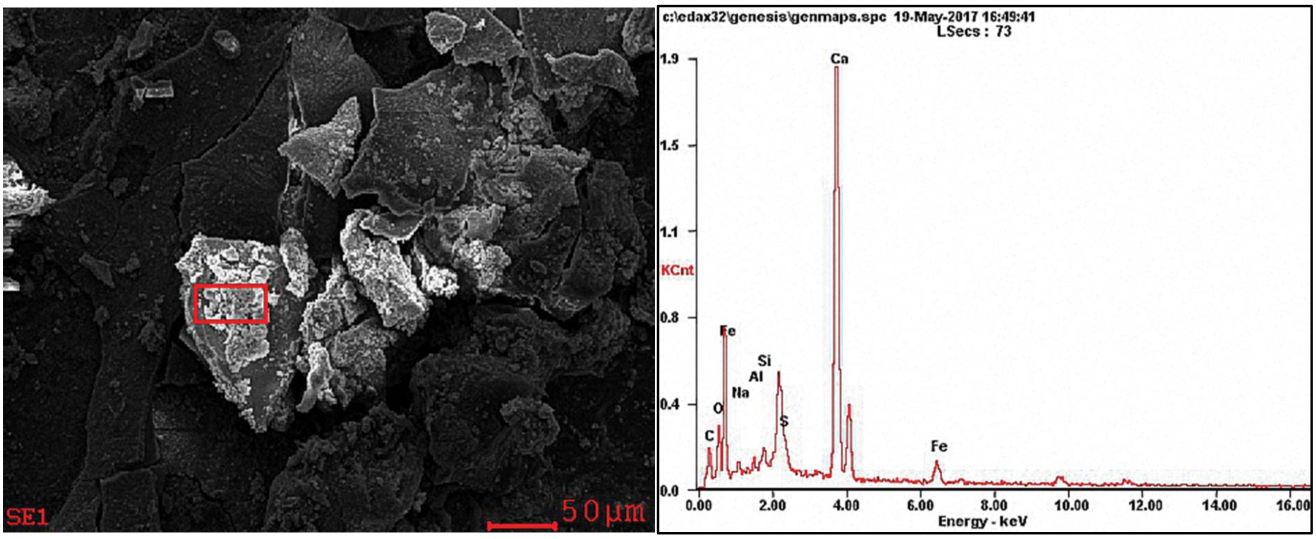

Fig. 3. SEM-EDS of the active layer of the fouled RO membrane.

Table 1
Characteristic parameters of RO influent, RO permeates, and RO concentrates

Parameter	RO influent	RO permeates	RO concentrates
pH	8.45 ± 0.02	8.67 ± 0.01	8.43 ± 0.01
COD (mg/L)	211 ± 2	107 ± 2	696 ± 4
TOC (mg/L)	176 ± 4	51 ± 2	323 ± 3
TN (mg/L)	19.48 ± 1	2.02 ± 0.4	83.40 ± 2
Conductivity (mS/cm)	21.5 ± 0.13	9.31 ± 0.14	35.84 ± 0.74
Turbidity (NTU)	1.54 ± 0.12	0.63 ± 0.04	188 ± 3
Aluminum (mg/L)	8.713 ± 0.06	0.123 ± 0.01	3.659 ± 0.03
Calcium (mg/L)	37.124 ± 0.04	4.732 ± 0.02	39.436 ± 0.02
Iron (mg/L)	6.426 ± 0.01	0.034 ± 0.0003	3.233 ± 0.04
Potassium (mg/L)	22.622 ± 0.5	14.109 ± 0.2	40.152 ± 0.7
Magnesium (mg/L)	5.510 ± 0.2	0.939 ± 0.001	6.767 ± 0.33
Silica (mg/L)	8.374 ± 0.01	4.910 ± 0.06	11.260 ± 0.05
Copper (mg/L)	0.458 ± 0.03	0.022 ± 0.0017	0.284 ± 0.01
Sodium (mg/L)	3465 ± 3.1	686 ± 5.7	3,650 ± 14.8

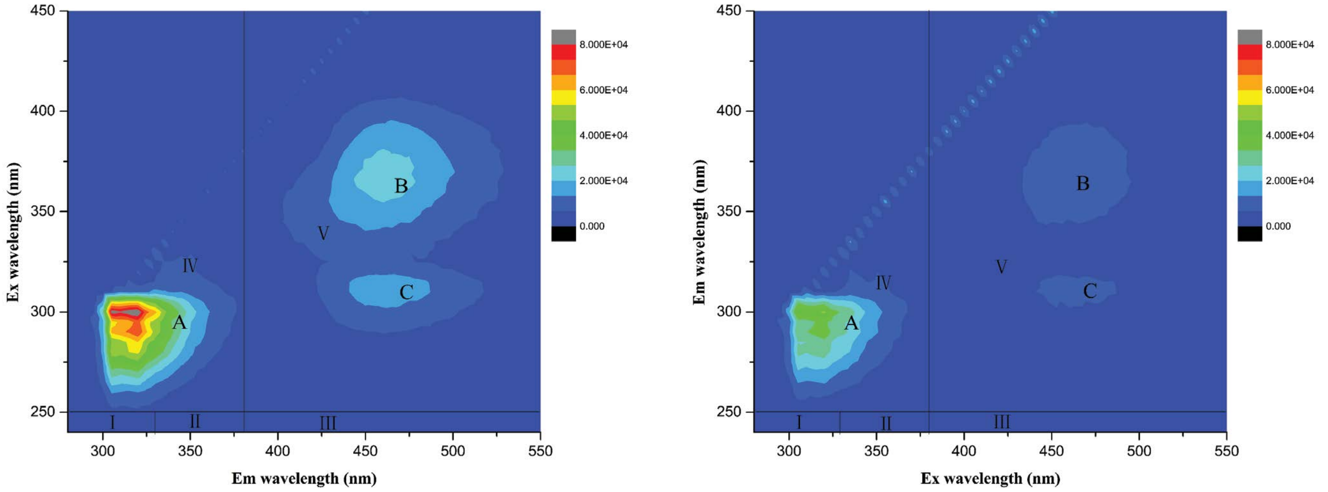

Fig. 4. Fluorescence EEM spectra of DOM in RO influent and effluent.

indicate aromatic protein-like organic matters; Region III (Ex < 250 nm; Em > 380 nm) and Region V (Ex > 250 nm; Em > 380 nm) account for fulvic-like and humic-like organic matters, respectively; and Region IV (Ex > 250 nm; Em < 380 nm) represents microbial-derived organic matters. Peak A is associated with microbial-derived organic matters; Peak B and Peak C are both associated with humic-like organic matters. Peak A, Peak B, and Peak C correspond to the apparent fluorescence intensity in the EEM spectra of the RO influent and the weak fluorescence intensity in the EEM spectra of the RO effluent. The results showed that organic deposits on RO membranes mainly consisted of large amounts of humic-like substances and microbial-derived organic substances. From the results of SEM-EDS of the membrane surface and EEM of the RO process influent and effluent, we can infer that organic matter and some ionic species, such as calcium ions, silica, and ion, interact to cause severe membrane fouling.

3.2. Optimization of chemical agents

To examine the optimization of cleaning by several kinds of chemical cleaning agents, cleaning efficiencies (η) and salt rejections of membranes under different cleaning agents were investigated. The cleaning agents used were (1) 0.5% (w/v) NaOH, (2) 0.5% (w/v) H_2SO_4, (3) 0.5% (w/v) Na_2-EDTA, (4) 0.5% (w/v) SDS, and (5) 0.5% (w/v) $KMnO_4$/0.2% (w/v) NaOH.

As shown in Fig. 5, the salt rejections ($MgSO_4$) of cleaned membranes ranged from 45.34% to 50.05%. The salt rejection of the fouled membrane is 56.7% ± 0.9%. This result suggests that the fouled RO membrane was damaged to some extent because of the long service time. There was no significant drop of salt rejections after chemical cleaning, indicating that the membrane surface was not damaged seriously by the chemical agents used in this study. For cleaning efficiencies (η), more effective cleaning led to higher η. The results indicate that H_2SO_4 exhibited a minimal efficiency for the removal of deposited foulants from the membrane surface. The value of η for SDS was higher than that of H_2SO_4. Na_2-EDTA showed a similar behavior to that of SDS. The optimum chemical agents were the combination of the two agents ($KMnO_4$ + NaOH) and NaOH, and the oxidant solution had higher cleaning efficiency. This result is consistent with the observation from SEM, as shown in Fig. 6.

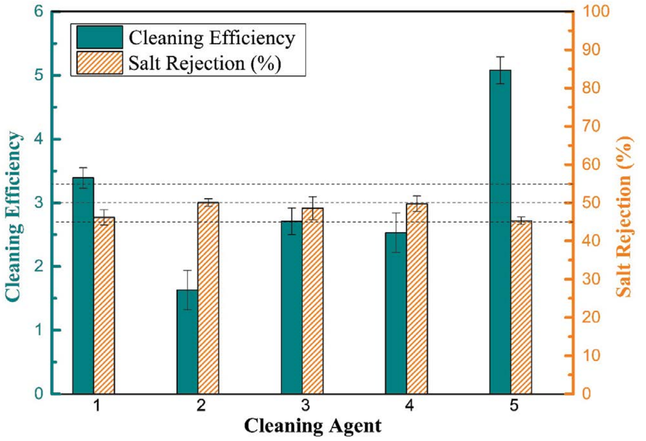

Fig. 5. Cleaning efficiencies and salt rejections of (1) 0.5% (w/v) NaOH, (2) 0.5% (w/v) H_2SO_4, (3) 0.5% (w/v) Na_2-EDTA, (4) 0.5% (w/v) SDS, and (5) 0.5% (w/v) $KMnO_4$/0.2% (w/v) NaOH on fouled membranes. Cleaning was performed for 1 h at 0.6 MPa, and the temperature during cleaning was maintained at 45°C.

To further analyze the inorganic matter and organic matter extracted in the chemical cleaning with the five cleaning agents, the results of ICP-AES and TOC analysis are exhibited in Table 2. The amounts of inorganic ions extracted were normalized to the membrane area. TOC analysis was not performed for Na_2-EDTA, because Na_2-EDTA is a kind of organic matter and will cause significant interference. As shown in Table 2, calcium and iron were extracted the most by H_2SO_4. Aluminum, silica, magnesium, and organic matter were notably removed by NaOH and $KMnO_4$/NaOH. The cleaning efficiencies of $KMnO_4$/NaOH and NaOH were greater than that of H_2SO_4, as shown in Fig. 5. Hence, pollutants that could be removed easily by NaOH and $KMnO_4$/NaOH but removed with difficulty by H_2SO_4 reflect differences in

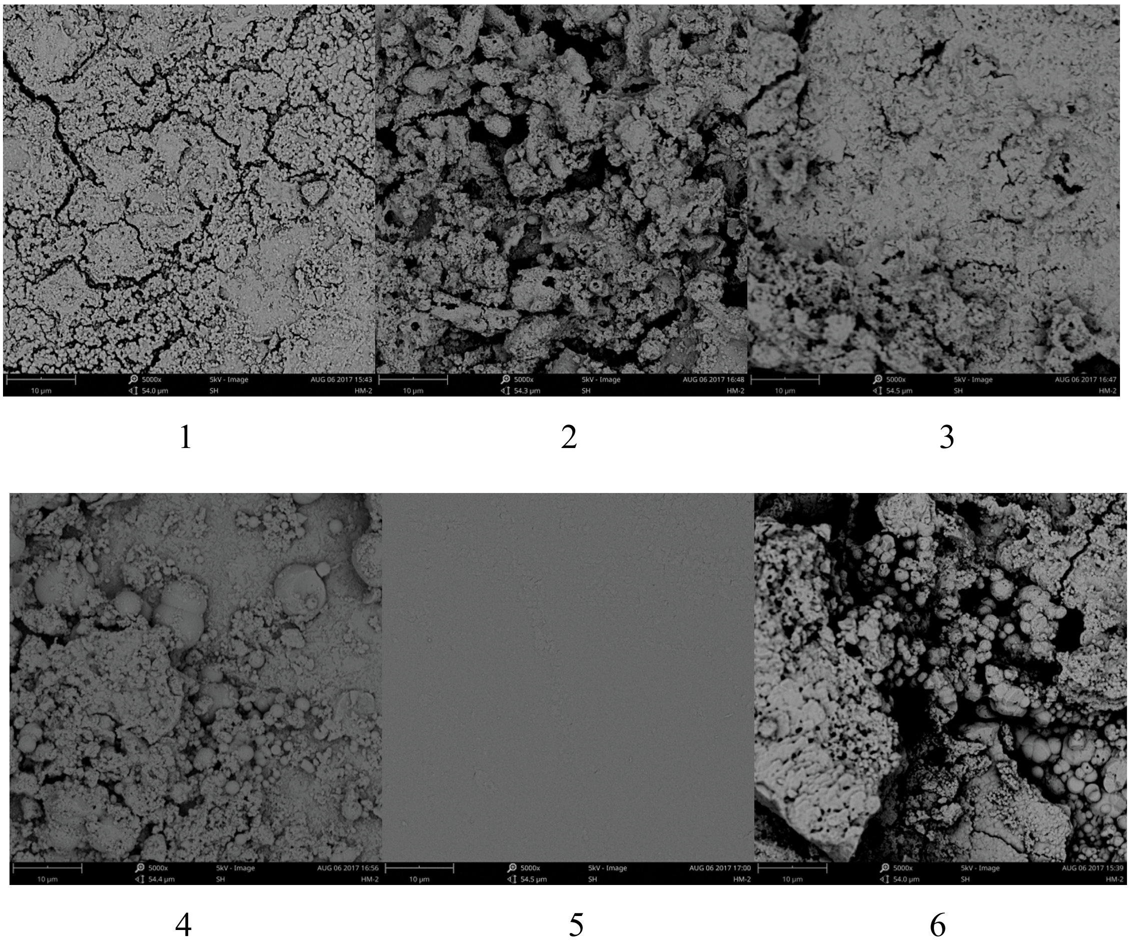

Fig. 6. SEM images of cleaned membranes: (1) 0.5%(w/v) NaOH, (2) 0.5% (w/v) H_2SO_4, (3) 0.5% (w/v) Na_2-EDTA, (4) 0.5% (w/v) SDS, (5) 0.5% (w/v) $KMnO_4$/0.2% (w/v) NaOH, and (6) the fouled membrane.

Table 2
Concentrations of inorganic ions and TOC in different chemical cleaning agents

	NaOH	H_2SO_4	Na_2-EDTA	SDS	$KMnO_4$/NaOH
Calcium (mg/m^2)	198.533 ± 1.472	293.14 ± 0.153	233.825 ± 1.357	67.165 ± 1.667	214.025 ± 2.411
Iron (mg/m^2)	17.670 ± 0.456	113.819 ± 0.218	63.150 ± 0.013	5.574 ± 0.003	22.769 ± 1.635
Aluminum (mg/m^2)	11.371 ± 0.011	8.310 ± 0.007	13.589 ± 0.001	4.405 ± 0.006	19.823 ± 0.274
Silica (mg/m^2)	24.513 ± 1.140	3.217 ± 0.063	17.93 ± 1.121	7.791 ± 0.011	23.334 ± 0.341
Magnesium (mg/m^2)	56.377 ± 1.553	43.165 ± 0.301	44.017 ± 1.554	15.182 ± 0.272	53.665 ± 2.152
TOC (mg/L)	188.71 ± 0.249	28.47 ± 1.172	–	89.50 ± 5.157	246.17 ± 0.620

cleaning efficiency among the cleaning agents. This implies a substantial contribution of organic matter (especially humic-like substances and microbial-derived substances) and their coexistence with some ions, such as aluminum, silica, and magnesium, to the severe membrane fouling in this study.

The AFM images (Fig. 7) show that the roughness of the membrane surfaces was consistent with the SEM images (Fig. 6). The fouled membrane has the largest RMS (399 nm) because of the presence of foulants [36]. The RMS decreased to 172 nm after cleaning by 0.5% (w/v) NaOH, indicating the removal of foulants. The RMS was 22.7 nm when the chemical agents were 0.5% (w/v) $KMnO_4$/0.2% (w/v) NaOH. It was noted that $KMnO_4$ played an important role in the removal of foulants.

On the basis of these results, we concluded that membrane cleaning performed using 0.5% (w/v) $KMnO_4$/0.2% (w/v) NaOH solution for 1 h is most efficient and leads to higher η without fracturing membrane surface.

3.3. Optimization of the reaction conditions

3.3.1. Effects of concentration

The effects of the concentration of $KMnO_4$ were investigated, and the results are shown in Fig. 8(a). The cleaning

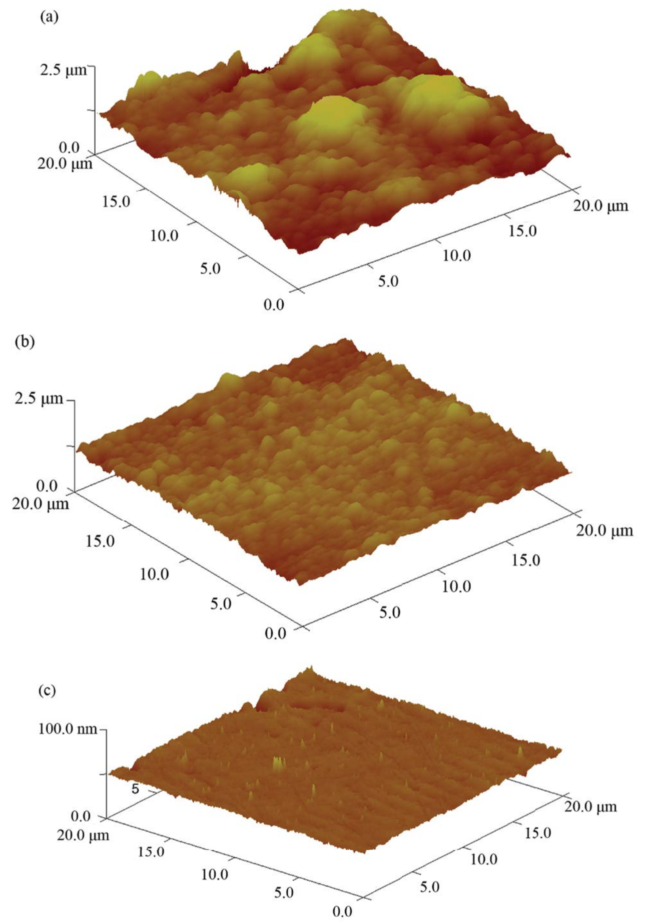

Fig. 7. AFM pictures of cleaned membranes: (a) the fouled membrane, (b) 0.5% (w/v) NaOH, and (c) 0.5% (w/v) $KMnO_4$/0.2% (w/v) NaOH.

procedure was using $KMnO_4$ + 0.2% (w/v) NaOH solution at a cleaning time of 50 min, followed by 0.5% (w/v) $NaHSO_3$. The value of η was apparently affected by the concentration of oxidants, with the value increasing as the concentration increased. The growth curve increased quickly, but rose more slowly as the concentration increased. The membrane surface may be damaged when the concentration of $KMnO_4$ exceeds a certain value (1% w/v) because of the sharp rise in the cleaned membrane flux and the reduction of salt rejection. This is because chemical agents used at higher concentrations could react with the membrane functional groups [11,37,38]. The optimum concentration of $KMnO_4$ was 0.5% (w/v), and η = 5.27 can be achieved at a cleaning time of 50 min. The effect of agent utilization is lower at higher dosages.

3.3.2. Effect of cleaning time

The effect of cleaning time on the efficiency and salt rejection of the RO membrane cleaning process at 0.5% (w/v) $KMnO_4$ + 0.2% (w/v) NaOH, followed by 0.5% (w/v) $NaHSO_3$, was examined, as shown in Fig. 8(b). The cleaning time is another crucial parameter that has a great impact on the operating costs [5]. By increasing the cleaning time from 20 to 60 min, η increased sharply, whereas it remained approximately constant at longer times (after 60 min). This behavior occurred because of the significant removal of the strongly adsorbed fouling materials in the early stages. Accordingly, the optimum cleaning time was 60 min, and the value of η can reach 5.87.

3.3.3. Effect of pH

Fig. 8(c) shows the impact of pH on the cleaning efficiency and salt rejection of RO membranes cleaned using 0.5% (w/v) $KMnO_4$ solution for 60 min. Apparently, the cleaning efficiency decreased with the increase of the pH from 2 to 12, indicating that the flux recovery rate of the fouled membrane in an acidic environment is higher than that in alkaline and neutral environments. This difference was caused by the higher oxidation–reduction potential of MnO_4^- in acidic solutions (E^0 = +1.51 V) than in neutral solutions (E^0 = +0.588 V) and alkaline solutions (E^0 = +0.564 V). The extent of foulant removal and membrane damage are different at different pH values. To investigate whether the chemical composition of the polyamide RO membrane surface is changed or not within a controlled cleaning time (60 min), FTIR spectra of membranes cleaned by $KMnO_4$ solutions at different pH values were employed, as shown in Fig. 9.

A broad band at approximately 3,100 cm^{-1} was assigned to the N–H stretching vibration (amide II) [37], and the adsorption band of the C=O stretching vibration was at 1,670 cm^{-1} (amide I). The peak at 1,542 cm^{-1} was assigned to the N–H bending vibration (amide II), and the peak at 1,610 cm^{-1} was assigned to the C=C stretching vibration of the benzene ring [39]. These four peaks are the characteristic absorption peaks that existed in the polyamide RO membrane [39]. Therefore, the peaks at 3,310, 1,679, 1,610, and 1,542 cm^{-1} were not observed on the membrane cleaned in an acidic environment, demonstrating that the active layer of the polyamide RO membrane was damaged. Similar results were reported in the literature [12]. $KMnO_4$ treatment degraded the active layer and increased the permeate flux at the expense of decreased salt rejection. The peaks were all observed on the membrane in the alkaline environment and were observed on some parts of the membrane cleaned in the neutral environment. It can be inferred that pH can control the cleaning degree of $KMnO_4$ chemical treatments of discarded RO membranes aimed at their reuse.

3.4. The cleaning mechanism

In the case of treated textile wastewater, reactive dyes, surfactants, and effluent organic matters (EfOMs) are the primary foulants causing RO flux decline through adsorption, covering, and plugging of the membrane surface and membrane pores [1,40–42]. Some ionic species (such as Ca^{2+} and Si^+) play an important role in the evolution of severe membrane fouling [4]. For the optimized cleaning agents used in this study, NaOH solution could clean the organic foulants by solution hydrolysis, thereby generating electrostatic interactions between the membrane and negatively charged foulants (such as anionic surfactant) [43,5]. $KMnO_4$ could reduce the molecular weight of organic matters and degrade the selective layer to improve the water permeate flux [12]. According to the changes in the membrane flux and

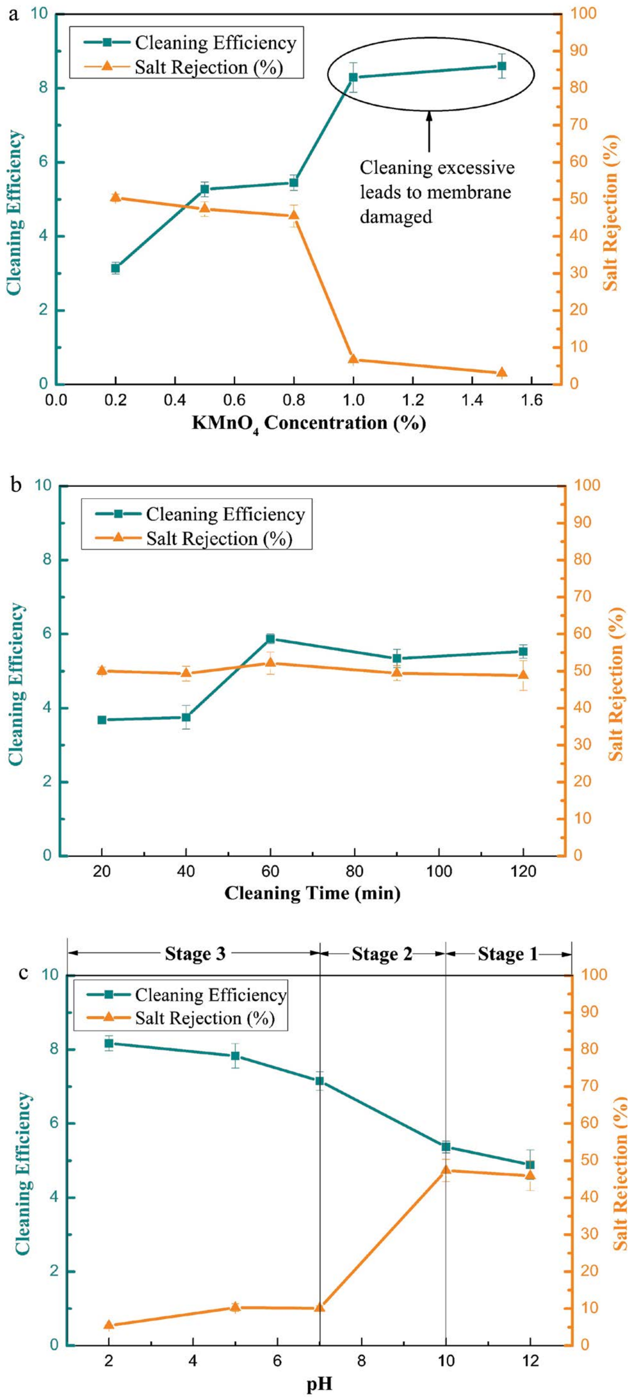

Fig. 8. Effect of (a) KMnO$_4$ concentration (% w/v), (b) cleaning time, (c) pH on the cleaning efficiency and salt rejection.

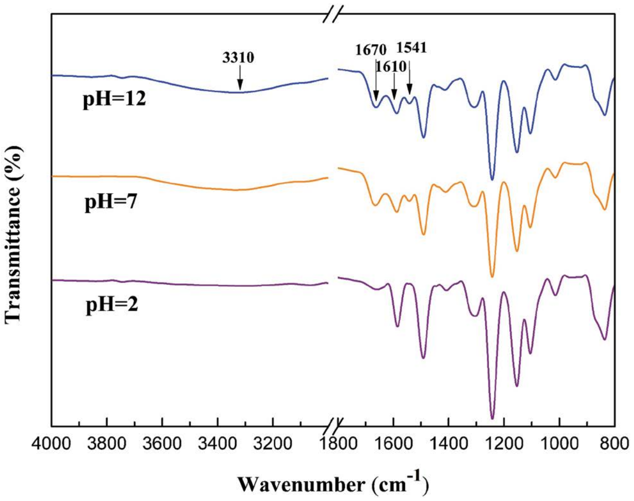

Fig. 9. FTIR spectra of the fouled RO membrane cleaned by KMnO$_4$ solution at different pH values.

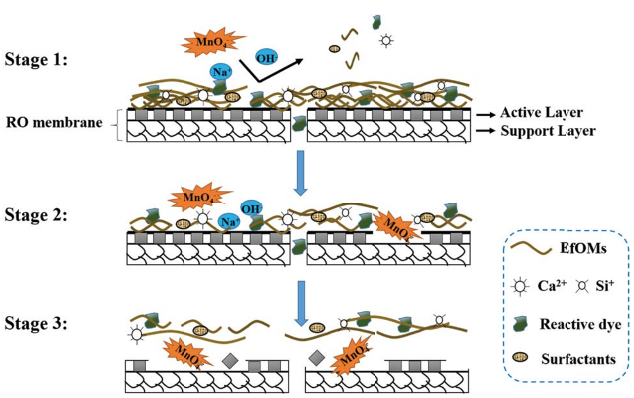

Fig. 10. Schematics of the cleaning mechanisms in the alkaline environment at 1% (w/v) KMnO$_4$ concentration for 2 h.

the salt rejection, as well as the applicable scope of the membrane flux, the cleaning procedure could be divided into three stages. Stage 1 is foulants removal stage. At this stage, with the removal of pollutants, the change in membrane flux was relatively stable, and the salt rejection remained approximately constant. There was no damage to the membrane surface. The flux of the recycled membrane is between the flux of RO membrane and that of the NF membrane. Stage 2 is mixed removal stage. In this stage, the foulants removal and selective degraded layer coexist simultaneously. At this stage, the rate of change of the membrane flux increased and the salt rejection decreased significantly. A large amount of pollutants was removed, and the selected layer was damaged to a certain extent. The flux of the recycled membrane is between the flux of NF membrane and that of the UF membrane. Stage 3 is selective layer degradation stage. In this stage, a large area of the selective layer is degraded. The changes in membrane flux and salt rejection were stable again. The discarded membrane can be recycled as an UF membrane. NaOH and KMnO$_4$ play a major role in the first two stages, while KMnO$_4$ plays a major role in Stage 3. Schematics of the cleaning mechanisms are presented in Fig. 10. The flux recovery rate of fouled membranes varies at different stages. On the basis of the experimental results, both the KMnO$_4$ concentration and pH can control the cleaning stage. Based on economic feasibility, controlling the solution pH with low KMnO$_4$ concentrations could lead to the transformation of used membranes into recycled membranes (such as RO, NF, and UF).

4. Conclusions

The regeneration and recycling of discarded membranes are of great importance for extending the membrane lifespan, and therefore, they are crucial to reduce the environmental impacts and permit the economic feasibility of the industrial scale membrane process. In this research, several chemical agents were investigated for cleaning severe irreversible foulants on RO membranes fouled by MBRs effluents of textile wastewater, including acid (H_2SO_4), base (NaOH), metal-chelating agents (Na_2-EDTA), surfactants (SDS), oxidizing agents ($KMnO_4$), and their combinations. Good regeneration of the membrane was achieved after each membrane was cleaned by following integrated procedure: (I) $KMnO_4$ + NaOH solution followed by (II) $NaHSO_3$ solution. To achieve high cleaning efficiency, the effects of oxidant concentration, cleaning time, and solution pH were studied. The optimum cleaning protocol was 0.5% (w/v) $KMnO_4$ + 0.2% (w/v) NaOH solution followed by $NaHSO_3$, and the optimum cleaning time was 60 min, under which condition the cleaning efficiency could reach 5.87. Furthermore, experimental results revealed that the cleaning procedure could be divided into three stages and both the $KMnO_4$ concentration and pH can control the cleaning stage. Based on economic feasibility, controlling the solution pH with low $KMnO_4$ concentrations could lead to the development of recyclable membranes.

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