Electrochemical impedance spectroscopy and surface properties characterization of anion exchange membrane fouled by sodium dodecyl sulfate

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Abstract

In this study, the fouling of anion exchange membrane (AEM) in electrodialysis was investigated using sodium dodecyl sulfate (SDS) as a model foulant, and the effect of membrane cleaning on the properties of the fouled AEMs was examined further. Results showed that the severer fouling of AEM was caused by the higher concentration of SDS in the feed solution, and a dense SDS fouling layer was formed on the AEM surface, causing the obvious increase of electrical resistance and the deterioration of desalination performance. Electrochemical impedance spectroscopy (EIS) indicated the SDS fouling layer on the AEM could hinder, even restrict completely the transmembrane migration of the ions, especially at high concentration of SDS. The cleaning experiment showed the cleaning effect of ultra-pure water was similar to that of HCl solution, but was better than that of NaOH solution, in which most SDS on the fouled AEM could be removed effectively by cleaned in ultra-pure water. EIS of the fouled AEMs before and after cleaned indicated that the remaining SDS on the cleaned AEM had almost no influence on the transmembrane migration of the ions through AEM.

Keywords: Anion exchange membrane; Membrane fouling; Electrochemical impedance spectroscopy; Surface properties; Membrane cleaning

1. Introduction

Electrodialysis (ED) has potential application in the treatment of industrial effluent from coal-power generation, food processing, steel and coal chemical industry because of the excellent characteristics of ion exchange membranes (IEMs): high chemical stability, low electrical resistance and good mechanical strength [1-6]. However, many organic foulants, especially, these with the negative charges from industrial wastewater can cause the serious fouling of anion exchange membranes (AEMs), resulting in an increase of the membrane electrical resistance and even causing the membrane to be damaged. Therefore, the fouling of AEM is a key factor for restricting the wide application of electrodialysis in the treatment of industrial wastewater and hence has been paid much attention by many researchers all along.

Many studies on organics fouling of AEM have been reported. Bukhovets et al. [7] found that the membrane fouling caused by aromatic amino acids would cause the membrane conductivity to decrease significantly and its surface hydrophobicity to increase. Lee et al. [8] examined the fouling potential of AEM caused by different foulants such as humate, bovine serum albumin (BSA) and sodium dodecyl benzene sulfonate (SDBS), and found that SDBS caused severer fouling on the AEM than the others. Tanaka et al. [9, 10] examined the organic fouling behavior of AEM by organic foulants with various alkyl chain, and found that affinity interaction was a more important factor in organic fouling than the electrostatic interaction and geometrical factor between the foulant and AEM. However, the study on the fouling behavior of AEM by sodium dodecyl sulfate (SDS), a common anionic surfactant appeared in industrial wastewater, with long

alkyl chain and strong charged groups but without benzene ring, hasn't been found so far.

Membrane cleaning with dilute solution of acids and bases is an effective method for restoring the membrane performance. Lee et al. [11] investigated that the removal of SDBS from the fouled AEM by cleaning with water and examined the respective contribution of irreversible fouling and reversible fouling caused by SDBS. Guo et al. [12] compared the cleaning effect of HCl and NaOH solution on the fouled AEMs and CEMs caused by oily wastewater and found that HCl solution was a more efficient cleaning agent for both of the fouled AEMs and CEMs. According to the literature [13], the organics with charged groups and aromatic rings might result in the irreversible fouling of AEM, which couldn't be removed effectively by membrane cleaning because of the strong affinity interaction between benzene rings of the organics and the membrane polymer matrix. Therefore, it's vitally important to examine the effect of membrane cleaning on performance recovery of the fouled AEM caused by SDS.

Electrochemical impedance spectroscopy (EIS) is a powerful technique to provide valuable information on the electrochemical properties of the membrane system [14-18]. The membrane resistance and the resistance of ionic transfer through the interface (i.e. the diffusion boundary layer and the electrical double layer) of the different commercial IEMs could be distinguished by the analysis of EIS under the condition of various salt concentration, liquid flow rate and temperature [16, 18]. Especially, the EIS study of the IEM system performed by Park et al. [19, 20] provided an approach of investigating the BSA fouling phenomena on the AEM and helped to get a better insight into the changes of the interfacial layers between the AEM and solution. Therefore, the EIS study of the fouled AEM before and after cleaned should be a good approach to examining the effects of membrane fouling caused by SDS and chemical cleaning on the electrochemical

properties of AEM.

The aim of the work was to study the fouling of AEM from SDS and to further examine the effect of membrane cleaning on the properties of the fouled AEM. The influence of the concentration of SDS on the surface properties and desalination performance of AEM was investigated systemically. The effects of membrane cleaning on the physicochemical properties of the fouled AEMs were characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), atomic force microscopy (AFM) and the measurement of electrical resistance. The EIS of the fouled AEMs and cleaned AEMs was measured to study the effects of membrane fouling and subsequent cleaning on the electrochemical properties of AEM.

2. Experimental

2.1 Materials

The commercial anion exchange membrane (AEM, NEOSEPTA AMX) and cation exchange membrane (CEM, NEOSEPTA CMX) provided by Astom Corp (Tokyo, Japan) were used in the experiment. The properties of the membranes were shown in Table 1, provided by the manufacturer. Sodium dodecyl sulfate (SDS) used as a model foulant was purchased from Alfa Aesar. Other reagents such as NaCl (A.R), HCl (A.R), Na₂SO₄ (A.R) were used to prepare the solutions in the experiment. All solutions were prepared using ultra-pure water (18.2 MΩ·cm⁻¹, Milli-Q, Millipore).

Table 1

The main properties of the ion exchange membranes used in the experiment.

Type	Cation exchange membrane	Anion exchange membrane
Thickness (mm)	0.17	0.14

Electrical resistance ($\Omega \cdot \text{cm}^2$)	3.0	2.5
Burst strength (MPa)	≥ 0.40	≥ 0.25
Temperature ($^{\circ}\text{C}$)	≤ 40	≤ 40
pH	0~10	0~8

2.2 Membrane fouling in electrodialysis

The fouling experiments and desalination experiments were performed in an electrodialysis apparatus. One AEM and two CEMs were contained in the ED stack, which was divided into three compartments, including the dilute, concentrated, and electrode compartments.

In the fouling experiments, the 500 mL feed solution in one beaker containing 0.1 M NaCl and a certain concentration of SDS (50~200 mg/L) was flowed through the dilute and concentrated compartments of ED stack, respectively, then into the same beaker to ensure that the electrolyte concentration of the feed solution was unchanged during electrodialysis. The feed solution was kept constant temperature of 25 $^{\circ}\text{C}$ by a thermostatic bath during the experimental process. The electrode rinse solution was 500 mL of 0.1 M Na_2SO_4 . All the circulated solutions were driven by a peristaltic pump at a flow rate of $100 \text{ mL} \cdot \text{min}^{-1}$. The effective area of each membrane was 50 cm^2 ($5 \text{ cm} \times 10 \text{ cm}$). The fouling experiments were carried out at a current density of $3 \text{ mA} \cdot \text{cm}^{-2}$. A couple of platinum plate electrodes were equipped between the both sides of AEM to record the change of the potential difference (ΔE) of AEM using a data logger connected to a computer during the fouling experiment. The fouling experiment at a certain concentration of SDS was repeated for three times and the potential difference (ΔE) was the average value of the three measurements. The AEMs after the fouling experiments were dried naturally or stored in ultra-pure water for further characterization.

In the desalination experiments, the initial solution in dilute compartment was 500 mL of 0.1 M NaCl and a certain concentration of SDS (50~200 mg/L), and the feed solution in the concentrated

compartment was 500 mL of 0.1 M NaCl, and the solutions in the two different beakers were circulated through the dilute and concentrated compartments, respectively, and then flowed into the two beakers. The desalination experiment was performed at a voltage of 4.0 V. The other experimental conditions of the desalination experiment were similar to that of the fouling experiment. The electrical conductivity of the solution in dilute compartment was measured online by a conductivity meter (S230, SevenCompact, Mettler Toledo) connected with a computer. Besides, the total organic carbon (TOC) of the solution in the dilute and concentrated compartments was measured by a TOC analyzer (Shimadzu TOC-V_{CPH}, Japan) to characterize the concentration change of SDS in the solution before and after the desalination experiment. The desalination experiment at a certain concentration of SDS was also repeated for three times.

2.3 Membrane cleaning

After the fouling experiment, the fouled AEM was taken out from the ED stack. The area electrical resistance of the fouled AEM was measured immediately by LCR Meter (NF2321, Japan) set at 100 kHz, 100 mV in 0.5 M NaCl at 25 °C and the details were described in the previous study [21, 22]. Thereafter, the membrane cleaning was performed by soaking the three fouled AEMs of equal size into ultra-pure water, 0.28 M HCl and 0.25 M NaOH at room temperature, respectively. The electrical resistance of the fouled AEMs after cleaned in the different solutions was measured at the same period of soaking time and the electrical resistance value of all the AEMs was the average of the five measurements.

2.4 Characterization of membrane properties and the foulant SDS

The ion exchange capacity (IEC) of AEM was expressed as millimole per gram of AEM (mmol/g chloride-ion-form dry AEM) and determined as follows. A sample of AEM with a size of

20 mm×20 mm was immersed in 20 mL of 1 M NaCl for 6 h. Then the sample was washed with ultra-pure water to remove the residual NaCl on the AEM surface and thereafter was put into conical flask with 30 mL of 1 M Na₂SO₄ for 12 h. After that, the sample was washed with ultra-pure water and then was wiped up with filter paper. The AEM was dried in an oven at 60 °C for 24 h and weighted as m_b . The Na₂SO₄ solution and washed water was titrated using 0.1 M AgNO₃ by adding three drops of potassium dichromate before titration and the number of moles of Cl⁻ was calculated as n_a . The IEC was obtained as:

$$IEC = \frac{n_a}{m_b} \quad (1)$$

The IEC value of AEM was the average of three repeated measurements.

The structure of AEM was characterized by ATR-FTIR using T27-Hyperion-Vector22 (Bruker, Germany) from 4000 to 600cm⁻¹. The surface morphology of AEM was observed by field emission scanning electron microscopy (FE-SEM, Hitachi SU8020, Japan) at an accelerating voltage of 5 kV and a current of 10 μA. To examine the distribution of the elements on the AEM surface, EDS was used to obtain the element mapping at an accelerating voltage of 20 kV and a current of 10 μA with a magnification of 5,000. The surface roughness of AEMs was measured by AFM using Bruker Multimode 8 (Veeco, Germany) with a Nanoscope IV controller in tapping mode. The details were described in the literature [22].

The critical micelle concentration (CMC) of SDS in the presence of 0.1 M NaCl in solution at 25 °C was determined by conductivity measurement using a conductivity meter (S230, SevenCompact, Mettler Toledo). The zeta potential of SDS was measured using the Particle Analyzer (DelsaNano C, Beckman Coulter, America) to characterize its surface potential.

2.5 Electrochemical impedance spectroscopy of AEMs

EIS measurement is performed by applying an alternating sinusoidal current $I(t) = I_0 \sin(\omega t + \varphi) = I_0 e^{j(\omega t + \varphi)}$ of a known frequency (f), angular frequency ω and voltage amplitude (E_0) to a membrane system, then the phase shift φ is measured and the voltage response is expressed as $E(t) = E_0 \sin \omega t = E_0 e^{j\omega t}$. Impedance is represented by a phasor and calculated according to Ohm's law as:

$$Z = \frac{E(t)}{I(t)} = \frac{E_0 e^{j\omega t}}{I_0 e^{j(\omega t + \varphi)}} = |Z| e^{-j\varphi} = |Z| \cos \varphi - j|Z| \sin \varphi \quad (2)$$

where $E(t)$ is the voltage at a certain time, E_0 is the voltage in phase, $I(t)$ is the alternating current at a certain time, I_0 is the alternating current in phase, φ is the phase shift and j is the imaginary unity ($j = \sqrt{-1}$). The impedance of the membrane system is defined as:

$$Z = \frac{1}{G + j\omega C} \quad (3)$$

where G is the conductance quantifying the ability of the system to conduct electric charge and C is the capacitance quantifying the capacity of the system to store the charge.

For an electrically homogeneous system G and C are independent of frequency. However, when the pristine AEM is immersed in an electrolyte solution, the electrical double layers and the diffusion boundary layers will be formed between the AEM and solution, therefore, the total G and C of the heterogeneous AEM system are strongly dependent on frequency [14, 23-25]. This dependency can be utilized to assess the electrochemical properties of the pristine AEM. For the fouled AEM, the additional SDS fouling layer might be formed or SDS molecular might block the membrane channel, which can cause the change of the total G and C of the heterogeneous AEM system. Therefore, the electrochemical properties of the fouled AEM can be examined according to the change of G and C of the heterogeneous AEM system at different frequencies. The Maxwell-Wagner model is fitted according to the measured G and C , and is used to yield an

equivalent circuit characterizing the conductance and capacitance properties of electrically distinct layers existing in the different AEM system [26]. Therefore, the total impedance of the AEM system can be defined as:

$$Z = \sum_{k=1}^K Z_k = \sum_{k=1}^K \frac{1}{G_k + j\omega C_k} \quad (4)$$

where G_k and C_k denote, respectively, the conductance and capacitance of the model, and Z_k is the impedance of the k_{th} layer such as the electrical double layer and the diffusion boundary layer, etc. Therefore, Eq. (3) can determine the individual contribution of the different layers (i.e. G_k and C_k) to the total impedance of the different AEM system, from which the effects of the membrane fouling because of SDS and subsequent cleaning on the electrochemical properties of AEM can be studied further.

In this work, the EIS of the pristine AEM and fouled AEMs was measured using an Autolab electrochemical workstation (PGSTAT302N, Metrohm) with a four-electrode setup, shown in Fig. 1. A couple of platinum sheet electrodes were used as the working electrode (WE) and the counter electrode (CE), respectively; and two saturated Ag/AgCl electrodes connected with Luggin capillaries, which were placed on both sides of AEM were used as the reference electrode (RE) and the sensitive electrode (SE), respectively, to measure the EIS of different membrane systems. The impedance contributions from all the electrode-solution interfaces can be avoided by using four-electrode measurements [23]. A 10 mV amplitude sinusoidal potential perturbation was applied ranging from 100 kHz to 1 mHz at a rate of 60 measurements frequencies in 0.1 M NaCl solution at 25 ± 1 °C.

Fig. 1. Schematic diagram of the experimental setup used for electrochemical impedance spectroscopy (EIS)

measurements (WE: working electrode, CE: counter electrode, SE: sensitive electrode, RE: reference electrode;

AEM: anion exchange membrane).

3. Results and discussion

3.1 Analysis of membrane fouling

3.1.1 Characterization of the foulant SDS

The micelle formation of SDS, which might affect the fouling behavior on the AEM, was related closely to the concentration of electrolyte and SDS. The CMC could be measured by different methods such as surface tension, UV absorbance, conductivity, turbidity and etc. [27]. In this work, the CMC of SDS in 0.1 M NaCl solution at 25 °C was determined by conductivity measurement and the result was shown in Fig. 2. It was found that the CMC of SDS in 0.1 M NaCl solution at 25 °C was 389 mg/L (1.35 mM), which was approximate to the result (1.33 mM) determined by surface tension measurement in the literature [28].

Fig. 2. Determination of the critical micelle concentration of SDS in 0.1 M NaCl solution at 25 °C.

The surface potential of SDS of different concentration in 0.1 M NaCl solution was determined according to the zeta potential measurement and the result was shown in Fig. 3. It indicated that the surface potential of SDS depended on its concentration and was more negative at the higher concentration of SDS, especially higher than CMC (389 mg/L). The results implied that the higher concentration of SDS might result in the fouling of AEM with positive charge more easily because of the stronger electrostatic interaction between the SDS and AEM.

Fig. 3. Zeta potential of SDS as a function of its concentration in 0.1 M NaCl solution.

3.1.2 The effect of the concentration of SDS on membrane fouling

During electrodialysis, the change of potential difference (ΔE) of AEM at the constant current could be used to evaluate the membrane fouling as the fouling of AEM caused an increase of electrical resistance. Fig. 4 showed the ΔE change of AEM during the fouling experiment to examine the effect of the initial concentration of SDS in the feed solution on the membrane fouling. It was seen that the ΔE of AEM began to increase slightly after 60 min and the final ΔE value of AEM exhibited a slight increase after 180 min when the feed solution contained 50 mg/L SDS. When the concentration of SDS increased to 100 and 150 mg/L, the ΔE of AEM began to increase after ~20 min and the difference between the ΔE of AEM under the two concentrations of SDS became more obvious with the extension of time. As the concentration of SDS in the feed solution increased to 200 mg/L, the ΔE of AEM increased sharply at the beginning of the fouling experiment and reached to 3.0 V after 100 min. The results indicated that with the increase of the concentration of SDS, the increased rate of the ΔE of AEM was faster and the ΔE of AEM was higher at the end of the experiment, which meant the higher SDS concentration in the feed solution could cause the severer fouling of AEM.

Fig. 4. The potential difference (ΔE) of AEM as a function of time during the fouling experiment of electrodialysis and the concentration of SDS in the feed solution was 50, 100, 150 and 200 mg/L, respectively.

In electrodialysis, the foulant SDS with strong charged groups could migrate from the bulk solution to the AEM surface under the electric field. However, the migration rate of SDS across the AEM was much slower than that in the bulk solution because of the long alkyl chain contained in SDS, which would lead to the accumulation of SDS in the interface between AEM and solution. It was inferred that the actual concentration of SDS on the AEM surface in ED stack could reach to even exceed its CMC (389 mg/L), although the concentration of SDS in the feed solution was all below CMC in the different fouling experiments. Therefore, the different types of micelles such as granular, rod-like and lamellar might be formed related to the different concentration of SDS contained in the feed solution. Similar to the results reported in literature [29], it was inferred that the lower initial concentration of SDS such as 50 mg/L in the feed solution might lead to the formation of some granular and rod-like micelles, which could result in the heterogeneous fouling on the AEM surface. With the increase of SDS concentration in the feed solution, more lamellar micelles could be formed in the interface between solution and AEM, which might lead to the formation of the dense fouling layer of SDS on the AEM surface. The different fouling behavior of SDS on the AEM surface could cause the difference in the electrical resistance of the fouled AEMs when the concentration of SDS was 50, 100, 150 and 200 mg/L in the feed solution, respectively. Therefore, the potential difference (ΔE) of AEM exhibited the obvious difference when the feed solution contained different concentration of SDS in electrodialysis.

In addition, as shown in Table 2, the area electrical resistance of the fouled AEMs by different concentration of SDS exhibited a various increase, which was consistent with that shown in Fig. 4; however, the ion exchange capacity of the different fouled AEMs exhibited no differences from that of the pristine AEM (2.19 ± 0.0235 mmol/g) as shown in Table 2. To further analyze the effect

of the concentration of SDS on membrane fouling, surface properties of the fouled AEM were also characterized.

Table 2

The area electrical resistance and the ion exchange capacity of the pristine AEM and the fouled AEMs by different concentration of SDS.

C _{SDS} /mg/L	0	50	100	150	200
Area electrical resistance ($\Omega \cdot \text{cm}^2$)	2.80±0.076	9.38±0.364	112.18±10.23	134.47±10.70	209.29±10.55
Ion exchange capacity (mmol/g)	2.19±0.0235	2.17±0.0192	2.03±0.0129	2.21±0.0133	2.01±0.0173

3.1.3 The effect of the concentration of SDS on ED performance

Fig. 5 showed the electrical conductivity of the solution in dilute compartment as a function of time. The electrical conductivity of the solution without the foulant SDS in dilute compartment decreased from approximately 10.78 mS/cm to 7.27 mS/cm after 180 min. However, the desalination rate of the feed solution containing 50 mg/L SDS began to slow down after 60 min and the electrical conductivity of the solution decreased to ~7.5 mS/cm after 180 min. The desalination rate began to slow down at the shorter time with the increase of SDS concentration in the solution and the electrical conductivity of the solution decreased to ~8.2, ~9.09 and ~10.3 mS/cm at the end of the desalination experiment, respectively, for 100, 150 and 200 mg/L SDS contained in the feed solution. The results meant that the higher concentration of SDS would accelerate the fouling of AEM, which restrained the transmembrane migration of Cl^- and Na^+ ions significantly. The main reason was that the current density through the system became lower at the constant voltage since the electrical resistance of the fouled AEM was larger, which resulted from the higher concentration of SDS contained in the feed solution, hence the migrated amount of Cl^- and Na^+ ions became smaller. Besides, it was inferred that a small amount of SDS could block the

channel of AEM because of the large volume of SDS when entering into the AEM under the electric field, which could restrict the migration of Cl^- ions into the concentrated compartment. Therefore, the desalination performance of AEM was deteriorated severely by membrane fouling from SDS contained in the feed solution in dilute compartment, especially at the higher concentration.

Fig. 5. Electrical conductivity of the solution in dilute compartment during ED desalination experiment and the concentration of SDS in dilute compartment was 50, 100, 150 and 200 mg/L, respectively.

To further investigate the fouling of AEM from SDS, the initial and end concentration of SDS in the dilute and concentrated compartments was analyzed by the measurement of TOC during the desalination experiments. The results in Table 3 showed that partial SDS could migrate to the concentrated compartment through AEM under the external electric field and the initial concentration of SDS had almost no influence on the migrated amount of SDS to the concentrated compartment. According to the concentration change of SDS in the dilute and concentrated compartments, it was seen that small amount of SDS could be adsorbed on the AEM surface and even block the membrane channel. When the concentration of SDS was above 50 mg/L, the adsorbed amount of SDS on the AEM increased significantly to cause the severer fouling of AEM

in the ED process. Therefore, the higher initial concentration of SDS led to the severer deterioration of desalination performance of AEM.

Table 3

TOC of the initial and end solution in the dilute (D) and concentrated (C) compartments during the desalination experiments. (1, 2, 3 and 4 represented the four desalination experiments in which the initial concentration of SDS in dilute compartment was 50, 100, 150 and 200 mg/L, respectively.)

	1		2		3		4	
	D	C	D	C	D	C	D	C
TOC in initial solution/mg/L	29.25±0.52	0	52.44±0.39	0	75.52±0.58	0	101.92±0.76	0
TOC in end solution/mg/L	13.77±0.24	12.43±0.13	24.21±0.48	14.36±0.12	48.95±0.34	14.36±0.21	77.65±0.32	13.33±0.14

3.1.4 SEM-EDS of the fouled AEM

To further analyze the fouling of AEM from SDS, the physicochemical properties of the fouled AEMs were characterized by spectrum analysis. Fig. 6 showed the SEM images of the pristine AEM and the fouled AEMs by different concentration of SDS. It was observed that the surface morphology of the fouled AEMs exhibited obvious differences from that of the pristine AEM. The surface of the fouled AEM by 50 mg/L SDS was covered by the granular and flake-like foulant. With the increase of the concentration of SDS in the feed solution, the fouling layer on the surface of the fouled AEMs was much denser and the surface morphology of the fouled AEMs had nearly changed completely.

It was inferred that when 50 mg/L SDS was contained in the feed solution, the lower actual concentration of SDS on the AEM surface was beneficial to the formation of the granular and rod-like micelles [29], which might lead to the heterogeneous membrane fouling on the AEM surface shown in Fig. 6 (b). The SEM images shown in Fig. 6 (c-e) indicated that, with the

increase of the concentration of SDS in the feed solution, the enrichment of more SDS in the interface between AEM and solution might make the actual concentration of SDS to reach to or above its CMC under the electric field, causing the formation of the lamellar micelle layer on the AEM surface, which was beneficial to the formation of a dense SDS fouling layer.

Fig. 6. SEM images of the pristine AEM (a) and the fouled AEMs by 50 mg/L SDS (b), 100 mg/L SDS(c), 150 mg/L SDS (d) and 200 mg/L SDS (e) in the feed solution.

3.2 Cleaning of the fouled AEM

After 180 min of the fouling experiment in which the feed solution contained 150 mg/L SDS and 0.1 M NaCl and was kept at 25 °C, the fouled AEM was cleaned in ultra-pure water, 0.28 M HCl solution and 0.25 M NaOH solution at room temperature, respectively. Fig. 7 indicated the electrical resistance changes of the pristine AEM and the cleaned AEM soaked in different

cleaning solution. It was found that the electrical resistance values of the pristine AEM soaked in different solutions were nearly unchanged during the whole soaking process. In contrast, the electrical resistance of the fouled AEM exhibited an obvious decrease with the extension of soaking time. The electrical resistance of the fouled AEM before soaked was $134.47 \pm 10.70 \Omega \cdot \text{cm}^2$, which was much higher than that of the pristine AEM. When soaked in the different solutions for 1 day, the electrical resistance values of the fouled AEMs decreased to 23.26 ± 0.449 , 27.17 ± 0.909 and $40.17 \pm 3.23 \Omega \cdot \text{cm}^2$, respectively, for ultra-pure water, HCl and NaOH. And the extension of soaking time was favorable to reducing the electrical resistance and restoring performance of the fouled AEM. After soaked for 7 days, the electrical resistance of the fouled AEMs in the different cleaning solutions all could reach approximately $7.5 \Omega \cdot \text{cm}^2$, but was still higher than that of the pristine AEM. The electrical resistance value of the fouled AEM decreased by 94.5% after soaked for 7 days, which meant that most SDS on the AEM could be removed by the membrane cleaning, but the properties of the fouled AEMs by SDS couldn't be restored completely after cleaned. Therefore, the membrane fouling from SDS belonged to the partially irreversible one, which was consistent with the result reported by the literature [11]. It was inferred that the partial SDS might enter into the interlayer of AEM, which was difficult to be removed completely by membrane cleaning using the present cleaning solutions, thus the electrical resistance of the cleaned AEM was still higher than that of the pristine AEM.

As shown in Fig. 7, the electrical resistance of the cleaned AEMs in ultra-pure water was similar to that in HCl after 7 days, and was slightly lower than that in NaOH. The results indicated that the cleaning effect of ultra-pure water on the fouled AEM by SDS was similar to that of HCl solution, and better than that of NaOH solution. It was inferred that the quaternary ammonium

groups of AEM might occur the Hofmann elimination reaction and nucleophilic substitution under the strong alkaline environment, which could cause the structure and morphology of AEM to change and the conductivity of AEM to decrease. The similar result was also reported by the researcher [30]. In fact, many reports indicated that the acid cleaning used to remove the membrane fouling was targeted to eliminate inorganic fouling from the Ca^{2+} , Mg^{2+} ions because of the better solubility of metal complex in acid solution [12, 31]. However, the SDS fouling layer on the AEM could be effectively removed by cleaned in ultra-pure water and HCl in this study. It was inferred that the electrostatic interaction between the organic foulant SDS and the AEM was weak; moreover, the SDS fouling layer could be soluble in ultra-pure water and HCl solution. Compared with NaOH, ultra-pure water and HCl were more suitable to be used in cleaning the fouled AEM caused by SDS.

Fig. 7. Electrical resistance of the pristine AEM and the fouled AEM soaked in ultra-pure water (H_2O), 0.28 M HCl and 0.25 M NaOH, respectively (fouling experiment condition: 150 mg/L SDS, 0.1 M NaCl at $25 \pm 1 \text{ }^\circ\text{C}$ for 180 min).

3.3 Characterization of the fouled and cleaned AEMs

The fouled AEM was obtained by the fouling experiment and the experimental condition was

described in Section 3.2. In order to avoid the effect of HCl and NaOH on the properties of AEM, the properties of the fouled AEM after cleaned in ultra-pure water were further characterized to investigate the effects of membrane cleaning. The fouled AEM before cleaned was named as M0, and the cleaned AEMs in ultra-pure water for 2 days and 7 days were labeled as M2 and M7, respectively. These membranes were chosen as the representative samples, whose properties were characterized by ATR-FTIR, SEM-EDS and AFM.

3.3.1 ATR-FTIR

Fig. 8 showed the IR spectra of the pristine AEM and the fouled AEM before and after cleaned in ultra-pure water. The pristine AEM presented several peaks at 3400 and 2922, 2852 cm^{-1} , corresponding to O-H stretching vibration and C-H ($-\text{CH}_2$ and $-\text{CH}_3$) stretching vibration. The characteristic peak at 1637 cm^{-1} was attributed to C=C stretching vibration, and the peaks at 1480, 1080 cm^{-1} were attributed to C-H bending vibration and C-N stretching vibration of quaternary ammonium group [32]. The new peaks at 1220 and 1030 cm^{-1} occurred in the spectra of M0, which should correspond to the anti-symmetric stretching vibration and symmetric stretching vibration of sulfonic group, respectively [33]; moreover, the characteristic peaks of C-H ($-\text{CH}_2$ and $-\text{CH}_3$) at 2922 and 2852 cm^{-1} became stronger than that of the pristine AEM, which were related closely to the alkyl chain of SDS, demonstrating that the foulant SDS was adsorbed on the AEM surface after fouled. The spectra of M2 and M0 exhibited no obvious difference, but the characteristic peaks of the foulant SDS of M7 became weaker than that of M0 and M2, which indicated that the partial SDS had been removed but not completely after cleaned in ultra-pure water for 7 days.

Fig. 8. ATR-FTIR spectra of the pristine AEM, the fouled AEM and the cleaned AEMs (fouling experiment condition: 150 mg/L SDS, 0.1 M NaCl at 25 ± 1 °C for 180 min; cleaning agent: ultra-pure water).

3.3.2 SEM-EDS

The surface morphology of the pristine AEM and the fouled AEMs cleaned in ultra-pure water for different time was shown in Fig. 9. It was seen that the surface morphology exhibited obvious differences among the fouled AEMs, the cleaned AEMs and the pristine AEM. The surface of M0 was covered with the dense fouling layer with many uneven wrinkles, causing the sharp increase of the electrical resistance (shown in Fig. 7). The fouling layer of M2 became loosened and many nubbly, granular foulants appeared on the surface of the fouled AEM after soaked in ultra-pure water for 2 days. After soaked for 7 days, the most nubbly and granular foulants on the surface of the fouled AEM disappeared and the surface morphology of M7 was similar to that of the pristine AEM, but the surface of M7 was still covered partly with the flake-like foulant, which couldn't be removed completely by soaked in ultra-pure water. It was inferred that the electrostatic interaction and the affinity interaction between the fouling layer and AEM wasn't strong enough that the fouling layer on the AEM surface would be destroyed and most SDS was dissolved in water again when the fouled AEM was immersed in ultra-pure water; therefore, the fouling layer became

loosened even disappeared with the extension of cleaning time.

Fig. 9. SEM images of the pristine AEM, the fouled AEM and the cleaned AEMs (fouling experiment condition: 150 mg/L SDS, 0.1 M NaCl at 25 ± 1 °C for 180 min; cleaning agent: ultra-pure water).

EDS was utilized to examine the element composition and obtain the element mapping on the surface of the pristine and fouled AEMs. The results in Table 4 and Fig. 10 indicated that, compared with that of the pristine AEM, the content of carbon reduced but the content of oxygen and sulfur exhibited obvious increase on the surface of M0 and the element composition of M2 was similar to that of M0, which meant that most SDS was still adhered to the surface of AEM after soaked in ultra-pure water for the shorter time. However, after soaked in ultra-pure water for 7 days, the relative content of the elements of sulfur and oxygen of M7 decreased from 2.66% and 6.74% to 1.89% and 3.29%, respectively, which also indicated that most SDS was removed from the surface of the fouled AEM, which was consistent with the results obtained by ATR-FTIR and SEM analyses. Besides, as shown in Fig. 10, the elements of carbon, oxygen and sulfur were

distributed relatively uniformly on the surface of M0, M2 and M7, indicating that the foulant SDS adsorbed on the membrane was also relatively uniform, which was closely related to the homogeneous surface of pristine AEM.

Table 4

Surface element compositions of the pristine AEM, the fouled AEM and the cleaned AEMs.

Type	The wt% of main elements contained in different AEMs			
	C	O	Cl	S
Pristine AEM	84.17	1.83	14.00	0.14
M0	79.41	6.74	11.19	2.66
M2	76.93	6.57	13.87	2.63
M7	81.41	3.29	13.41	1.89

Fig. 10. The carbon, oxygen, sulfur elements mapping of the pristine AEM, the fouled AEM and the cleaned AEMs

obtained by EDS (fouling experiment condition: 150 mg/L SDS, 0.1 M NaCl at 25±1°C for 180 min; cleaning

agent: ultra-pure water).

3.3.3 AFM

Fig. 11 showed the AFM 3D images of the pristine AEM, the fouled AEMs before and after cleaned. The surface morphology of M0, M2 exhibited significant differences from that of the pristine AEM, while the surface morphology of M7 was similar to that of the pristine AEM. The results of AFM analyses were consistent with that of SEM. The roughness value of the pristine AEM, M0, M2 and M7 was 25.7, 30.3, 33.4 and 23.8 nm, respectively. The result indicated that the fouling of AEM from SDS would cause the increase of the surface roughness of AEM, which could be reduced by the membrane cleaning. It was inferred that the SDS fouling layer might be adsorbed unevenly on the AEM surface in the form of different micelles, which could cause the increase of the roughness of the fouled AEM. After cleaned for enough time, most of the heterogeneous fouling layer on the AEM surface was almost removed completely and made the roughness of the cleaned AEM reduced. The small amount of residual foulant SDS in the cleaned AEM might be kept in the crack and defects of AEM and made the surface of AEM smoother.

Fig. 11. AFM 3D images of the pristine AEM, the fouled AEM and the cleaned AEMs (fouling experiment condition: 150 mg/L SDS, 0.1 M NaCl at 25 ± 1 °C for 180 min; cleaning agent: ultra-pure water).

3.4 EIS analysis of AEMs

3.4.1 EIS analysis of the fouled AEMs

Fig. 12 (1) showed the impedance spectra of the pristine AEM and the fouled AEMs by different concentration of SDS in electrodialysis. In Nyquist plot of the cell with the pristine AEM, two arcs appeared on the impedance spectrum, which was divided into a geometric arc determined by the geometric capacity at high frequencies (above 1000 Hz) and a diffusional arc of finite-length Warburg-type impedance at low frequencies (below 1000 Hz), which was similar to that reported by Literature [14, 15]. It was inferred that the first geometric arch at high frequencies was associated with the charge transport onto the surface of electrode and the ion transport in the electrical double layer between the solution and AEM, and the right intersection point of the Nyquist plot with axis Z' was related to the total ohmic resistance (R_{SM}) of the membrane and solution; and the second diffusional arc at low frequencies was related to the migration of ions through the diffusion layer, electrical double layer and the AEM, which was also demonstrated by comparing the impedance spectra of the systems with the pristine AEM and without the AEM.

The notable difference appeared on the impedance spectra of the fouled AEMs and the pristine AEM as shown in Fig. 12 (1). The diameter of the first geometric arch at high frequencies of the fouled AEMs by SDS increased gradually with the increase of the concentration of SDS in the feed solution and the R_{SM} value increased significantly, which meant that the electrical resistance of the fouled AEMs exhibited a larger increase at a higher concentration of SDS. Besides, the shape of the impedance spectra at low frequencies of the fouled AEMs by SDS had changed completely. The additional arch B (shown in Fig. 12 (1)) appeared following the second arch at low frequencies on the impedance spectrum of the fouled AEM (50 mg/L SDS), which was

inferred that the SDS fouling layer (shown in Fig. 6) deposited on the AEM surface or the blockage of SDS molecular in the AEM channel restricted the ionic transport, which led to the formation of the additional arch on the impedance spectrum. The similar result was observed on the impedance spectrum of the fouled membranes by BSA over the limiting current density [19]. As the concentration of SDS was above 100 mg/L, the second diffusional arc at low frequencies of the fouled AEMs almost disappeared, and the imaginary part of the impedance of the fouled AEMs was approximately zero and the real part exhibited a decrease with the frequency decreasing. It was inferred that the sharp increased electrical resistance of the fouled AEMs was the dominant part of the total resistance of the cell and the dense SDS layer appeared on the fouled AEMs shown in Fig. 6, which had restricted completely the transmembrane migration of the ions through the fouled AEMs; therefore, the second diffusional arc at low frequencies representing the process of the ion migration through the AEM disappeared. It was inferred that the decrease of the real part of the impedance of the fouled AEM might result from the partial removal of SDS fouling layer adsorbed on the fouled AEM when immersed in electrolyte solution during the measurement of EIS, which was also demonstrated in Fig. 7.

Fig. 12. Electrochemical impedance spectroscopy of (1) the pristine AEM and the fouled AEMs by different concentration of SDS (fouling experiment condition: 0.1 M NaCl at 25 ± 1 °C); (2) the cleaned AEMs for different

soaking time (fouling experiment condition: 150 mg/L SDS, 0.1 M NaCl at 25 ± 1 °C for 180 min; cleaning agent: ultra-pure water). The values were obtained from measurements in 0.1 M NaCl solution at 25 ± 1 °C.

3.4.2 EIS analysis of the cleaned AEMs

The effect of membrane cleaning on the electrochemical properties of the fouled AEMs was examined by EIS analysis and the results were shown in Fig. 12 (2). It was found that with the cleaning time extended, the shape of the impedance spectra of the cleaned AEMs became more similar to that of the pristine AEM. The diameter of the first geometric arch at high frequencies of the cleaned AEMs decreased obviously, and the second diffusion arch at low frequencies appeared again after cleaned. However, the additional arch B (shown in Fig. 12 (2)) caused by the SDS fouling layer still existed following the second arch at low frequencies on the impedance spectrum of M2. The EIS indicated that the transmembrane migration of the ions through the cleaned AEM M2 might be only restored partly, and the fractional SDS remaining on the AEM surface (shown in Fig. 9) still restricted the ionic transport through the AEM after soaked in ultra-pure water for 2 days.

After soaked in ultra-pure water for 7 days, the shape of the second diffusion arch at low frequencies was similar to that of the pristine AEM, which demonstrated that the transmembrane migration of the ions through M7 wasn't almost affected by the flake-like foulant on the AEM (shown in Fig. 9) even though the electrical resistance of M7 was still a little higher than that of the pristine AEM. The results indicated that the dense fouling layer on the fouled AEM was the dominant factor in restraining the transmembrane migration of the ions through AEM but the dense fouling layer could be removed partly by membrane cleaning.

3.4.3 Equivalent circuit of the AEM systems

To obtain the quantitative analysis of the impedance spectra, the equivalent circuit fitted using NOVA 1.9 software was used to characterize the electrochemical properties of the different AEM systems. As was depicted in Section 2.5, the system with a pristine AEM immersed in electrolyte solution contained the electrical double layer and diffusion boundary layer besides the membrane and solution. Therefore, the equivalent circuit [R(RQ)(RQ)] was proposed to characterize the process of the migration of the ions through the AEM, electrical double layer and diffusion layer [16-19]. The fitting results of the pristine AEM system were shown in Fig. 13 (1) and Table 5 (1). The results indicated that the membrane resistance could be obtained by subtracting the solution resistance R_s (measured without the membrane, $R_s=32.0 \Omega \cdot \text{cm}^2$) from the resistance of membrane and solution R_{SM} . In the system with the pristine AEM, the diffusion boundary layer resistance R_{dbl} was about $2.49 \Omega \cdot \text{cm}^2$ and had a slightly lower contribution than the membrane resistance. The electrical double layer resistance R_{edl} , about $0.341 \Omega \cdot \text{cm}^2$, was relatively small, which had only a very minor contribution to the overall resistance of the system with the pristine AEM.

Considering the effect of the SDS fouling layer on the transmembrane migration of the ions through the AEM, an additional parallel element of resistance and capacitance was added to the originally proposed equivalent circuit (shown in Fig. 13 (1)), and the fitting results of the system with the fouled AEM (by 50 mg/L SDS) were shown in Fig. 13 (2) and Table 5 (2). It was found from the impedance analyses that, the membrane resistance exhibited obvious increase, but the resistances of the diffusion boundary layer and electrical double layer were almost unchanged. The results meant that the resistance of the fouling layer of SDS made a significant contribution to the overall resistance of the system with the fouled AEM. The fitting results of the modified equivalent circuit [R(RQ)(RC)(RQ)] showed good agreement with the real impedance spectra of

the fouled AEM, indicating that the SDS fouling layer could be reasonably explained by the additional parallel element of resistance and capacitance.

The impedance spectra of the system with the cleaned AEMs for different time were also fitted using the different equivalent circuit. Because the SDS fouling layer still existed on the cleaned AEM M2 due to the shorter cleaning time, the additional arch following the second arch was still presented at low frequencies on the impedance spectrum of M2. It was proved that the equivalent circuit $[R(RQ)(RC)(RQ)]$ also presented the good agreement with the real impedance spectra of the M2, shown in Fig. 13 (2) and Table 5 (2). The results showed that, the membrane resistance of M2 was still much higher than that of the pristine AEM, and the electrical double layer resistance also exhibited a slight increase. Accordingly, the resistance of the SDS fouling layer had still a major contribution to the overall resistance of the system with the cleaned AEM M2.

With the extension of the cleaning time, the additional fouling arch on the impedance spectrum of M7 disappeared and the EIS of M7 could be fitted better using the originally proposed equivalent circuit for the system with the pristine AEM. The results shown in Fig. 13 (1) and Table 5 (1) indicated that, the membrane resistance of M7 had decreased significantly after cleaned for enough time, but was still a little higher than that of the pristine AEM; moreover, the diffusion boundary layer resistance was also higher than that of the pristine AEM. It was inferred that the partial foulant SDS on the AEM could make the diffusion boundary layer thicker and the resistance of ionic migration increased because of the electrostatic repulsion between Cl^- and SDS. The fitting results of the impedance spectrum of M7 presented the good consistency with the experimental data, which also indicated the transmembrane migration of the ions through the cleaned AEM M7 was almost unaffected by the residual flake-like foulant on the AEM, which

confirmed further the results shown in Section 3.4.2.

Fig. 13. The fitting results of the electrochemical impedance spectroscopy at low frequencies of (1) the pristine AEM and the cleaned AEM M7; and (2) the fouled AEM by 50 mg/L SDS and the cleaned AEM M2 according to the different equivalent circuit.

Table 5

Fitting results of the impedance spectra shown in Fig. 13 obtained in the AEM systems according to the different equivalent circuits.

(1)

	R_{SM}	R_{edl}	Q_{edl}		R_{dbl}	Q_{dbl}	
	$/\Omega \cdot cm^2$	$/\Omega \cdot cm^2$	$Y_{edl}/S \ s^n/cm^2$	n	$/\Omega \cdot cm^2$	$Y_{dbl}/S \ s^n/cm^2$	n
Pristine AEM	34.9	0.341	7.75	0.756	2.49	29.9	0.889
M7	39.6	0.205	10.1	0.836	4.83	19.0	0.787

(2)

	R_{SM}	R_{edl}	Q_{edl}		R_{SDS}	C_{SDS}	R_{dbl}	Q_{dbl}	
	$/\Omega \cdot cm^2$	$/\Omega \cdot cm^2$	$Y_{edl}/S \ s^n/cm^2$	n	$/\Omega \cdot cm^2$	F/cm^2	$/\Omega \cdot cm^2$	$Y_{dbl}/S \ s^n/cm^2$	n
SDS50	39.6	0.600	5.03	0.463	0.844	64.3	2.40	96.4	0.913
M2	68.3	1.12	1.73	0.661	1.32	35.0	2.10	141	0.916

R_{SM} was the resistance of the solution and membrane ($R_S=32.0 \pm 0.1 \ \Omega \cdot cm^2$), R_{edl} was the resistance of the electrical double layer, Q_{edl} was the capacitance of the electrical double layer (constant phase element-non-ideal capacitor), R_{dbl} was the resistance of the diffusion boundary layer, Q_{dbl} was the capacitance of the diffusion boundary layer

(constant phase element-non-ideal capacitor), n was the parameter for the constant phase element (Q), R_{SDS} was the resistance of the SDS fouling layer, C_{SDS} was the capacitance of the SDS fouling layer.

4. Conclusions

The fouling of AEM caused by different concentrations of SDS contained in the solution was characterized during electrodialysis. Surface morphology analyses of the fouled AEMs showed that the higher concentration of SDS could cause the formation of a dense SDS fouling layer on the AEM surface, which led to a sharp increase of the electrical resistance during the fouling experiment. The desalination performance of the fouled AEM by SDS was also deteriorated obviously at higher concentration of SDS. The AEM fouling from SDS could almost restrict completely the transmembrane migration of ions during electrodialysis when the concentration of SDS in the feed solution was above 100 mg/L.

The membrane cleaning experiments showed that the SDS fouling layer on the AEM could be effectively removed in the different solutions. The cleaning effect of ultra-pure water on the fouled AEM by SDS was similar to that of HCl solution, but was better than that of NaOH solution. The electrical resistance of all the fouled AEM decreased gradually with the extension of cleaning time, but the value of the fouled AEM after cleaned for 7 days was still higher than that of the pristine AEM, which meant that the fouling of AEM from SDS was partial irreversible. The result was also proved by the analyses of ATR-FTIR, SEM and AFM.

According to the EIS results, the formation of the additional arch on the impedance spectrum of the fouled AEMs by 50 mg/L SDS indicated that the SDS fouling layer could restrict the ionic migration through AEM. At the higher concentration of SDS, the increased diameter of the first geometric arch at high frequency and the disappearance of the second diffusional arch at low

frequency meant that the dense SDS fouling layer led to a sharp increase of membrane resistance and restricted completely the ionic migration through the AEM. EIS analyses of the cleaned AEMs further demonstrated that the dense SDS fouling layer could be removed effectively by cleaned for enough time, and the transmembrane migration of the ions through the AEM was almost not restricted though the electrical resistance of the cleaned AEM was still higher than that of the pristine AEM.

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Nomenclature

ED	Electrodialysis
IEM	Ion exchange membrane
AEM	Anion Exchange Membrane
SDS	Sodium Dodecyl Sulfate
BSA	Bovine Serum Albumin
SDBS	Sodium Dodecyl Benzene Sulfonate
EIS	Electrochemical Impedance Spectroscopy
ΔE	Potential Difference (V)
G	Conductance (S/m^2)
C	Capacitance (F/m^2)

R_{SM}	Resistance of the solution and membrane in the equivalent circuit ($\Omega \cdot \text{cm}^2$)
R_{edl}	Resistance of the electrical double layer in the equivalent circuit ($\Omega \cdot \text{cm}^2$)
R_{dbl}	Resistance of the diffusion boundary layer in the equivalent circuit ($\Omega \cdot \text{cm}^2$)
R_{SDS}	Resistance of the SDS fouling layer on the AEM in the equivalent circuit ($\Omega \cdot \text{cm}^2$)
C_{SDS}	Capacitance of the SDS fouling layer on the AEM in the equivalent circuit ($\Omega \cdot \text{cm}^2$)
Q_{edl}	Constant phase element parameter of the electrical double layer in the equivalent circuit
Q_{dbl}	Constant phase element parameter of the diffusion boundary layer in the equivalent circuit
n	constant phase element exponent

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