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Effect of hypochlorite cleaning on the physiochemical characteristics of polyvinylidene fluoride membranes

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ABSTRACT

Traditionally, the chemical cleaning is unanimously considered to be an effective means to restore membrane permeability. However, the chemical solutions can also be responsible for changes in membrane properties and thus affect the life-span of membranes. The aim of this study was to gain a better understanding of the effect of sodium hypochlorite cleaning solutions on the changes of physiochemical characteristics of microfiltration (MF) flat sheet membranes made from polyvinylidene fluoride (PVDF). A pilot-scale MBR was operated for 63 d and frequent and high dose sodium hypochlorite cleaning was carried out. The properties of the original and cleaned membranes were compared by pure water flux evaluation, contact angle measurement, mechanical testing, and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra analysis. Effective removal of the foulant from the membrane surface resulted in more severe fouling. The pure water flux decayed faster with the extension of operation time and the membrane became more and more hydrophilic. The deterioration of ultimate tensile strength and the improvement of the ultimate elongation of membranes showed that membrane became more weak and flexible after hypochlorite cleaning. The results of ATR-FTIR indicated that the sodium hypochlorite cleaning had no vital damage to the chemical structure of PVDF membrane, but exerted impacts on its surface properties.

1. Introduction

Membrane bioreactors (MBRs) processes have been applied more and more extensively for both municipal and industrial wastewater treatment, because they offer remarkable advantages over conventional activated sludge (CAS), including a higher biomass concentration, reduced footprint, and highly improved effluent, etc. [1–3]. However, membrane fouling is a big obstacle in the wide-spread application of MBR for wastewater treatment. Membrane fouling results in reduced performance, severe flux decline, high energy consumption, and frequent membrane cleaning or replacement. Recently, the fouling mechanisms have been well studied, and related measures were adopted to mitigate the membrane fouling. Attention has been paid to various design and operating parameters such as hydrodynamic conditions in the reactor [4,5], air flow rate [6], reactor configuration [7], membrane characteristics [8,9], membrane flux [10] and mixed liquor characteristics [11,12]. Although membrane fouling was reduced to some extent by employing fouling control measures, the fouling and cleaning were unavoidable.

Chemical cleaning is the primary method to restore the membrane flux and permeability. There are several categories of cleaning chemicals (caustic, oxidants/disinfectants, acids, chelating agents, and surfactants) [13], and hypochlorite remains a popular choice because of its availability, reasonable price, and capacity to remove biofouling via efficient cleaning and bio-sanitation. At present, there are a variety of reports about the impact of hypochlorite cleaning on properties and function of ultrafiltration (UF) polymer membranes. For instance, Arkhangelsky et al. [14] used a solution of 0.3 g of bovine serum albumin (BSA) per liter of phosphate buffer solution (pH 7.2) to perform the fouling experiment. They found that effective removal of the foulant from the polyethersulfone membrane surface resulted in more severe fouling and the deterioration in the mechanical strength of hypochlorite-treated membranes which was ascribed to a loss of membrane integrity. Gaudichet-Maurin et al. [15] investigated various cleaning agents and their concentration, time of clean-in-place treatment and cleaning frequency for UF membranes fouled by BSA. It was found that higher dosage of cleaning agents resulted in complete restoration of the initial flux at the first step, but led to more severe fouling, which thus required more frequent clean-in-place operations in the long term. Chain breaking in polysulfone molecules after extended exposure to hypochlorite was observed by Rouaix et al. [16]. It was also reported by Gitis et al.

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[17] that the oxidation of cellulose triacetate (CA) could lead to the formation of various end groups, such as carboxyl, aldehyde, and ketone. Although the intensive efforts mentioned above are very helpful to understand the role of membrane cleaning in MBR operation, the effect of hypochlorite cleaning on membrane properties in real applications is insufficient. This is partly attributed to that the PVDF membranes were not well investigated in previous studies. PVDF membranes are one of widely used membranes in MBRs for wastewater treatment nowadays. Another important reason is that BSA was conducted as a sole fouling agent to simulate the actual operation in the previous literature. It is well known that in wastewater treatment systems membrane polymers are in continuous interaction with both complicated organic and inorganic substances. Hence, BSA alone cannot fully reflect the actual situation of real applications.

The aim of this study was, therefore, to gain better understanding of the effect of sodium hypochlorite on PVDF microfiltration (MF) membranes. A pilot-scale MBR at an existing wastewater treatment plant (WWTP) was operated for 63 d in order to investigate the effects of frequent and high dose sodium hypochlorite solution on the membrane characteristics. The pure water flux, contact angle, mechanical properties, and Fourier transform infrared (FTIR) spectra of membranes were analyzed and discussed. The results obtained in this study are expected to provide a sound understanding on the role of chemical cleaning in MBRs.

2. Materials and methods

2.1. Experimental setup

The pilot-scale submerged MBR with a total volume of 504 L is shown in Fig. 1, which was located at the Quyang Municipal WWTP of Shanghai, China. Twenty flat sheet membrane modules (SHZZ-30, Zizheng Environment Incorporated, Shanghai, China) were mounted vertically in the reactor. The microfiltration membranes made from PVDF polymer with a mean pore size of 0.20 μm were used in this study. The effective filtration area for each module was 0.17 m^2. Air diffuser was placed under the membrane modules and aeration was continuously carried out in order to supply oxygen demanded by the microorganisms and to induce a cross-flow velocity (CFV) along membrane surfaces. The CFV was kept at about 0.3 m/s by aeration with an average air flow rate of 6 m^3/h.

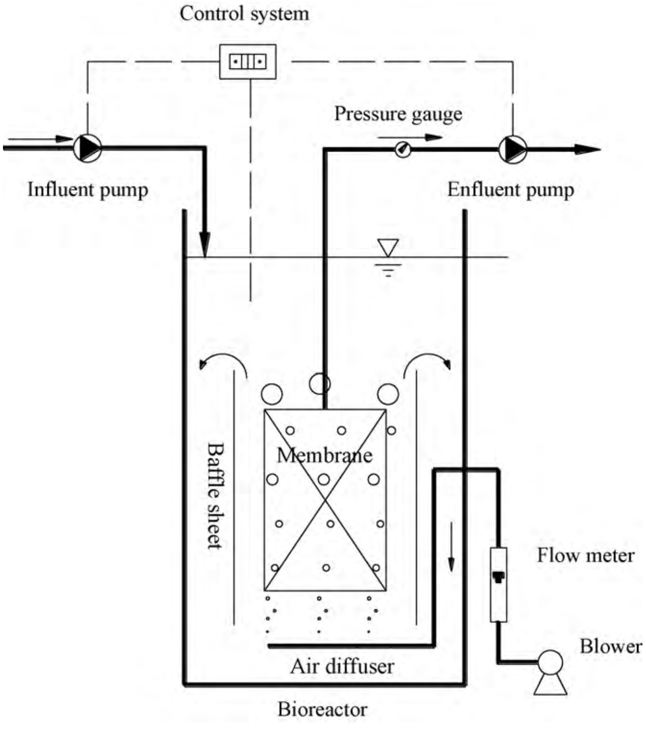


Fig. 1. Diagram of the pilot-scale MBR.

The characteristics of the raw wastewater can be found elsewhere [3,18]. The influent pump was controlled by a water level sensor to maintain a constant water level in the bioreactor. The effluent flow rate and the trans-membrane pressure (TMP) were monitored by a water meter and a pressure gauge, respectively.

2.2. Operating conditions

Membrane filtration was carried out by peristaltic pumps, and the constant flow rate mode of operation was employed. Membrane flux was maintained at 20 L/(m^2 h) which was lower than the critical flux 33.5 L/(m^2 h). The critical flux of membrane was measured using the stepwise method described by Cho and Fane [19] before the experiment was started. Intermittent operation of the suction pumps (2 min pause for every 12 min of operation) was carried out to mitigate membrane fouling in the operation. The membrane modules were taken out of the reactor every 3–7 days and immerged in sodium hypochlorite solution after the physical washing. Solutions were prepared from sodium hypochlorite concentrates (33% in chlorine) diluted by tap water. The dose of hypochlorite is expressed as the product of the concentration C times the contact time t, i.e., $C \times t$ in units of g h/L. The membranes were soaked for various times to give doses (concentration $C \times$ contact time t) of chlorine of 7.92 g h/L. The agent concentration was doubled and the soaking time was twelve times as much as mentioned in the literature [20].

Twenty modules were divided into four groups, and each group (five modules) was sucked by one pump. When the chemical cleaning was performed for the fourth, fifth, sixth, tenth and twelfth times, one module of a group was taken out, respectively, and named A1, A2, A3, A4, and A5. Contact times corresponded to 1.85, 2.31, 2.77, 4.62, and 5.54 equivalent years on site for the unfavorable conditions (one cleaning step of 2 h at 165 mg/L of chlorine once a week). The original membrane was named A0. All the membranes were stored dry under ambient conditions and tested after pretreatment. The hydraulic retention time (HRT) of the MBR was 4.9 h. The sludge in the system was not discharged during the experiment. During this study, the temperature in the mixed liquor of the process was in the range of 23 and 27 °C.

2.3. Analytical methods

2.3.1. Pure water flux

The pure water flux was measured by a dead-end filtration apparatus. The area of tested membrane was 12.6 cm^2. Each sample was soaked in de-ionized water for 24 h before testing and pre-compacted for 30 min at 0.08 MPa. Then, the trans-membrane pressure was lowered and the pure water flux (J) was obtained at 0.03 MPa by measuring permeate volume in a certain period of time. To minimize the experimental error, each membrane was measured at three random locations and the average of three values was reported. The pure water flux was calculated according to the following equation.

$$J = \frac{V}{St} \tag{1}$$

where J is the pure water flux (L/(m^2 h)), V volume of permeated water (L), S virtual area of tested samples ($S = 0.00126\,m^2$), and t record time (h).

2.3.2. *Contact angle*

The hyrophilicity of membrane top surface was characterized on the basis of a water contact angle system (OCA20, Dataphysics, Germany) equipped with video capture at room temperature. To minimize the experimental error, the contact angles were measured in triplicate at random locations for each sample and the average value was reported.

2.3.3. *Mechanical properties*

The mechanical properties of the membranes were tested using a CMT4204 Microcomputer Controlled Electronic Universal Testing Machine (Sans Material Testing Corporation, China) at room temperature. All samples were cut into the standard shape before testing. The sample was clamped at the both ends and pulled in tension at constant elongation velocity of 50 mm/min with an initial gauge length of 20 cm. One holder was attached to the lower stage of the CMT, and the other was attached to a strain-gauge-based force sensor. The time taken for mounting and testing of the sample was kept constant. The ultimate tensile strength σ_T (MPa), the ultimate elongation ε (%) and Young's modulus were then obtained through the specific formulas as reported in the literature [21]. For each test, five samples were evaluated. The average values for tensile strength and elongation were reported.

2.3.4. *Fourier transform infrared (FTIR) spectrometry*

To study the surface chemical composition changes of the PVDF membranes, attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were collected using a Nicolet 5700 spectrometer (Thermo Electron Corporation, USA) set at a 4 cm^{-1} resolution. The spectra were measured at wave numbers in the range of 4000–400 cm^{-1}.

2.3.5. *Other item analysis*

The sludge samples were brought to the laboratory within 30 min after sampling, and the experiments were started immediately. Measurements of chemical oxygen demand (COD), ammonia, nitrate and nitrite in the membrane effluent, mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS) and pH of the influent and in the reactor were performed according to Chinese NEPA standard methods [22]. CFV was determined using a Cup-type Current Meter (Model LS45A, Chongqing Hydrological Instrument Incorporated, Chongqing, China).

3. Results and discussion

3.1. *Process performance*

During the operation, the MLSS concentration in the MBR was maintained at about 8 g/L. Table 1 summarizes the average characteristics of the treated water and the removal efficiency in the MBR. It can be seen that the removal of COD, ammonia, TN and suspended solids (SS) was quite successful.

The variations of membrane flux and TMP with operation time are demonstrated in Fig. 2. An arrow indicates that chemical cleaning of membrane was performed on that day to remove membrane foulant and to recover the membrane's permeability. It can be observed that a total of 12 times chemical cleaning was carried out throughout the running cycles. A1, A2, A3, A4 and A5 in Fig. 2 represent that one group of modules were taken out when the chemical cleaning was performed for the fourth, fifth, sixth, tenth and twelfth times, respectively. It can also be seen that the TMP increased with the increase of operation time in each period while the flux maintained at about 20 L/(m^2 h) (sub-critical flux) except in the initial period. In the first three cycles, the TMP had a sharp growth rate because the activated sludge was not stabilized when the filtration was started, and the initial start-up pressure of the three cycles gradually increased after each cleaning. In the subsequent courses of operation, the TMP showed a slow increase and the initial start-up pressure tended to restore to the initial level and then became stable in the last four cycles. Another phenomenon was that the TMP had a faster growth in the terminate courses than in the former courses. That indicates although the chemical cleaning had a good restoration of permeability for PVDF membrane in the last four cycles, it led to more severe fouling during the subsequent operation. The result is in accordance with the conclusions of the literature [14,15,23].

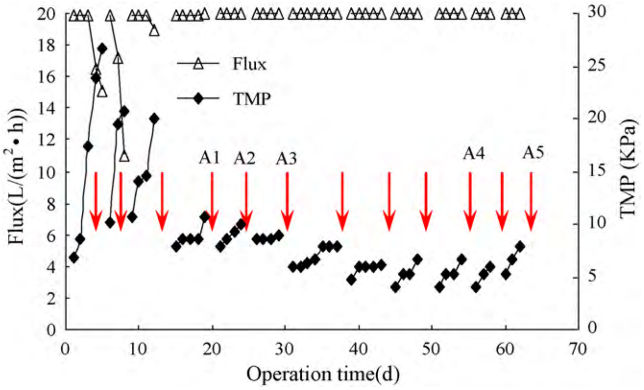


Fig. 2. Variations of membrane flux and TMP during the experiment.

3.2. *Variations of the pure water flux*

The pure water fluxes of the cleaned membranes for various cleaning times by the sodium hypochlorite and of the original one (A0) are presented in Table 2. From Table 2, it can be observed that the pure water flux decreased after each chlorine treatment. In the initial six cleaning processes, the pure water flux showed a sharp decline particularly from A0 to A1 (after the fourth cleaning), and then a smaller decline. The result obtained from this experiment is inconsistent with the result in the literature [24,25] in which UF membranes exhibited a flux increase in hypochlorite-treated membranes. It can be ascribed to the differences of fouling agents. The fouling agent used in the literature was purified BSA, while the real municipal wastewater which was comprised of complicated chemicals was used in our experiment. Membrane fouling of the

Table 1
Average characteristics of the treated water ($n = 7$).

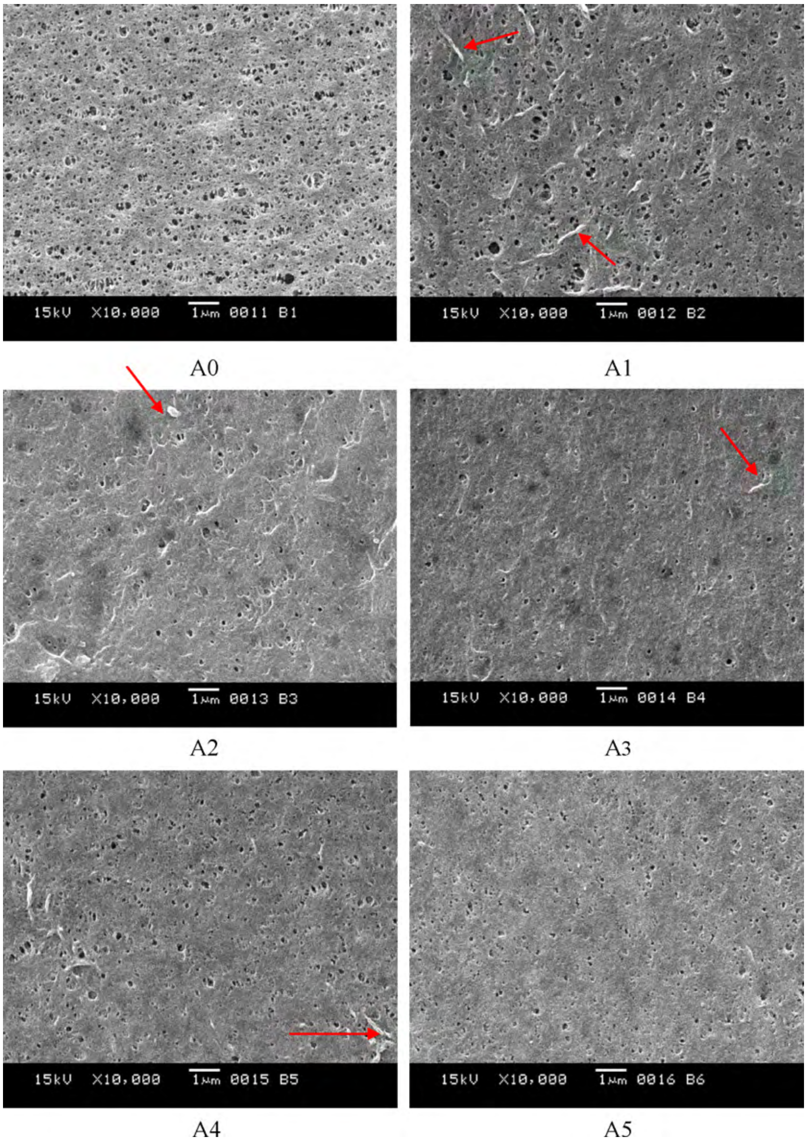
Items	Mean concentration	Removal efficiency (%)
COD (mg/L)	17.9 ± 4.7	95.0 ± 1.3
TN (mg/L)	26.7 ± 5.3	41.5 ± 11.6
NH_3–N (mg/L)	0.9 ± 0.5	96.8 ± 2.0
TP (mg/L)	2.8 ± 0.9	59.6 ± 13.6
SS (mg/L)	0.0	100.0

Values are given as mean value ± standard deviation.

Table 2
Pure water flux of new and hypochlorite-cleaned membranes.

Items	Pure water flux (L/m^2 h)
A0	299 ± 16
A1	167 ± 8
A2	143 ± 3
A3	108 ± 6
A4	96 ± 5
A5	72 ± 5

Values are given as mean value ± standard deviation.



A0 A1

A2 A3

A4 A5

Fig. 3. SEM images of new and hypochlorite-cleaned membranes.

real MBR is not only due to organic matters, but some inorganic substances. It is well accepted that oxidants or alkaline solutions can effectively remove organic substances while acids perform well in removing inorganic foulants [26]. In this study, sodium hypochlorite as an oxidizing agent was used to clean the membrane, and the organic matters such as the proteins, carbohydrates, etc. could be removed from the membrane by oxidation. However, the inorganic substances could be remained on/in membranes, which can be observed in Fig. 3. Hence, the pure water flux might not be effectively restored in our study.

3.3. *Contact angle*

The contact angle is an important parameter in measuring the surface hydrophobicity. In general, the higher the contact angle, the higher is the hydrophobicity of the membrane surface. The membrane is considered to be hydrophilic when contact angle is less than 90° [27–29].

It can be seen from Fig. 4 that the new membrane showed a hydrophobic surface, with an angle of 91.8°. The subsequent fouling and cleaning cycle made membranes become more hydrophilic, changing the contact angle from 91.8° to 75.8°. Although the contact angle of membrane A2 had a slight increase compared with membrane A1, the overall trend was down. In other words, the membrane became more and more hydrophilic as the cleaning times increased. Interestingly, when PVDF membrane was only

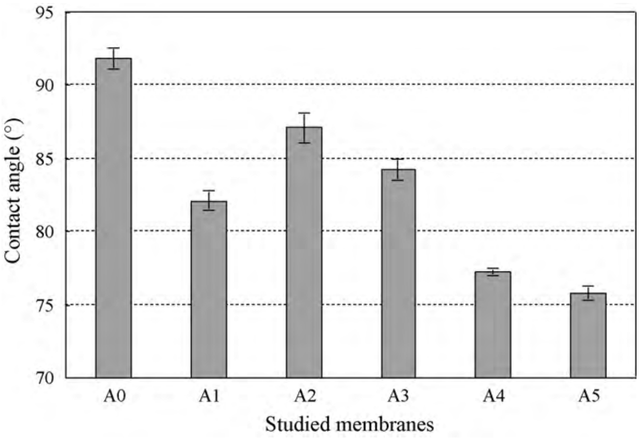


Fig. 4. Contact angles of new and hypochlorite-cleaned membranes.

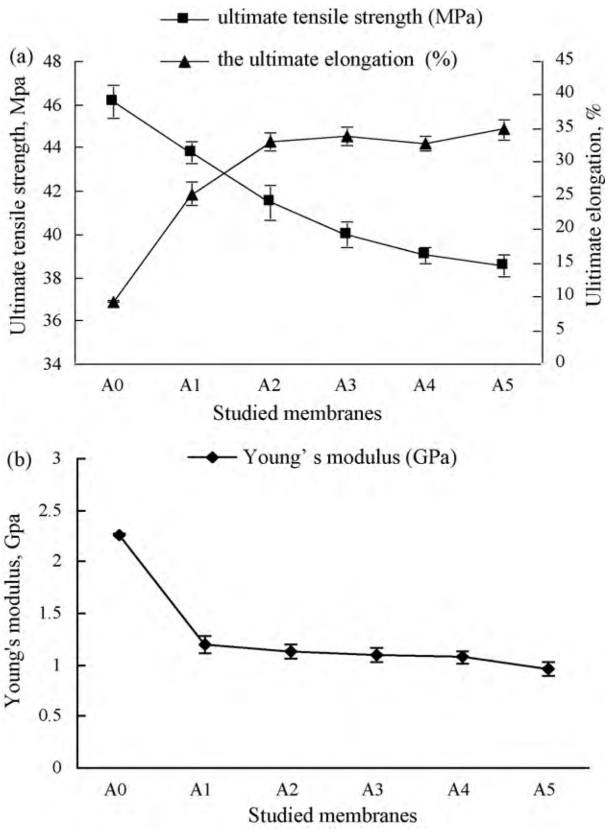


Fig. 5. Ultimate tensile strength, ultimate elongation (a) and Young's modulus (b) of A0, A1, A2, A3, A4 and A5 membrane.

cleaned once, the hydrophilicity did not change very significantly. For instance, the contact angle measurement of membrane reduced from 87.1° to 84.2° after a single cleaning cycle. When the membrane was cleaned twice or more, the surface then became more hydrophilic (with contact angle of 84.2° and 77.3° for membranes A3 and A4, respectively). This phenomenon was previously found by other authors [29,30]. It was explained that surfaces were either modified by foulant, cleaning agents or both. The contact angle of membrane A1 was lower than that of membrane A2, which should be attributed to that some foulants still remained on the membrane A1. In the initial three cycles, the membrane fouling was very serious due to the unstable situation of the activated sludge and contaminants were not completely removed at the same dose of chemical cleaning agents compared with other cycles. Therefore, membrane A1 was more hydrophilic.

3.4. *Mechanical properties test results*

Fig. 5 presents the values of ultimate tensile strength and the ultimate elongation of various membranes. It is evident from Fig. 5 that the ultimate tensile strength of membranes showed a continuous decrease with the extension of cleaning time. Moreover, the ultimate tensile strength decreased sharply from the 46.2 to 41.5 MPa after five times hypochlorite cleaning. Afterwards the decline slowed down in the subsequent cleaning processes and the ultimate tensile strength decreased from 40.0 to 38.6 MPa. Besides that, the Young's modulus decreased from 2.3 to 1.2 GPa after the fifth time cleaning, which meant that membrane rigidity was declined sharply, and gradually reduced to 1.0 GPa at the end of the experiment. That indicated the rigidity of this membrane decreased rapidly after it was put into use, while it varied slightly in the following operating time. It was also confirmed by other researchers that the ultimate tensile strength and Young's modulus decreased after hypochlorite cleaning [14,21].

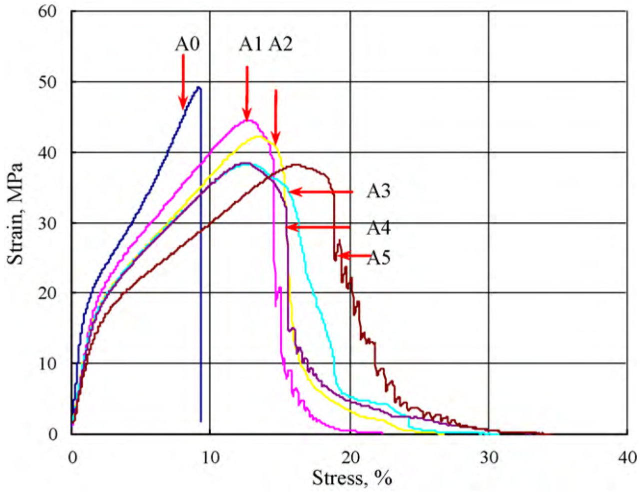


Fig. 6. The stress–strain curves of A0, A1, A2, A3, A4 and A5 membrane.

In addition, the ultimate elongation tended to increase as the cleaning time prolonged, presenting a similar changing trend with the Young's modulus. It can be observed from Fig. 5(a) that the ultimate elongation showed a faster increase in the course of first five times cleaning and tended to level off at last. This result is inconsistent with the report of the literature [14,21]. In other words, the membranes used in the literature became brittle, while our membranes became flexible. Besides, as shown in Fig. 6, there is an obvious difference in the stress–strain curves between the new and the used one. A0 was burst into fracture when the stress reached a certain value. The cross-section had an even fracture indicating strong brittle. However, the membranes after hypochlorite cleaning did not show a sudden fracture as soon as the ultimate stress was exerted. When the membrane was stretched, the stress was focused on some position where the interaction force among the polymer macromolecules was weak, resulting in the rupture at that location. Afterwards, the stress was transferred to other parts resulting in fracture in another place, and then the membrane fractured asynchronously due to an uneven section structure.

Arkhangelsky et al. [14] and Rouaix et al. [16] ascribed the decline of the ultimate tensile strength and the ultimate elongation to the polymer chain scission of polyethersulfone and polysulfone membranes after sodium hypochlorite cleaning. As a result, the interaction between polymer molecules was weakened and easier to crack. Furthermore, in the relevant literature [14,15,21], BSA was taken as a fouling agent and a short running time was performed, so the membranes could be well cleaned and almost no substances remained within the membrane pores. In our experiments, different results were obtained. It might be due to the fact that PVDF membrane was used in our experiment and submerged in the activated sludge to run for a long time. In the practical application process, the sodium hypochlorite cleaning may cause damage to the PVDF membranes together with other chemical process like plasticization. The specific reasons need further studying.

3.5. *Surface chemistry (FTIR)*

ATR-FTIR provides a convenient and effective way to determine the composition of a thin-film composite membrane [31], which was employed to analyze the chemical changes of PVDF layer before and after chemical cleaning. Fig. 7 shows the ATR-FTIR spectra of PVDF membranes treated with sodium hypochlorite solutions for

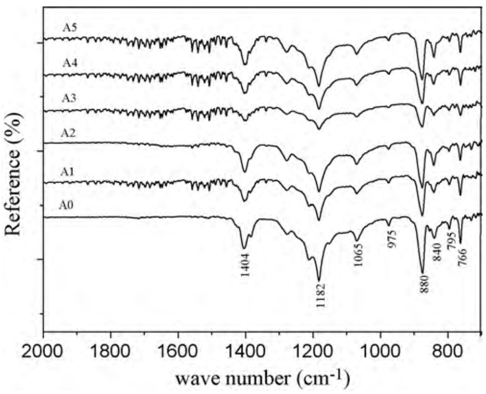


Fig. 7. ATR-FTIR spectra of new and hypochlorite-cleaned membranes.

various times. The typical spectrum of an original PVDF membrane (as represented by A0), as depicted in Fig. 7, exhibited the following characteristic intense bands: 1404 cm^{-1}, 1182 cm^{-1}, 975 cm^{-1} and 880 cm^{-1} for CH out of plane deformation vibrations, 1065 cm^{-1} for C–C vibrations, 840 cm^{-1} and 795 cm^{-1} for CH_2 rocking vibrations, 766 cm^{-1} for CF_2 bending and skeletal vibrations [32]. Compared with the spectrum of the new one, there are no other new peaks appearing or disappearing in the spectra of cleaned membranes. It is apparent that polymer did not change appreciably except a significant changing of the relative intensity of the bands with the increase of sodium hypochlorite cleaning times. The peak strength decreased with the increase of cleaning times until after the sixth time. And then the peak strength showed a gradual rise in the subsequent cleaning process. Ultimately, however, the intensity was not restored to the original level. In addition, it can also be observed the relative intensity of all the characteristic peaks changed simultaneously, rather than of a single band. That was inconsistent with the reports that the intensity of some particular band changed and resulted in chain scission of the polymer after treatment [14,33]. It suggests that the sodium hypochlorite cleaning did not damage the chemical structure of PVDF membrane. Interestingly, the variation of the peak strength was closely related to the initial start-up TMP in the operation process. The initial start-up TMP rose gradually after the sixth time cleaning while the peak strength decreased. Afterwards, the former decreased and the latter increased. It is well known that if the cleaning cannot completely remove the foulant, the initial start-up TMP will be higher. Hence, that indicated the residues after cleaning were covered on the membrane surface, and that weakened the infrared absorption of membrane. The peak strength could not been fully recovered even the initial start-up TMP of the ultimate membrane was as high as of the new one. That showed that the sodium hypochlorite cleaning did have an impact on the surface of PVDF membrane. The particular mechanism needs further studying.

4. Conclusions

The influences of chemical cleaning on PVDF membrane characteristics were carried out in an MBR. The sodium hypochlorite cleaning had a relatively good recovery of TMP, but led to more severe fouling in the subsequent operation. The pure water flux decayed faster with the extension of operation time. It was found that the chemical cleaning could modify the contact angle of membranes, and the membrane became more and more hydrophilic as the cleaning times increased. Besides that, the mechanical properties were also strongly modified. The ultimate tensile strength of studied membranes was weakened and the Young's modulus also decreased, while the ultimate elongation showed a fast increase with the extension of operation time. However, with the increase of cleaning times, all the values of membrane parameters tended to level off. ATR-FTIR indicated that the sodium hypochlorite cleaning did not damage the chemical structure of PVDF membrane, but had impacts on its surface properties. The results indicated that PVDF membranes could stand normal chemical cleaning conditions over several years.

Acknowledgements

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