On the cleaning procedure of reverse osmosis membrane fouled by steel wastewater

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Abstract−The proper cleaning procedure for reverse osmosis (RO) membranes holds the key to achieving sustainable operation of RO processes during long-term filtration such as the reclamation of wastewater. In this study, the most adequate cleaning protocol was tested for RO membranes fouled by the steel wastewater. X-ray photoelectron spectroscopy (XPS) analysis of the fouling layer revealed the presence of the aromatics, aliphatic hydrocarbons, metallic oxides and hydroxides. An integrated cleaning procedure was developed for flux recovery. That is, metal chelating agent (MCA) plus alkaline-oxidant cleaning procedure consisting in one cleaning stage or two cleaning stages in series. MCA cleaning with 2 mM disodium ethylenediaminetetraacetate (Na$_2$-EDTA) solution followed by alkaline-oxidant cleaning with 5 mM NaOCl+NaOH/pH 12.0 solution provided the maximum cleaning efficiency.

Keywords: Reverse Osmosis, Cleaning, Steel Wastewater, Integrated Cleaning, Metallic Oxides

INTRODUCTION

Reverse osmosis (RO) has been extensively used in wastewater treatment due to membrane cost and operating cost reduction. However, the management of membrane fouling remains as the main challenge of this technology, as it results in increased operating cost and decreased membrane life. Membrane fouling is a multidimensional phenomenon that depends on several factors, including membrane morphology, chemical nature of membrane surface, the feed water composition and the operating conditions [1-3]. Membrane fouling is divided into reversible and irreversible fouling according to the attachment strength of foulants to the membranes. Reversible fouling caused by loose deposits can be controlled by strong washing. Otherwise, irreversible fouling caused by strong attachments such as cake is difficult to remove. Several technologies have been investigated to minimize membrane fouling, including membrane modification [4] and the pretreatment of wastewater [5]. But these technologies can only mitigate membrane fouling, which means fouling is still inevitable in most cases. Hence, membrane cleaning including physicochemical, biological or enzymatic cleaning will be needed.

Membrane cleaning has been used widely to remove foulants during operating terms. It has become an integral part of the membrane system and it plays an important role on industrial scale membrane process [6,7]. Membrane cleaning and its procedure depend on the nature of foulants on the membrane surface. Fouling varies, so does the membrane cleaning procedure. For instance, alkaline solutions can effectively remove organic and microbial foulants [8], while metal chelating agents (MCA) such as citric acid are effective in removing iron-containing deposits [9]. For the combined foulants, the individual agent shows a limited ability. Higher clean-

ing efficiency can be attained by strategically pairing chemical agents because of the complementary mechanisms. Dual-step cleaning is sometimes carried out for achieving higher efficiency. Optimization of cleaning is therefore essential to permit the economic feasibility and reduce the damage of membrane integrity.

Steel production requires large amounts of fresh water, meanwhile producing a very great amount of wastewater. RO is generally used as steel wastewater recycling technology. Deleterious membrane fouling constricts the efficiency of this technology. The most adequate cleaning protocol is therefore needed for fouled RO membrane after the treatment of steel wastewater. As shown in our previous study, RO membranes in service for steel wastewater recycling can be regenerated by oxidative cleaning under the optimal cleaning conditions [10]. However, the complete regeneration of fouled membranes is hardly achieved. Some metal ions convert to highly insoluble metal oxyhydroxide and the rest associated with dissolved organic molecules. A portion of these foulants will deposit on membrane surface and form a cake layer [11]. The layer of metal oxides may protect the organics from being oxidized and removed. If the metal layer can be removed or becomes looser, a higher cleaning efficiency can be achieved by oxidative cleaning. MCA such as citrate and disodium ethylenediaminetetraacetate (Na$_2$-EDTA) may promote removal of metal layer from the membrane surface via ligand-promoted dissolution [12].

In this study, we evaluated the cleaning procedure of RO membranes fouled by the steel wastewater. MCA and alkaline-oxidant solutions are used as cleaning agents. MCA includes Na$_2$-EDTA, sodium oxalate and sodium citrate. The models for oxidants are NaClO and H$_2$O$_2$. The membranes are cleaned in various protocols: individual cleaning, various combined cleaning by MCA and oxidant and individual cleaning in two cleaning stages in different series to investigate the cleaning efficiency. The results demonstrate the maximum cleaning efficiency is achieved when the MCA cleaning is followed by alkaline-oxidant cleaning.

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MATERIALS AND METHODS

1. Membranes and Test Setup

A fouled membrane (CPA2, Hydranautics) in almost one-year service in a steel plant (Wuhan, Hubei Province, China) was selected for this work. CPA2 is a typical thin composite membrane with aromatic polyamide active layer supported by polysulfone layer. The average flux of fresh membrane is 2.1 μm/s as determined using de-ionized (DI) water at an applied pressure of 20 bar and a crossflow velocity of 9.8 cm/s. The flux of fouled membranes is only 1.01 μm/s determined at the same conditions. Cleaning is performed with a laboratory scale crossflow test setup, which can be found elsewhere as well as our previous study [10]. The setup consists of a round membrane cell, a high-pressure pump, an electromagnetic mixer and a feed tank with a temperature control system. The cleaning solution is held in the tank and the membrane is placed in the membrane cell.

2. Cleaning Agents

The cleaning agents used are NaClO and H_2O_2 as oxidative solution. The oxidative cleaning is performed in alkaline environment (pH 12.0). Certified grade Na_2-EDTA, sodium oxalate, sodium citrate and citrate acid are used as a MCA. All agents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification. The stock solutions were freshly pre-

pared by dissolving each agent in DI water.

3. Cleaning Experiments

Cleaning was performed at ordinary pressure and a cross flow velocity of 20 cm/s. The solution was continuously circulated from the feed tank to the membrane for a period of 0.5 h. At the end of the cleaning, the setup was rinsed with DI water to flush out the chemical residue. Then, the flux of the membrane was tested at the conditions as section 1. The effects of solution component, concentration and pairs of cleaning agents on the cleaning efficiency were investigated. The cleaning efficiency (η) is evaluated as follows:

$$\eta = \frac{J_c}{J_f} \tag{1}$$

where J_c and J_f are flux through a cleaned membrane and fouled membrane, respectively.

4. Analysis Methods

4-1. XPS

The foulants on the membrane surface are stripped off the membrane by a clean sterile spatula. After being dried, the foulant information is detected by X-ray photoelectron spectrophotometer (XPS) (ESCALABMK-II, Thermo Fisher Scientific, US) using monochromatic Al $K\alpha$ X-rays (1,480 eV). C, O, N, Si, Al, Na and Fe are recorded and XPS peak 4.1 software is used to fit the spectra to identify the different oxidation states of C, O, N, Si and Al.
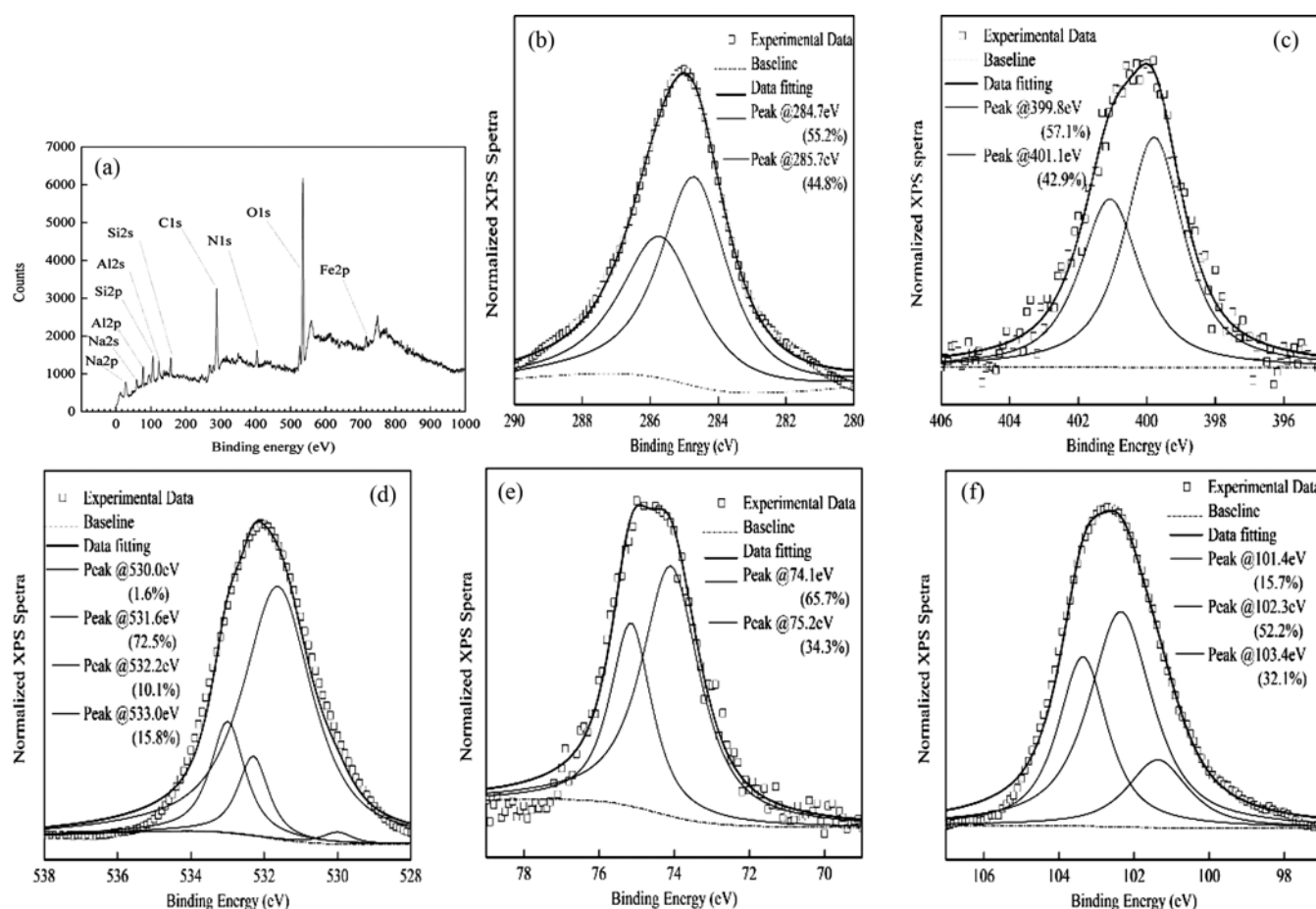

Fig. 1. XPS spectra of foulants. (a) Wide scan spectrum; (b)-(f) XPS peak fitting for elements: (b) C1s, (c) N1s, (d) O1s, (e) Al2p, (f) Si2p.
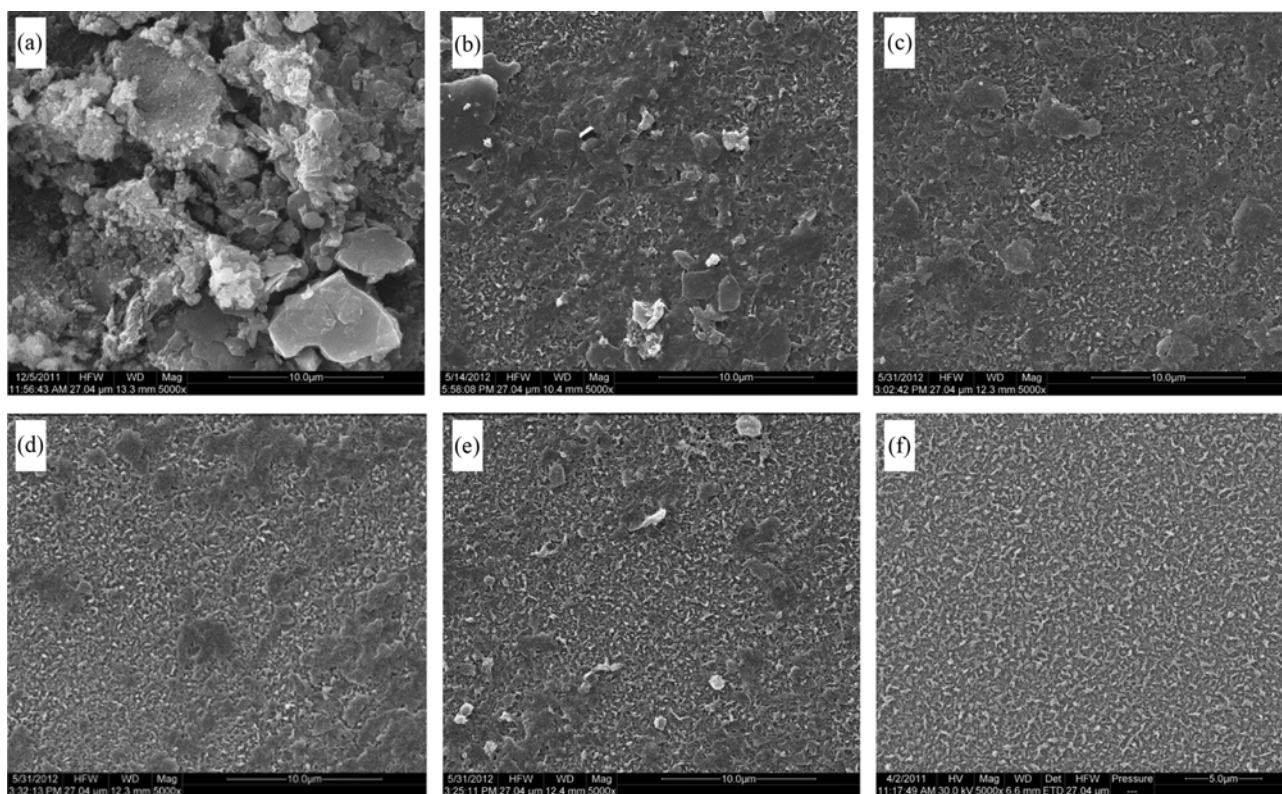
Fig. 2. SEM pictures of cleaned membranes: (a) the fouled membrane, (b) 2 mM Na$_2$-EDTA/pH 12, (c) 40 mM H$_2$O$_2$/pH 12, (d) 2 mM Na$_2$-EDTA/40 mM H$_2$O$_2$/pH 12, (e) 3 mM Na$_2$-EDTA/40 mM H$_2$O$_2$/pH 12, (f) the virgin membrane.

4-2. SEM

The surface morphologies of the fouled and cleaned membranes were analyzed by a scanning electron microscope (SEM) (FEI Quanta 200, Holland). All membranes were dried at 80 $^{\circ}$C and coated with a conductive sputtered gold layer before the analysis.

4-3. AFM

Surface roughness is tested by an SPM-9500J3 atomic force microscope (AFM) (Shimadzu, Kyoto, Japan) in the contact mode. Silicon probes were coated by 30 nm thick aluminum. Membrane surface roughness was characterized by the root mean square, which is the deviation of the peaks and valleys from the mean plane [13].

RESULTS AND DISCUSSION

1. XPS of Foulants

In our previous study, foulants on the membrane surface were removed by oxidative cleaning and the flux of the membrane was restored [10]. But for the heavily fouled membrane in rather long time term, the flux was hardly to be completely recovered by an individual cleaning. The thick dark brownish yellow layer could be effectively removed by oxidative cleaning. There was a thin yellow layer that remained on the membrane surface. To improve the efficiency, the cleaning protocol should be modified. To realize this purpose, the nature of foulants stripped off membranes was precisely analyzed by XPS. As shown in Fig. 1, C, O, N, Si, Al, Fe and Na were found at 284 eV, 533 eV, 400 eV, 103 V, 74 eV, 716 eV and 27 eV, respectively. The main elements including C, O, N, Si and

Al were further analyzed by peak fitting to identify the different oxidation states.

The binding energy shift (δ_{BE}) depends on the valence and structure of element. C1s spectrum had been only fitted to two peaks: a major peak at 284.7 eV (δ_{BE}=0 eV) that accounts for 55% of carbon atoms, and another peak at 285.7 eV (δ_{BE}=1.0 eV) (Fig. 2(b)). The peak without a δ_{BE} might be assigned to aromatic and aliphatic carbons with no adjacent electron withdrawing groups [14]. The peak with 1.0 eV shift corresponds to carbon atoms in an electron withdrawing environment. The little shift might be assigned to carbon atoms bonded to hydroxyl groups (-COH) [15]. The results indicate the presence of the aromatics and aliphatic hydrocarbons in the foulants, which accord with previous study [10]. N1s peaks indicate two kinds of N (Fig. 1(c)): amines in polymer (Al-NH-C-, -NH-CH$_2$COO-) at 399.8 eV [16] and positively charged N atoms (NO$_2^-$ and NO$_3^-$) at 401.1 eV [17]. As shown in Fig. 1(d), the peaks located at 530 eV, 531.6 eV, 532.2 eV and 533 eV correspond to oxygen atoms in oxides, hydroxides, sulfates and water, respectively [18]. Al2p peak in Fig. 1(e) at 74.1 eV and 75.2 eV shows the presence of Al$_2$O$_3$ in foulants [19]. Si2p peak in Fig. 1(f) indicates the bonds of C-Si-O$_3$ (101.4 eV), Si-O$_4$ (103.4 eV) and Si-O$_2$ (102.3 eV) [20]. The XPS results testified the presence of aromatic and aliphatic hydrocarbon, metal oxides and hydroxides.

2. Membrane Cleaning Efficiency

2-1. Effect of Agents Combinations

According to XPS results, cleaning agents were modified and MCA was added into the oxidant solution. The results are shown

Table 1. Cleaning efficiency of various cleaning agents

Cleaning agent	Efficiency (η)
40 mM H_2O_2, pH=12	1.60
4 mM NaClO, pH=12	1.62
2 mM Na_2-EDTA, 40 mM H_2O_2, pH=12	1.85
500 mM NaCl, 40 mM H_2O_2, pH=12	1.67
18 mM sodium oxalate, 40 mM H_2O_2, pH=12	1.80
9 mM sodium citrate, 40 mM H_2O_2, pH=12	1.79
2 mM Na_2-EDTA, 5 mM NaClO, pH=12	1.91
500 mM NaCl, 5 mM NaClO, pH=12	1.72
18 mM sodium oxalate, 5 mM NaClO, pH=12	1.83
9 mM sodium citrate, 5 mM NaClO, pH=12	1.81
2 mM Na_2-EDTA, 500 mM NaCl, pH=12	1.37

Table 2. The effect of concentration on the cleaning efficiency

Cleaning agent	Efficiency (η)
2 mM Na_2-EDTA, 40 mM H_2O_2, pH=12	1.85±0.02
2 mM Na_2-EDTA, 20 mM H_2O_2, pH=12	1.70±0.04
2 mM Na_2-EDTA, 30 mM H_2O_2, pH=12	1.81±0.03
1 mM Na_2-EDTA, 30 mM H_2O_2, pH=12	1.68±0.02
3 mM Na_2-EDTA, 30 mM H_2O_2, pH=12	1.89±0.03
2 mM Na_2-EDTA, 5 mM NaClO, pH=12	1.91±0.02
2 mM Na_2-EDTA, 4 mM NaClO, pH=12	1.88±0.01
2 mM Na_2-EDTA, 2 mM NaClO, pH=12	1.79±0.03
1 mM Na_2-EDTA, 4 mM NaClO, pH=12	1.75±0.02
3 mM Na_2-EDTA, 4 mM NaClO, pH=12	1.95±0.03

in Table 1. Compared with the base oxidative cleaning, the η was significantly elevated after the addition of MCA into the cleaning solution. For example, after the Na_2-EDTA addition, the η of 40 mM H_2O_2/pH 12.0 solution increased from 1.60 to 1.85 and that of 5 mM NaClO/pH 12.0 solution increased from 1.62 to 1.91. At pH 12.0, a soluble complex is formed after the reaction between Na_2-EDTA and the metal oxides and it is flushed away from the membrane surface. On the other hand, at high pH level, the fouling layer becomes looser that propelled the MCA and oxidant to enter the fouling layer [21]. Therefore, the foulants are more likely to be fully oxidized. The more effective cleaning leads to the higher η.

2-2. Effect of Concentration

The increase of the η was greatest after the addition of Na_2-EDTA into oxidant solution. Therefore, the concentration of the cleaning formula was investigated in detail and the results are described in Table 2. The η was apparently affected by the concentration of both Na_2-EDTA and oxidants. And it was raised with the concentration increasing. The growth curve started off quickly and increased slower and slower as the concentration increased. For cleaning agent Na_2-EDTA/H_2O_2/pH 12.0, the rate of change with respect to H_2O_2 concentration ($d\eta/dc_{H_2O_2}$) was 11 L·mol^{-1} when the concentration of H_2O_2 increased from 20 mM to 30 mM. $d\eta/dc_{H_2O_2}$ decreased to 4 L·mol^{-1} when the concentration of H_2O_2 further increased from 30 to 40 mM. dh/dc_{Na_2-EDTA} had essentially the same changing tendency with $d\eta/dc_{H_2O_2}$. The decline in change rate of the η is related to the dosage effect of cleaning agents [22]. The effect agent utilization is lower at the higher dosages. The change rate of η is also

controlled by the dosage effect of Na_2-EDTA/NaClO/pH 12.0.

2-3. Effect of Cleaning Sequence in Dual-step Cleaning

The fouled membrane was cleaned by single and dual step cleaning. The cleaning agents selected were 5 mM NaClO (pH 12.0), 40 mM H_2O_2 (pH 12.0), 2 mM Na_2-EDTA, 18 mM sodium oxalate, 9 mM sodium citrate and 500 mM NaCl. Table 3 presents a summary of the η measured for all cleaning procedures. The membrane was cleaned for 0.25 h in both first and second step. The shaded lattices refer to one cleaning agent used in both step for 0.5 h. The η shown in brackets was obtained when the membranes were cleaned by the combined agents for 0.5 h.

The η varied when the dual-step cleaning was performed in different sequence. The highest η was obtained when the membrane was cleaned by MCA followed by oxidants. The main foulants deposited on the membrane surface were verified to be the organics in our previous study [10]. For RO filtration of a steel wastewater during a long time, the characteristic of foulants on the membrane surface can be surmised as the following: the inorganic foulants, i.e., metal oxides and hydroxides, are located at the top layer; the organic foulants, i.e., aromatic and aliphatic hydrocarbon, are located at the bottom of the fouling layer and closely bonded with the membrane. Periodic cleaning is performed by a 2 wt% citric acid solution (pH 4) during the reclamation of the steel wastewater. The inorganic foulants are easily removed, but the organic compounds accumulate on the membrane surface gradually. So the organic foulants locate below the inorganics. The most inorganics are removed by the MCA in the first step. As a result, the mass transfer is elevated in the second step cleaning, which leads to the higher
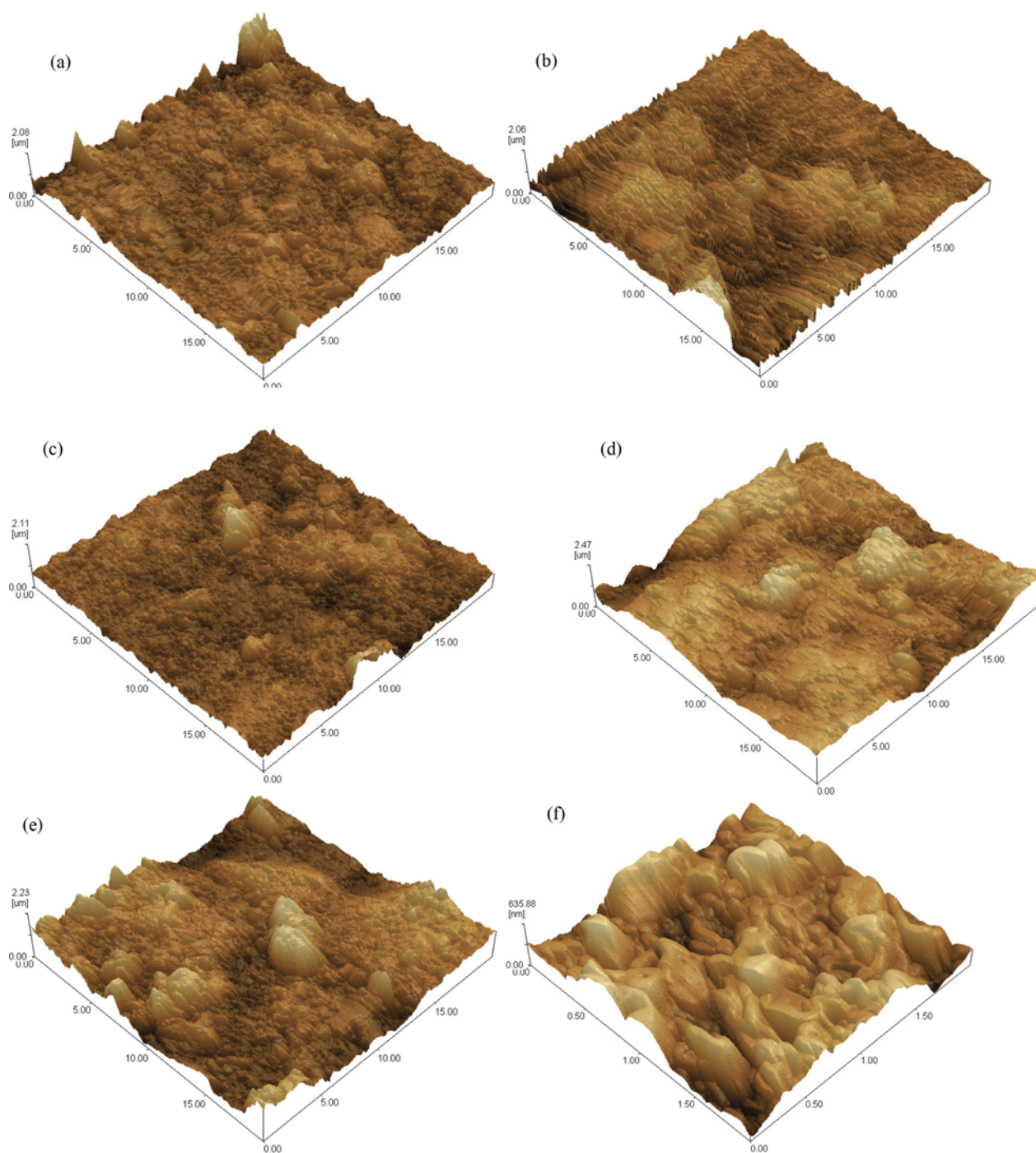
Table 3. The effect of cleaning order on the cleaning efficiency

		First step cleaning 0.25 h					
		NaClO	H_2O_2	Na_2-EDTA	Sodium oxalate	Sodium citrate	NaCl
Second step cleaning 0.25 h	NaClO	1.62	1.59 (-)	1.98 (1.91)	1.89 (1.83)	1.87 (1.81)	1.81 (1.72)
	H_2O_2	1.61 (-)	1.60	1.89 (1.85)	1.88 (1.80)	1.85 (1.79)	1.76 (1.67)
	Na_2-EDTA	1.89 (1.91)	1.82 (1.85)	1.42	1.29 (-)	1.28 (-)	1.47 (-)
	Sodium oxalate	1.85 (1.83)	1.83 (1.80)	1.37 (-)	1.37	1.35 (-)	1.30 (-)
	Sodium citrate	1.79 (1.81)	1.78 (1.79)	1.34 (-)	1.32 (-)	1.35	1.29 (-)
	NaCl	1.70 (1.72)	1.71 (1.67)	1.31 (-)	1.32 (-)	1.32 (-)	1.29

( ) The data in brackets were the η of the combined agents for 0.5 h cleaning; - No test

Table 4. The salt rejection of various membranes

Membranes	Rejection (%)
Fouled	90.2
Cleaned by 2 mM Na$_2$-EDTA/pH 12	91.3
Cleaned by 40 mM H$_2$O$_2$/pH 12	92.6
Cleaned by 2 mM Na$_2$-EDTA/40 mM H$_2$O$_2$/pH 12	95.8
Cleaned by 2 mM Na$_2$-EDTA followed by 40 mM H$_2$O$_2$/pH 12	97.3
Cleaned by 40 mM H$_2$O$_2$/pH 12 followed by 2 mM Na$_2$-EDTA	94.2

Fig. 3. AFM pictures of cleaned membranes: (a) The fouled membrane, (b) 2 mM Na$_2$-EDTA/pH 12, (c) 40 mM H$_2$O$_2$/pH 12, (d) 2 mM Na$_2$-EDTA/40 mM H$_2$O$_2$/pH 12, (e) 3 mM Na$_2$-EDTA/40 mM H$_2$O$_2$/pH 12, (f) the virgin membrane.

η. It was also noted that the combined agents, i.e., MCA/oxidants/pH 12.0, were more effective than the individual cleaning agents. The higher η is attained by strategically pairing MCA and oxidants that have complementary cleaning mechanisms [23].

3. Characterization of the Cleaned Membranes

Table 4 shows that the separation properties of membranes were improved after the cleaning. For example, the rejection slightly increased from 90.2% to 92.6% after the membrane cleaned by 40 mM H_2O_2/pH 12. When 2 mM Na_2-EDTA was added into the solution, it further increased to 95.8%. The highest rejection was obtained when the membrane was cleaned with 2 mM Na_2-EDTA followed by 40 mM H_2O_2/pH 12. The rejection results were concordant with the cleaning efficiency. The improved rejection and water flux suggested that the structure was not damaged by the cleaning.

The SEM images (Fig. 2) showed the changes of membrane surface morphology after various cleanings. The virgin membrane possessed a pebble-style surface with peaks and valleys. In comparison, a fouling layer was clearly found on the surface of fouled membranes. After cleaning, the fouling layer disappeared and the pebble-style surface reappeared. The surface morphology of the cleaned membranes became similar to that of the virgin membrane. Many foulants remained on the membrane surface after the single cleaning. For example, precious few of the areas showed the pebble-style after cleaning by 2 mM Na_2-EDTA/pH 12. The pebble-style areas were significantly enlarged after cleaning by 40 mM H_2O_2/pH 12, but the improvment was not enough. For oxidative cleaing, the bonds, especially unsaturated hydrogen bond of foulants, break down and the foulants decompose to small molecules [24]. Then, the oxidation products are removed because of either hydrolysis or shear force during the cleaning. Howere, most metal oxides and hydroxides remain on the membrane surface. The pebble-style surface was more obvious after the cleaning by the combined agents (2 mM Na_2-EDTA/H_2O_2/pH 12). The area covered by foulants was further constricted with Na_2-EDTA concentration increasing. These results indicated that the removal of foulants was facilitated by the use of the combined agents.

The AFM images of the membrane surface (Fig. 3) indicate that the changes on the membrane surface were largely consistent with the SEM images (Fig. 2). The fouled membrane shows the largest surface roughness (379.8 nm) because of the presence of fouling layer. The surface roughness decreased to 358.5 nm and 159.7 nm after the cleaning by 2 mM Na_2-EDTA/pH 12 and 40 mM H_2O_2/pH 12, respectively, indicating the removal of foulants from the membrane surface. It was noted that the concentration of Na_2-EDTA played an important role in the combined cleaning. The surface roughness was 137.4 nm when the combined agents included 2 mM Na_2-EDTA. With the concentration of Na_2-EDTA increasing to 3 mM, it decreased to 120.1 nm, which was extremely close to that of the virgin membrane (111.8 nm). The results indicated that almost all foulants were removed from the polymer surface.

CONCLUSIONS

The cleaning protocol shows a great importance on industrial scale membrane processes, especially in a large water-consuming industry like steel plants. Good regeneration of the membrane can be achieved after the membranes are cleaned by the combined agents, including MCA and oxidants. The cleaning efficiency is affected by both concentration and cleaning sequence in second step cleaning, i.e., MCA cleaning followed by oxidative cleaning provided the greatest cleaning efficiency. For complex foulants, the synergistic effect by the combined agents leads to a higher cleaning efficiency. Therefore, an experiment is necessary to determine the cleaning procedure.

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