

Studies on textile effluent for desalination using electrodialysis and its membrane fouling analysis

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ABSTRACT

The reuse of the printing and dyeing wastewater is limited by its large chromaticity, high alkalinity, high chemical oxygen demand (COD_{Cr}), high salinity. In this study, electrodialysis, as a promising technology, was applied for the advanced treatment for printing and dyeing wastewater. With the Design-Expert software and Box–Behnken central composite design method, the optimal operating condition was: operating voltage 85 V, inlet flow rate 1,000 L/h, temperature 25°C, in which the energy consumption was 3.52 kW h/m³ and the desalination processing cost was 0.33 \$/m³. The characteristics of the desalination process and membrane pollution were further revealed and discussed. The maximum concentration was obtained at 15,000 mg/L during the concentrated water circulation. And the cation exchange membrane pollution was mainly calcium carbonate, while the anion exchange membrane pollution was organic. In addition, the reversal time fixed at 2 h could effectively reduce membrane fouling. The present work is expected to provide reference technical support for practical industrial applications.

Keywords: Electrodialysis; Printing and dyeing wastewater; Membrane fouling; Desalination; Optimization; Concentration effect

1. Introduction

Printing and dyeing industry is a large domestic industrial wastewater discharge, the daily discharge of which, according to incomplete statistics, is about 4×10^6 – 5×10^6 m³, accounting for 35% of the total industrial wastewater discharge [1]. With the continuous improvement of national discharge standards, industrial water price and product water quality requirements, it is increasingly important to solve the problems of printing and dyeing wastewater treatment and reuse [2]. Printing and dyeing wastewater is characterized by high chemical oxygen demand (COD_{Cr}), high alkalinity, large chromaticity and high salinity [3],

and the obstacle of removing the chromaticity and salinity needs to be overcome in the reuse of printing and dyeing wastewater [1].

Membrane technologies as reverse osmosis (RO) and electrodialysis (ED) have been widely employed to produce freshwater from seawater, industrial wastewater, and underground water by desalting it to a desired quality level [4–7], which have the advantages of operating at room temperature, concentrating and separating at the same time, low energy consumption, stable operation and so on [8].

For RO, high inlet quality is needed. Besides, a large amount of concentrated water [9] is to be discharged and further treated. In addition, RO usually relies on high pressure

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to realize the separation of water molecules and ions, which results in higher energy consumption than ED.

The ED, employing ion-exchange membranes (IEMs), with an electrical potential difference as the driving force, so that ions in solution migrate through the membranes (cation- and anion-exchange) in an electric field [10,11], can significantly increase the concentration of concentrated water, greatly improve the recovery rate of freshwater and reduce the emission of concentrated water. And it can also reduce the pollution of the IEM by frequent reversal, thus improving system operation stability [12]. In addition, the electro-dialysis process is suitable for the treatment of salt-containing water with 1,000–5,000 mg/L owing [13] to its low pressure, which is consistent with the water quality characteristics of printing and dyeing wastewater.

Based on the advantages of electro-dialysis above, many studies have been conducted. Tang and Ling [14] conducted an electro-dialysis desalination study on ammonia nitrogen wastewater, which reduced the concentration of ammonia nitrogen from 534.59 to 13 mg/L to meet the emission standards, meeting the demand for recycling. Peng and Tang [15] used electro-dialysis method to carry out the advanced treatment of wastewater containing NaBr. The study showed that after desalination treatment, the concentration of NaBr was low to 120 mg/L, and freshwater could be discharged directly or used as the industrial cooling water cycle. Chandramowleeswaran and Palanivelu [16] studied the desalination of printing and dyeing wastewater, which made the water outlet of the electro-dialysis water chamber meet the standard of water reuse of industrial water, with minimum energy consumption.

However, there are still few studies on advanced treatment of printing and dyeing wastewater by electro-dialysis and the research is not systematic enough, so this study aims to investigate the influence of multiple factors on the effect of electro-dialysis desalination and optimize the operating conditions of electro-dialysis machines, thus reducing the energy consumption. And also to further explore electro-dialysis desalination concentration characteristic of IEM, explore the pollutant characteristics of printing and dyeing outlets, characterize and analyze the characteristics of the membrane pollution, and expound the control of membrane fouling and cleaning, so as to lay a theoretical foundation for the electro-dialysis desalination industrialization application.

2. Experimental material and method

2.1. Water quality of influent (textile effluent)

Since the membranes used in the electro-dialysis are sensitive to the suspended solids, a sand filter was applied for pretreatment, which combined to “coagulation- sand filter-electro-dialysis” process for the advanced treatment of the textile effluent. The characterization of the influent (after sand filter) is listed in Table 1.

2.2. Electro-dialysis setup configuration

The electro-dialysis unit was equipped with electro-dialysis, raw water pump, electrode rinse pump, concentrated water pump, three-rotor flow meters, raw water tank,

electrode rinse tank and concentrated water tank. The effective volume of the electro-dialysis was 0.19 m³, along with the raw water tank, electrode rinse tank and concentrated water tank of 1,000 L volume. The electro-dialysis was assembled as a “three-electrodes - three directions” module (Fig. 1), which included 160 membrane pairs (one anion exchange membrane (AEM) and one cation exchange membrane (CEM)). The anode, cathode and intermediate electrode all employed titanium mesh coated ruthenium electrodes. The size of the membrane was 400 mm × 800 mm, with the active area of 360 mm × 600 mm, and the material of the membrane was out-phase polyethylene (0852 for CEM and 0851 for AEM) whose characterization was listed in Table S1. The CEM had a strong acidic active exchange group R-SO³⁻, which formed a negative electric field, enabling positively charged ions to pass through. The AEM had a strong alkaline active exchange group R-N⁺(CH₃)_y, which formed a

Table 1
Influent of electro-dialysis after sand filter

COD (mg/L)	100–130
Conductivity (μS/cm)	7,000–8,500
TDS (mg/L)	3,500–4,500
Hardness (mmol/L)	0.7–0.9
Calcium ion (mmol/L)	0.6–0.8
Chlorine ion (mg/L)	1,700–1,900
Turbidity (NTU)	<3

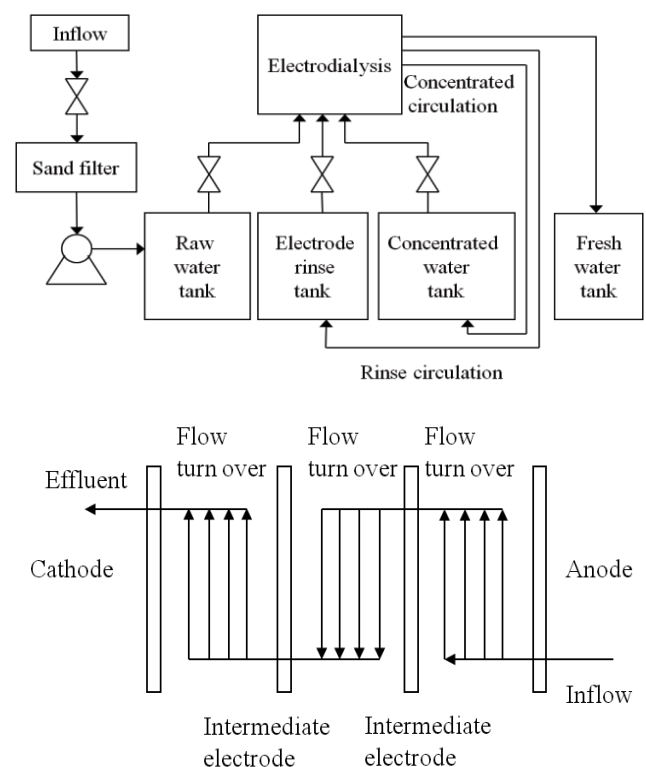


Fig. 1. (a) Process of the electro-dialysis and (b) sketch of electro-dialysis structure.

positive electric field, enabling negatively charged ions to pass through. Five membranes stack voltages (75, 80, 85, 90, and 95 V), inflow rates (800; 900; 1,000; 1,100; and 1,200 L/h) and temperatures (15°C, 20°C, 25°C, 30°C, and 35°C) were designed to explore the electro dialysis optimum operating conditions.

2.3. Analytical methods

The electrical conductivity was measured using a conductivity meter. Total dissolved solids (TDS) and chloride were measured by gravimetric and argentometric methods respectively as previous [17]. Calcium was determined by ethylene diamine tetraacetic acid titrimetric method [17]. Other ions were monitored by ion chromatography (IC).

Images were taken on new and fouled membrane pieces to examine the membrane fouling situation with a scanning electron microscopy (SEM; S-4800, Hitachi High-Technologies Corporation, Japan). Elemental analyses were performed on an energy-dispersive X-ray spectrometer.

3. Result and discussion

3.1. Influence factors of electro dialysis reversal and its optimization

3.1.1. Influence factors of electro dialysis performance

The TDS removal ability of the electro dialysis can be affected by so many parameters that the targeted study on

the influence factors was necessary. The textile wastewater was characterized by various water yields with different temperatures. Therefore the inflow rate and temperature were the subjects in our study. Besides, the operational voltage related to the energy cost, which also should be taken into consideration.

3.1.1.1. Operational voltage effect

The voltage played a dominant role in ion migration [18]. The operational voltage of electro dialysis was restricted by the limited current [19], which has been investigated before in our previous work [20]. Therefore, a series of membrane stack voltage gradient of 75, 80, 85, 90, and 95 V were selected, and the performance comparison is shown in Fig. 2.

Fig. 2 shows that the highest performance was obtained at 85 V, including the highest TDS, conductivity, chlorine ion and hardness reduction of 78.0%, 88.0%, 89.0%, and 72.2%, respectively. The TDS removal rate could reach 56.35 mg/(L s) at 85 V, which reduced the conductivity of textile effluent below 1,000 $\mu\text{S}/\text{cm}$. When the voltage further increased (to 95 V), the performance decreased instead. This was because when the voltage increased from 85 to 95 V, the polarization phenomenon led to the decrease of the ion removal rate. Then it could be concluded that the desalination performance increased as the voltage rising within the limited current, however, decreased when exceeding the limited current.

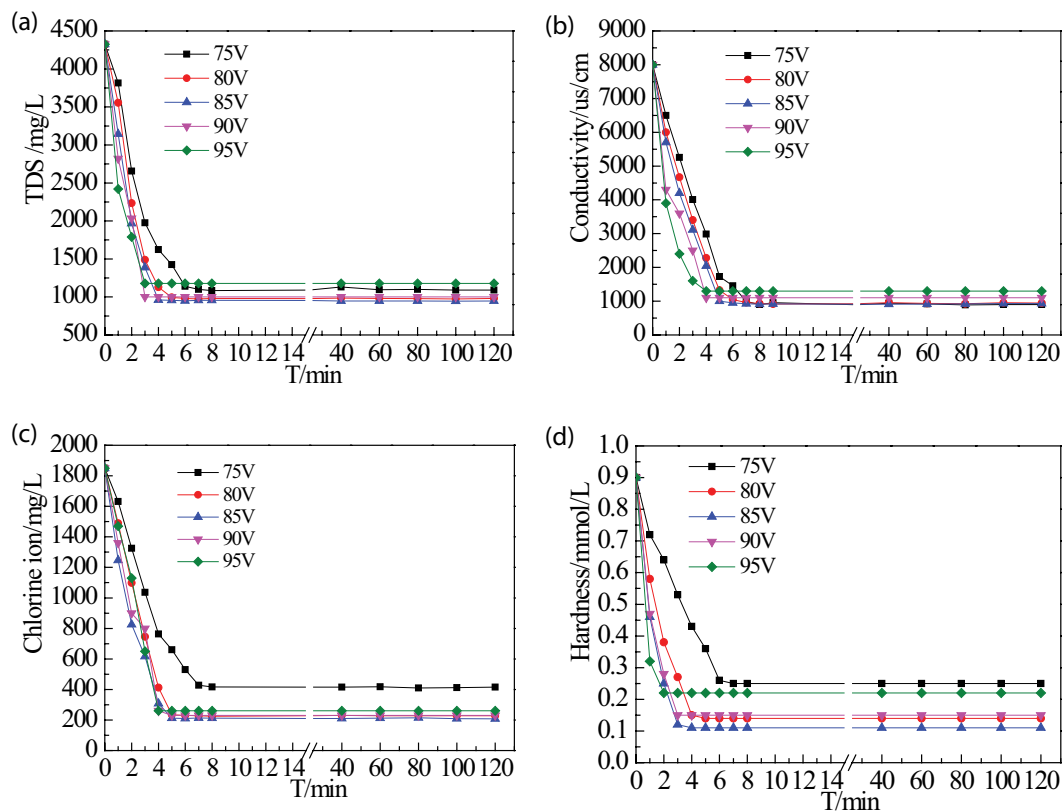


Fig. 2. Performance comparison among different operational voltage: (a) TDS, (b) conductivity, (c) chlorine ion, and (d) hardness.

3.1.1.2. Inflow rate effect

The textile wastewater usually suffered from varies water yield so the study on inflow rate effect was necessary. Based on the experiment above, the voltage 85 V was fixed, and an array of inflow rate 800; 900; 1,000; 1,100; and 1,200 L/h was investigated.

The results (Fig. 3) showed that at 800 L/h, the TDS, conductivity, chlorine ion and hardness reduction were 77.50%, 88.2%, 88.3%, and 74.1%, respectively. When the inflow rate increased from 800 to 1,000 L/h, the performance displayed first increase, which was because when the flow rate was relatively low, water molecules on the membrane surface underwent electrolysis, and the ions were difficult to penetrate the membrane, resulting in a small desalination rate. When the flow rate reached 1,000 L/h, the content of ions in the wastewater met the demand for ion migration, thus the desalination rate raised. With the continuous increase of the flow rate, there were more ions in the wastewater, and the current increased rapidly beyond the limit current, then the polarization phenomenon occurred, leading to the decrease of ion removal rate.

Therefore, the highest performance was obtained at 1,000 L/h, with the TDS removal rate 57.25 mg/(L s).

3.1.1.3. Temperature effect

The effluent temperature from different processes varied much [21], which would influence the performance of electrodesialysis. The previous study demonstrated that the size of membrane pore would increase as the temperature

rose [22], leading to higher TDS removal, especial for the bivalent ion. Based on the experiments above, the voltage 85 V and inflow rate 1,000 L/h were fixed, the effect of gradient temperatures of 15°C, 20°C, 25°C, 30°C, and 35°C was investigated, according to different processes and seasons.

According to Fig. 4, as the temperature decreased, the conductivity of effluent became higher gradually, reaching as high as 2,000 $\mu\text{S}/\text{cm}$ at 15°C. This was because at low temperature, the thermal motion of ion reduced and solution viscosity increased, which hindered the ionic migration. Correspondingly, the TDS removal rate was as low as 46.2 mg/(L s), much lower than the 55.75 mg/(L s) at 25°C. When the temperature further increased (over 25°C), the membrane pore became larger, leading to backflow of ion (based on differential concentration), which was probably responsible for the lower performance.

3.1.2. Economy optimization by response surface

So many factors affected the electrodesialysis performance. In order to further optimize the operational parameters, response surface analysis was applied. Both performance and energy consumption (i.e. the economy of operation) of the electrodesialysis reactor were considered.

The energy consumption of electrodesialysis mainly consists of three parts: electrode, membrane stack, and the pump. The current variation at different operational conditions was shown in Fig. S1, which demonstrated the current was always increasing along with time as these three parameters (voltage, inflow rate, temperature) rises. It was because

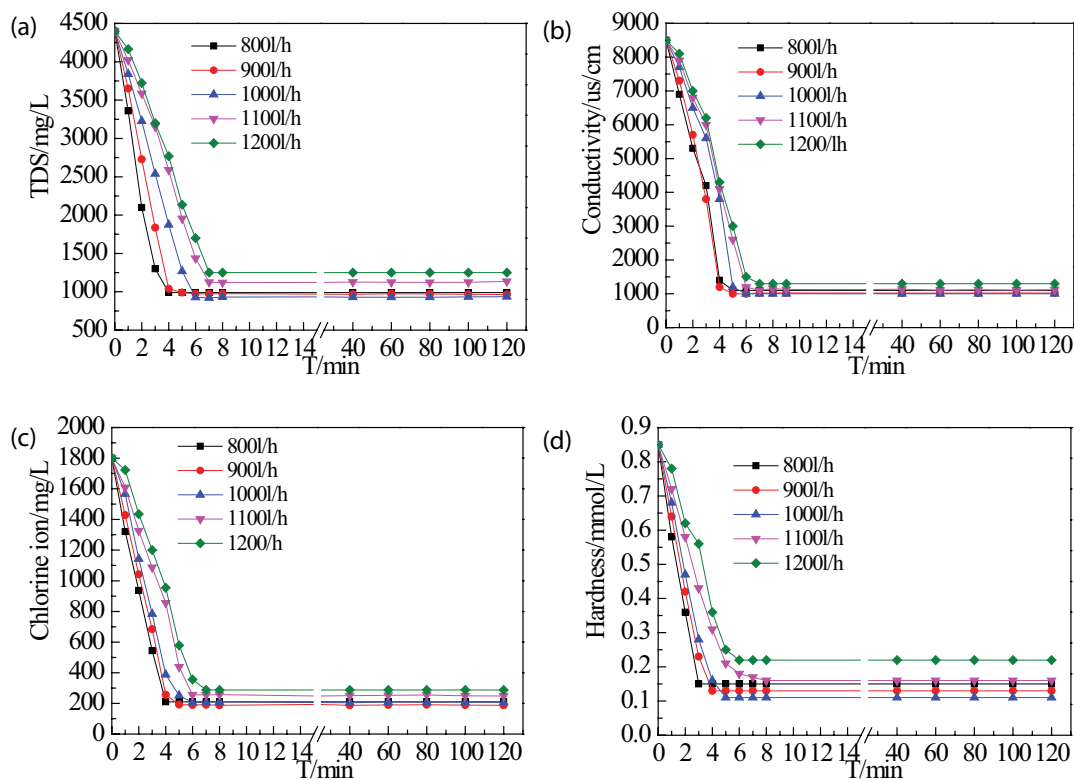


Fig. 3. Performance comparison among different inflow rate: (a) TDS, (b) conductivity, (c) chlorine ion, and (d) hardness.

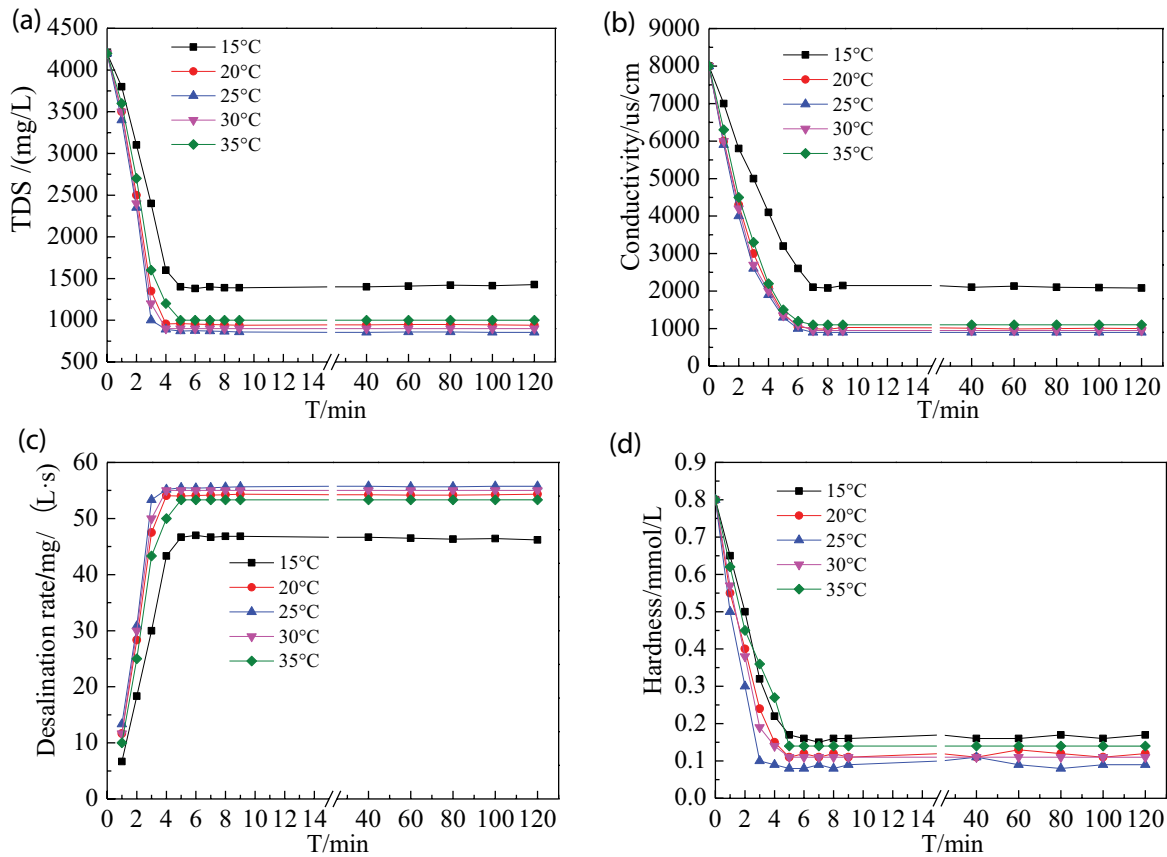


Fig. 4. Performance comparison among different inflow temperature: (a) TDS, (b) conductivity, (c) chlorine ion, and (d) hardness.

the removed ions entered into the concentrated circulation, leading to a higher accumulation. Therefore, the operational parameters had to be controlled within the limited current (25A for this study) in the practical application, otherwise, unnecessary energy consumption would be increased and membrane fouling would be accelerated.

The response surface analysis was applied to investigate the effects on TDS removal and energy consumption by operational voltage, inflow rates, and temperature. The Box-Behnken central composite design method [23–25] and software Design-Expert 8.0 was used to establish the quadratic regression model of TDS removal vs. the three parameters (DS–TDS removal, A –voltage, B –inflow rate, C –temperature):

$$DS = 78.23 + 2.02 \times A - 1.40 \times B + 5.83 \times C + 0.4 \times A \times B + 0.12 \times A \times C - 1.82 \times B \times C - 1.01 \times A \times A - 0.13 \times B \times B - 6.70 \times C \times C.$$

The significance testing showed $F = 54830.14$, $P < 0.0001$; and the loss effectiveness testing showed $F = 1.74$, $P = 0.2972 > 0.05$.

Correspondingly, the quadratic regression model of energy consumption (EC) vs. the three parameters:

$$EC = 1.59 + 0.046 \times A + 0.13 \times B + 0.14 \times C - 0.017 \times A \times C + 0.018 \times B \times C + 0.024 \times A \times A - 0.036 \times B \times B - 0.063 \times C \times C.$$

The significance testing showed $F = 47.73$, $P < 0.0001$; and the loss effectiveness testing showed $F = 6.56$, $P = 0.0504 > 0.05$.

The surfaces were shown in Fig. 5.

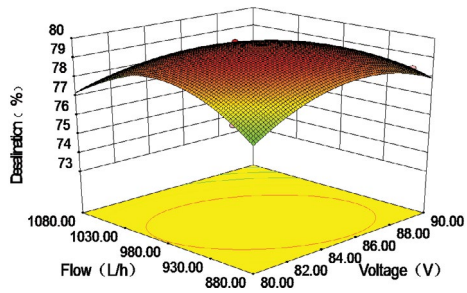
Therefore, in view of integrated TDS removal and energy consumption, the theoretical optimal parameters (operational condition) were: voltage 85.2 V, inflow rate 976 L/h

and temperature 25.2°C. At this condition, the (theoretical) maximum TDS removal could reach 83.16% and the energy consumption was 3.52 kW/h m³, far lower than that of the RO, 10 kW/h m³ [26]. The cost of TDS removal for textile wastewater (secondary effluent) was 0.33 \$/m³, according to the average electric charge for commercial power 0.1 \$/(kW/h).

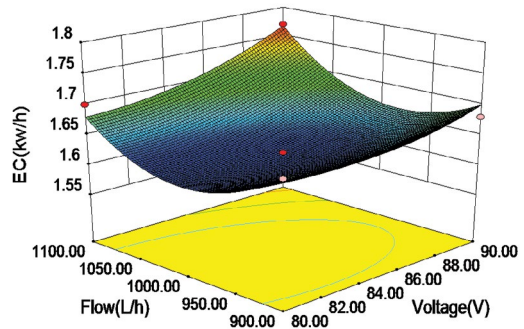
Operated under the condition of optimal parameters, the water quality comparison of electrodesalination freshwater chamber and printing and dyeing reuse water is shown in Table 2.

The results showed that [27] when the conductivity of printing and dyeing reuse water exceeded 3,000 μS/cm, the inorganic salts in the wastewater tended to stain the fabric, and the quality indexes such as the evenness, reproducibility, freshness and color fastness of the products would be affected. In addition, the high content of inorganic salts would inhibit the activity of anaerobic activated sludge, as well as reduce the removal efficiency of organic matter. In this experiment, the conductivity of electrodesalination freshwater chamber was less than 1,000 μS/cm, which met the standard of printing and dyeing reuse water.

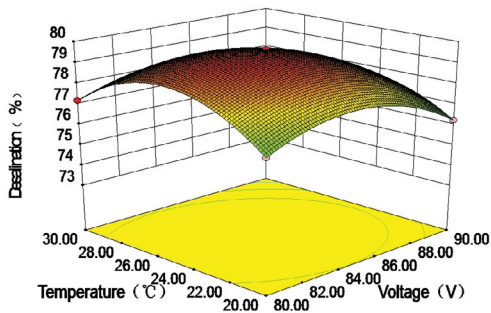
Dyeing and finishing process water also has strict requirements for hardness. A large number of surfactants will be consumed and precipitation will be produced with high-hardness water, which will affect the quality of the product. In the production water supply, the hardness of raw water which was less than 1.5 mmol/L could be used for



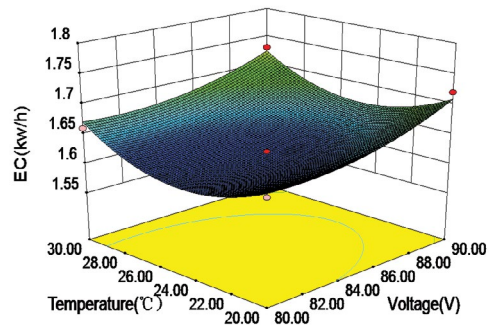
(a) TDS removal vs. voltage and inflow rate



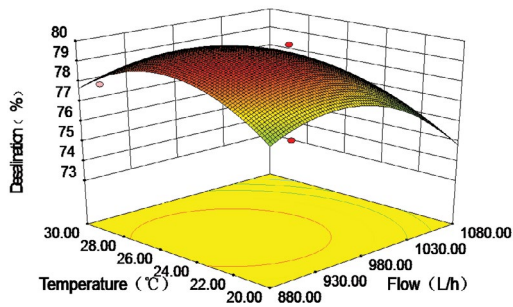
(d) Energy consumption vs. voltage and inflow rate



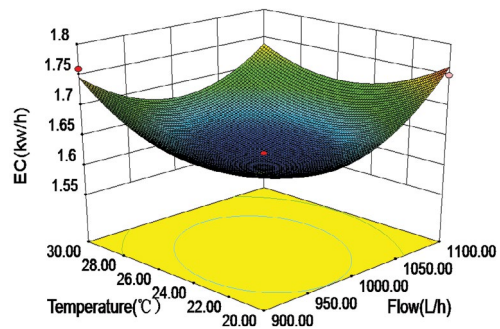
(b) TDS removal vs. voltage and temperature



(e) Energy consumption vs. voltage and temperature



(c) TDS removal vs. inflow rate and temperature



(f) Energy consumption vs. inflow rate and temperature

Fig. 5. Three-dimensional response surface analysis.

Table 2
Water quality comparison of electro dialysis freshwater chamber and printing and dyeing reuse water

Index	COD (mg/L)	pH	Suspended solids (mg/L)	Conductivity (μS/cm)	Hardness (mmol/L)
Electrodialysis freshwater chamber effluent	≤50	6–9	≤30	≤1,000	≤1.0
Standard of water reuse for printing and dyeing	≤50	6–9	≤30	≤2,500	≤4.5

production. The hardness of the effluent in this experiment was less than 1.0 mmol/L, which was far less than the index of printing and dyeing reuse water, and even reached the index of production water supply.

3.1.3. Electrodialysis reversal effect

3.1.3.1. Effect of reversal

The membrane life can be prolonged and freshwater effluent quality can be stabilized with electrodialysis reversal. Dong et al. [28] mentioned that the freshwater conductivity could be as low as 700 $\mu\text{S}/\text{cm}$ when using electrodialysis reversal, Liang [29] also pointed out that the freshwater conductivity could reach 254.6 $\mu\text{S}/\text{cm}$, which could fully meet the drinking water quality standards.

Fig. 6 shows that when the electrodialysis started with a positive electrode, after an operation, the freshwater chamber effluent quality was basically stable, the conductivity was kept below 1,000 $\mu\text{S}/\text{cm}$, and the calcium ion content was slightly fluctuated, which might be caused by the fluctuation of electrodialysis inflow. With the extension of running time, the conductivity of freshwater, after 8–9 h, was significantly increased, and the hardness content in freshwater was gradually increased, as well as the chloride ion content. At this time, the positive and negative electrode of electrodialysis was manually reversed, and the conductivity of freshwater was gradually decreased after polarity reversal, with the ion content in freshwater decreasing significantly. After a period of time running, a similar phenomenon occurred, the electrode was reversed again to guarantee the stability of freshwater. In addition, in the actual operation process, the reverse operation should be

carried out prior to the increase of freshwater outlet conductivity, so as to avoid the fluctuation of freshwater outlet quality, which influenced the subsequent recycling process.

3.1.3.2. Effect of reversal time interval

From the test above, during the electrodialysis operation, the reversal time should not be more than 6 h, therefore, a series of reversal time-interval gradient of 0.5, 1, 2, 3, and 4 h, respectively, was selected. The results are shown in Fig. 7.

With the number of times increasing, once reaching 40 times, the conductivity of the electrodialysis freshwater chamber outlet was significantly increased every 4 h, which, however, began to rise every 3 h when up to 85 times. However, with the reversal time interval of 0.5, 1, and 2 h, there was no obvious increase in the conductivity of the water outlet. It was because when the electrodialysis reversal time was too long, the IEM pollutants, especially for the calcium carbonate and organics, would be more closely combined with a membrane. Each reversal could only remove a small number of pollutants. While the short time was capable of eliminating most of the contaminants, which really served to delay the membrane fouling, however, would greatly increase the amount of operation and waste of running time. Therefore, the reversal time used in this study was once every 2 h.

3.2. Discussion on ion concentration effect (ion comparison)

3.2.1. Maximum concentration

In the use of electrodialysis method to desalinate wastewater, the properties of IEM and the type of ions had an effect

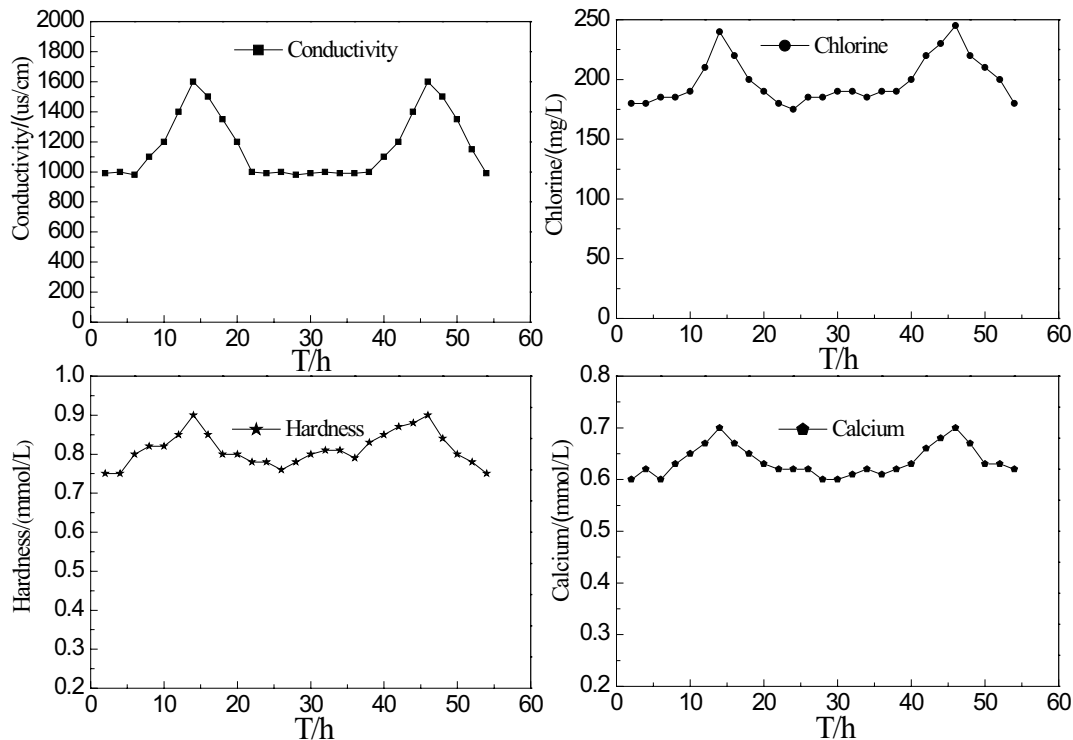


Fig. 6. Comparison of water quality before and after electrodialysis reversal.

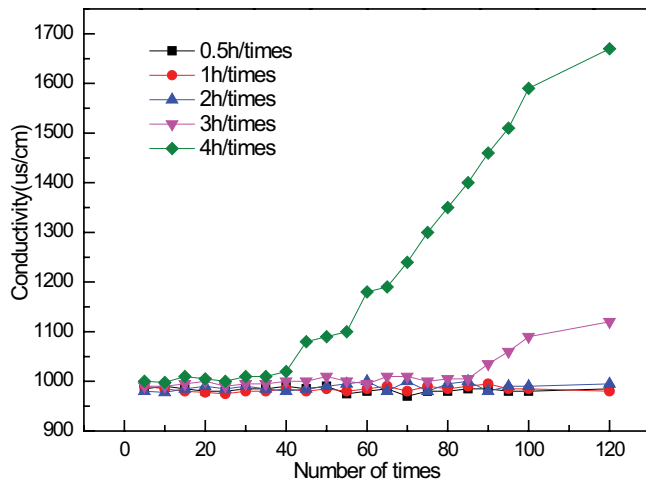


Fig. 7. Effect of the number of reversals on the electro dialysis effluent conductivity.

on the maximum concentration of some ions, which can be expressed as the Eq. (1) below [30]:

$$C_{\max} = \frac{(t_c + t_a - 1) \frac{I}{F} - K_s \Delta c}{\beta I + K_w \Delta c} \quad (1)$$

where t_c and t_a are migration numbers of cations and anions in the exchange membrane respectively, I is operating current, F is Faraday's constant, K_s is diffusion coefficient of salt ($\text{mmol}/(\text{cm}^2/\text{h}/\text{mol/L})$), Δc is average concentration difference between the concentrated and freshwater chamber, β is water electric permeability coefficient ($\text{mL}/(\text{mA h})$), K_w is water concentration permeability coefficient ($\text{mL}/(\text{cm}^2/\text{h}/\text{mol/L})$).

To further explore the characteristics of the type 0581 and 0582 polyethylene IEM, the maximum desalination concentration of the secondary treatment effluent was tested by means of concentrated water circulation, and the results are shown in Fig. 8.

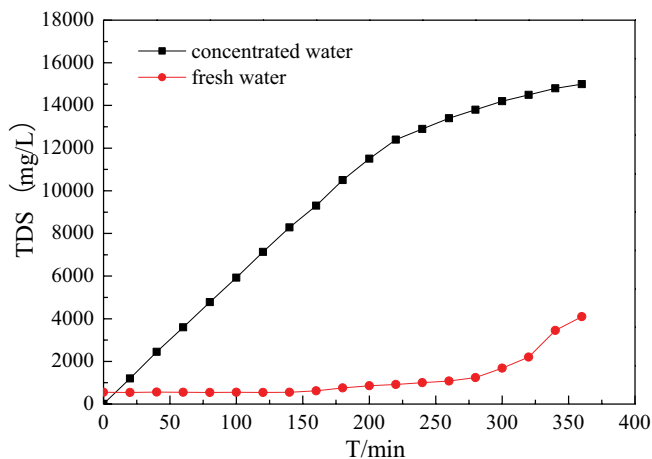


Fig. 8. Maximum concentration of TDS.

In the process of concentrated water circulation, the concentration of TDS in the concentrated water chamber, gradually condensed from 10 mg/L to the maximum concentration of 15,000 mg/L. At the beginning of the cycle, the concentration of TDS in the electro dialysis showed good concentration performance, with the TDS concentration of freshwater effluent stable and the TDS removal rate high. However, as the TDS concentration in the concentrated water chamber increased, the concentration difference between the concentrated water chamber and the freshwater chamber occurred, which resulted in the decrease of electro dialysis concentration and desalination, as well as the TDS content of freshwater was significantly increased. In the later stage, the TDS removal rate of the wastewater was very low, which demonstrated that the concentration and desalination effect was not ideal.

3.2.2. Concentration effect

In order to explore the concentration performance of different ions in the process of desalination and concentration, IC was used, and the raw water, electro dialysis freshwater, concentrated water were detected. The specific detection result is shown in Table 3.

According to Table 3, in raw water, sulfate, bicarbonate and chloride ions were the main anions, accounting for 40.19%, 16.53%, and 14.31% respectively, calcium, magnesium, potassium, potassium, and sodium, as the cationic, accounting for 0.9%, 0.21%, 1.04%, and 25.47% respectively. While in the concentrated water, the corresponding anions were 30.33%, 21.64%, and 22.25%, respectively, and the cationic were 1.54%, 6.29%, 1.53%, and 19.58%, respectively.

The study of Sadrzadeh et al. [31] showed that, when the ionic valence was the same, the removal rate of different ions was related to the relative molecular mass and activation energy of ions. In this study, there was a significant increase in the percentage of anions, such as hydrogen carbonate and chloride ions, which was caused by the small molecular weight, and the activation energy of calcium ions and magnesium ions in cationic ions was higher, so the removal rate was higher than that of the monovalent cation. Thus, the anion exchange membrane used in the experiment had a good removal effect on the monovalent anions, while the cation exchange membrane had a good removal effect on the divalent cations, which was in agreement with the study of Sadrzadeh et al. [31], and it was further proved that when the relative molecular mass was smaller and the activation energy was higher, electro dialysis was better for ion removal. The maximum desalination concentration of the secondary treatment outlet was 15,000 mg/L.

The cation exchange membrane played a vital role in the removal of calcium and magnesium divalent ions. Bazinet and Araya-Farias [32] studied the cation exchange membrane fouling with different concentrations of carbonate ions and calcium ions. The test results showed that when the carbonate ions existed, the buffer properties of carbonate ions made the cationic exchange membrane penetrate more calcium ions, thus forming calcium carbonate pollution.

The persad of anion exchange membrane had positive charges, which took responsibility for the removal of the

Table 3
Ion detection results in wastewater

Detection items	Detection results			Measure unit
	Raw water	Concentrated water	Freshwater	
F ⁻	0.67	0.99	0.17	mg/L
Cl ⁻	660	588	53.55	mg/L
NO ₃ ³⁻	59.7	28.7	3.31	mg/L
SO ₄ ²⁻	1854	801.6	746	mg/L
HCO ₃ ⁻	762.5	571.9	91.5	mg/L
NH ₄ ⁺	1.88	6.07	0.95	mg/L
Cu	0.03	0.02	0.02	mg/L
Ca	41.35	71.08	7.20	mg/L
Mg	9.60	16.61	1.37	mg/L
K	48.08	40.38	8.75	mg/L
Na	1,174.75	517.44	237.9	mg/L

monovalent anions, whereas the organic matter and colloidal substances in the water generally had negative charges, and the attraction between the opposite charges made these macromolecules close to the anion exchange membrane pores, however, the particle size of the organic ions was greater than the pore diameter of the membrane, forming a blockage of the membrane, thus other anions' passing through was impeded.

3.3. Membrane fouling and cleaning

3.3.1. Occurrence of membrane fouling

The reversal of the operation of the electrode could reduce membrane pollution, but after operating the electro-dialysis for a period of time, the phenomenon of pollution inevitably occurred. After 50 d of electro-dialysis operation, the effluent quality of freshwater was deteriorated, with various ions gradually increasing.

Seen from Figs. 9 and 10, at the beginning of the operation, the outlet quality was stable, with the conductivity between 900–1,000 $\mu\text{S}/\text{cm}$, inlet pressure at 0.025 MPa, the

content of chlorine ion water fluctuated slightly, but was basically kept at 210 mg/L, the hardness and calcium ion, almost unchanged, at 0.1 and 0.075 mmol/L respectively. After 50 d of operation, each index rise significantly, with the outlet conductivity of freshwater chamber up to 2,000 $\mu\text{S}/\text{cm}$ at 60 d, the inflow pressure increasing twice to 0.05 MPa, the chloride ion content rising to 310 mg/L, meanwhile, the hardness and the calcium ion concentration were 0.22 and 0.15 mmol/L, respectively, which affected the reutilization of desalinated water, showing that the IEM used in the test was polluted.

The SEM results are shown in Fig. 11, under the voltage of 10 kV, it could be observed that a large number of particles were accumulated on the cation exchange membrane, and from the surface morphology, it was preliminarily judged that the surface pollution of the cation membrane was mainly crystalline material, which was agreed with Zou's cleaning experiment [2]. Under the voltage of 50 kV, the contaminant of the cation exchange membrane was covered on the surface, which required further analysis to determine the type and the form of the contaminant.

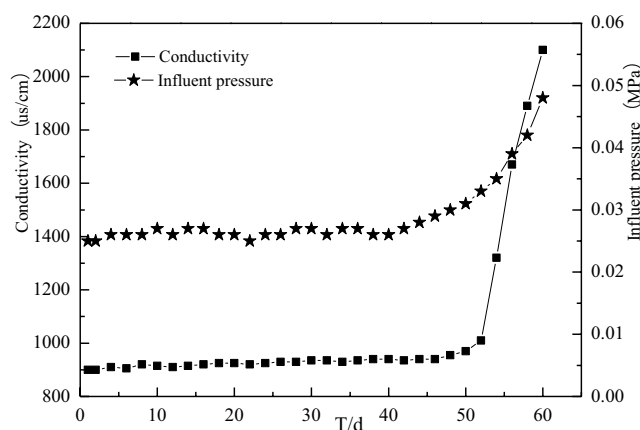


Fig. 9. Changes in water outlet conductivity and inlet pressure in freshwater chamber.

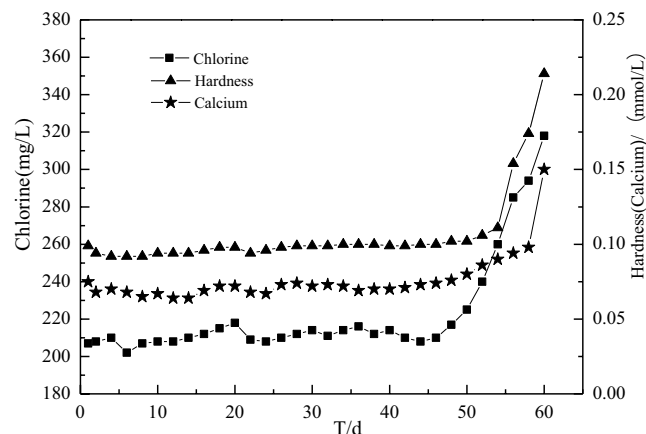


Fig. 10. Changes of chlorine ions, hardness and calcium ions content in freshwater chamber.

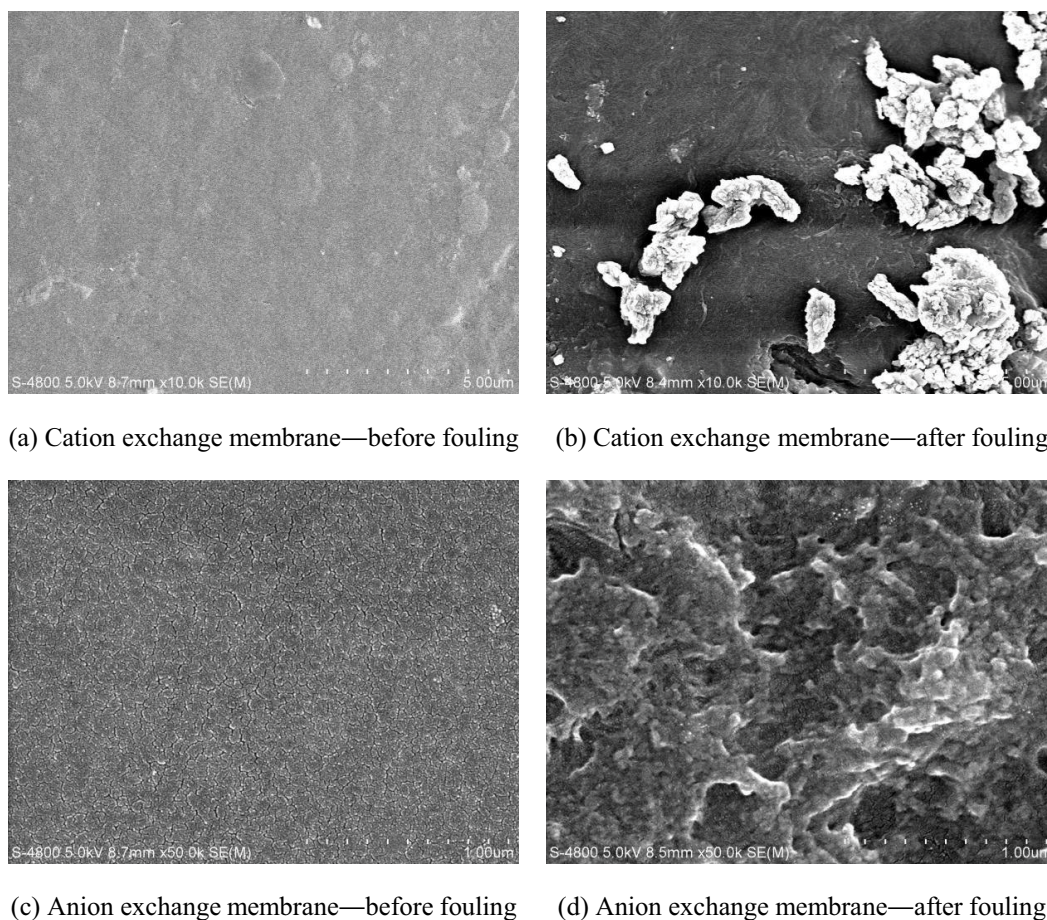


Fig. 11. Changes in cationic and anion exchange membranes before and after fouling.

Cation exchange membrane fouling spectrum analysis results were shown in Table 4, the composition of the uncontaminated surface elements of the cation membrane in the figure mainly consisted of carbon and oxygen, where the weight and the atomic percentage of the carbon were 84.72% and 88.42%, respectively, while the other metal ions were almost absent. However, after pollution, the weight and the atomic percentage of the carbon accounted for only 5.81% and 10.73%, respectively, while the calcium ions increased significantly, which was almost not detected before uncontaminated. However, the weight and the atomic percentage of the calcium were almost 50% after the pollution, which was 47.96% and 26.54%, respectively. There was also a significant increase in oxygen content. In addition, there was little increase in magnesium atom, which was consistent with the result of calcium ion accounting for more than 80% in the previous hardness test. This indicated that there was a large amount of calcium carbonate crystals on the surface of cation exchange membrane, which is consistent with Li's and Zhang's research [33,34]. Therefore, calcium carbonate was the main pollutant of the cation exchange membrane, and the calcium sulfate, magnesium sulfate, magnesium carbonate, and magnesium carbonate barely existed.

The anion exchange membrane spectrum results were shown in Table 4, carbon, nitrogen and oxygen were mainly formed in the non-polluted surface elements of the anion

membrane, in which the weight and the atomic percentage of the carbon were 69.81% and 74.37% respectively, and the weight and the atomic percentage of the carbon were only a small increase after contaminated, accounting for 81.58% and 87.49% respectively. The membrane surface contained a certain amount of nitrogen, which was because the material of the membrane was styrene-polyamine, containing the strong alkaline active group $R-N^+(CH_3)_3$, but the content of nitrogen was decreased after the pollution, while the chloride ion had a small increase, which was related to the high concentration of chloride in the electro dialysis intake.

Above all, there was a large amount of organic matter on the surface of the anion exchange membrane, so organic matter was the main pollutant, of which the specific ingredients required further analysis. Gas chromatography-mass spectrometry (GC-MS) was adopted to further identify the pollution component and type of anion exchange membrane, as shown in Fig. S2.

Li's research [34] showed that the main functional groups in organic pollutants were hydroxyl, amino, and carboxyl groups, and the main types of pollutants were polysaccharides, aromatic proteins, humic acids and fulvic acids. Wu et al. [35] and Chen et al. [36] found that the characteristic pollutants in the printing and dyeing wastewater could be divided into two categories, one was the various auxiliaries added in the process of textile printing and dyeing, the other

Table 4
Surface element content of cationic and anion exchange membranes before and after fouling

Element	Cation exchange membrane (Atom%)		Anion exchange membrane (Atom%)	
	Before fouling	After fouling	Before fouling	After fouling
C	88.44	10.73	74.37	87.49
N	0	0	15.32	4.2
O	11.13	60.92	9.87	5.58
Na	0.01	0.01	0	0
Mg	0	0.94	0	0
Al	0.01	0	0	0
P	0.39	0.62	0.4	0.49
S	0.03	0.19	0.01	0.62
Ca	0	26.54	0	0
Fe	0	0.02	0	0
Zn	0	0.02	0	0
Cl	0	0	0.02	0.62

was the small molecular pollutants, such as phenol and aniline. Huang [37] found that 1,2-benzisothiazole and other organic substances existed in the residual products of azo dyes, through anaerobic and aerobic biological treatment.

In this study, the main pollutants on the surface of the anion exchange membrane were hydrocarbons, ketones and esters with a benzene ring structure, which were the main products of dyes and additives after biodegradation. Among them, N-[(4-hydroxy) hydroxycinnamic acid]-phenylethylamine was the characteristic substance of the intermediate product of dyes, and the 4-phospho-butyrate triethyl ester, phthalate 3-chlorophenyl tetradecyl ester and 2-thiophene acetate were mainly the characteristic products of surfactants, and (2-methyl-3-nitrophenyl) methanol dimethyl pentafluorophenyl silicate was the product of the decomposition of the auxiliary agent used in printing and dyeing.

3.3.3. Membrane wash

3.3.3.1. Wash methods

In this study, the chemical wash method of the non-fluidisation tank was used, and hydrochloric acid with a mass fraction of not more than 3% was selected as the cleaning agent for the anion exchange membrane. After the first cleaning of the IEM, the electro dialysis normally operated. The water outlet of the freshwater chamber was basically the same as that of the unpolluted water, as shown in Figs. 12 and 13.

3.3.3.2. Wash times

After the first occurrence of pollution in the IEM, the electro dialysis was carried on, the time interval between the two IEM fouling was shortened, and the frequency of washing was gradually increased after the membrane fouling.

From Figs. 14 and 15 it can be found that, when reaching three times, the outlet conductivity of the freshwater chamber had increased from 985 to 1,070 $\mu\text{S}/\text{cm}$, and the concentration of chloride ions had increased from 195 to 235 mg/L , with a tendency to continue to increase. On the contrary, the

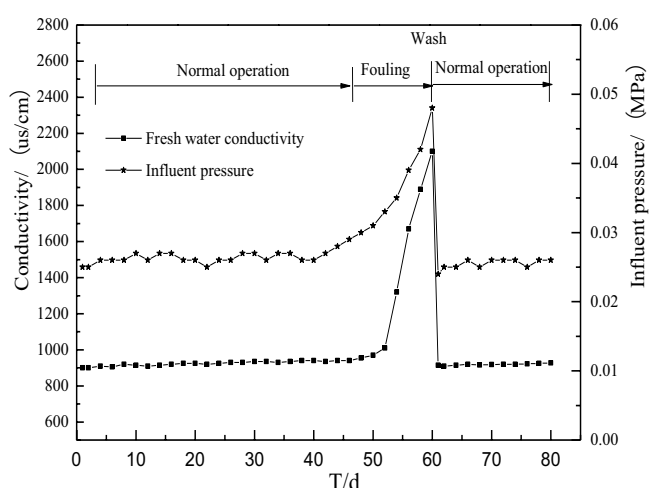


Fig. 12. Changes in freshwater conductivity and inlet pressure before and after membrane fouling.

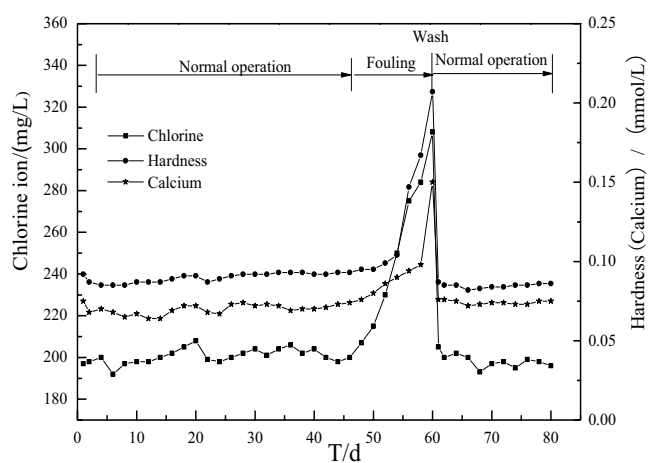


Fig. 13. Changes of chlorine ion, hardness and calcium ion before and after membrane fouling.

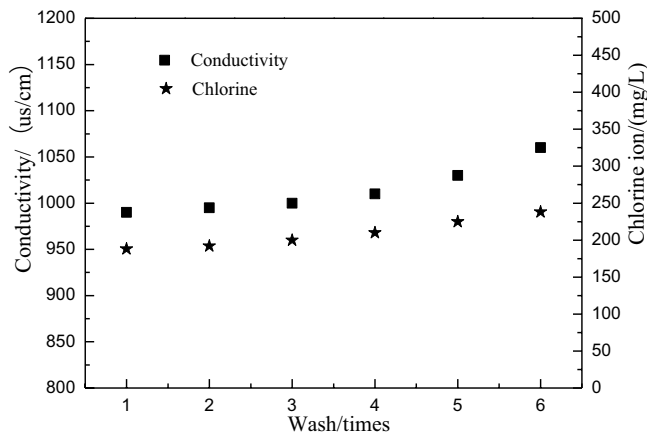


Fig. 14. Effect of membrane pollution wash times on water conductivity.

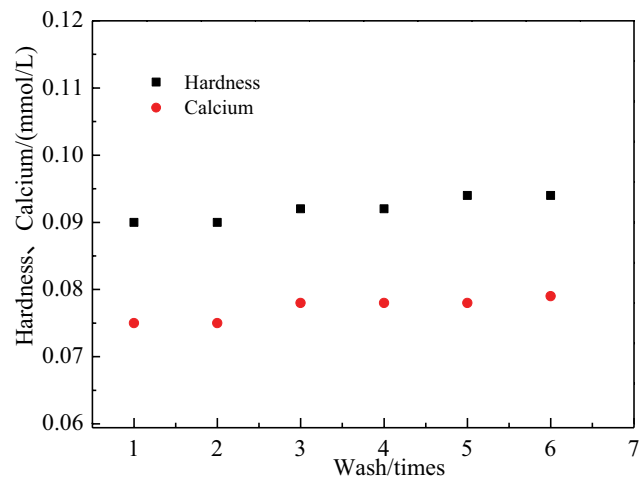


Fig. 15. Effect of membrane pollution wash times on water hardness and calcium ion concentration.

hardness and calcium ion concentration of freshwater chamber did not fluctuate significantly, which basically remained at 0.093 and 0.078 mmol/L, indicating that the hydrochloric acid cleaner used in the experiment could clean the calcium carbonate precipitation on the cation exchange membrane better, however, the inorganic pollution of the anion exchange membrane did not achieve the desired effect, which led to the reduction of the removal rate of the anion, especially the chloride ion.

4. Conclusion

Based on the advantages of electro dialysis, the desalination process of printing and dyeing wastewater was systematically studied. The optimal operating conditions of electro dialysis were determined by adjusting the parameters of voltage, flow rate, temperature and conducting the reversal experiment. Thus the minimum energy consumption was acquired. The highest salt concentration was obtained, the characteristics and regular of membrane fouling were studied, and finally, the fouling membrane was cleaned, to

determine the appropriate membrane cleaning agent. The fouling situation and mechanism of a membrane (electrodialysis membrane-printing and dyeing tailwater) were mainly discussed. The feasibility and superiority of electro dialysis in treating printing and dyeing water were confirmed, which could provide reference technical support for practical industrial application. The conclusions of this experiment are as follows:

- During the trial, the best operating conditions of the optimized electro dialysis were concluded: operating voltage 85 V, inlet flow rate 1,000 L/h, temperature 25°C, with the energy consumption 3.52 kW h/m³ and the printing and dyeing wastewater desalination processing cost 0.33 \$/m³, which had a strong economic advantage compared to RO. The reversal of the electrode could effectively reduce the membrane fouling, and 2 h was determined as the optimal reversal time.
- The experiment further discussed the desalination characteristics of the IEM, the electro dialysis desalination rate in the initial stage of operation could reach 79%, with the water outlet conductivity of the freshwater chamber remaining below 1,000 μS/cm. The concentration of 15,000 mg/L was the highest salt concentration of the polyethylene heterogeneous IEM, 0581 and 0582.
- The contaminant of the cation exchange membrane was identified as calcium carbonate, while the anion exchange membrane contaminant was characterized as organic matter. In this study, hydrochloric acid, with a mass fraction of less than 3%, was used as a membrane cleaning agent, which was able to better clean the calcium carbonate precipitation on the cation exchange membrane, whereas the organic pollution of the anion exchange membrane did not achieve the desired effect.

Acknowledgments

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Supplementary information

Table S1

Characterization of the ion exchange membrane of 0851 (AEM) and 0852 (CEM)

	Unit	Parameter	
		0581 (AEM)	0582 (CEM)
Thickness	mm	0.42	0.42
Moisture	%	35–50	30–45
Exchange capacity	(mmol/g dry membrane)	2.0	1.8
Resistance	(Ω/cm^2)	10	10
Transmittance ratio	%	90	89
Desalination ratio	%	40	40

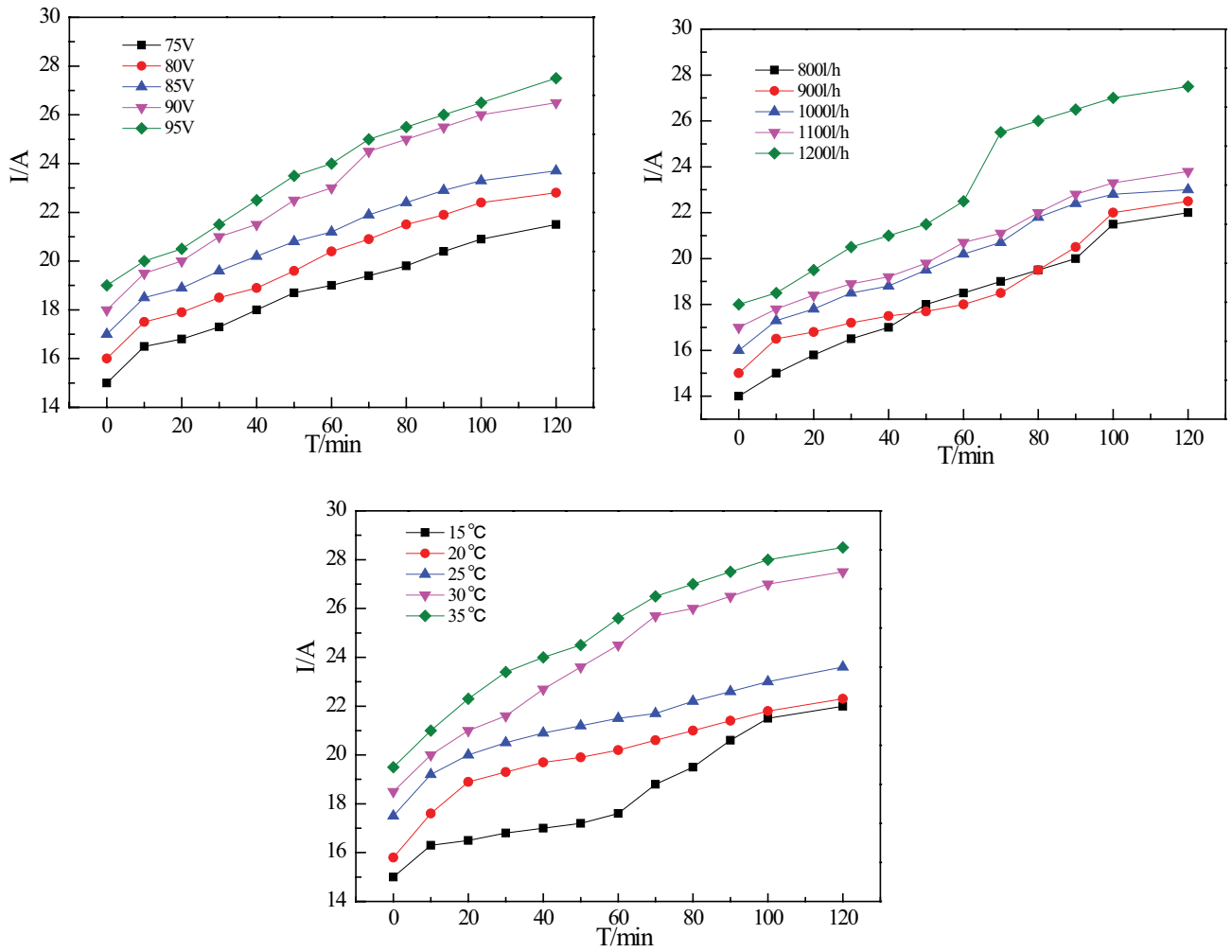


Fig. S1. Current variation at different operational conditions.

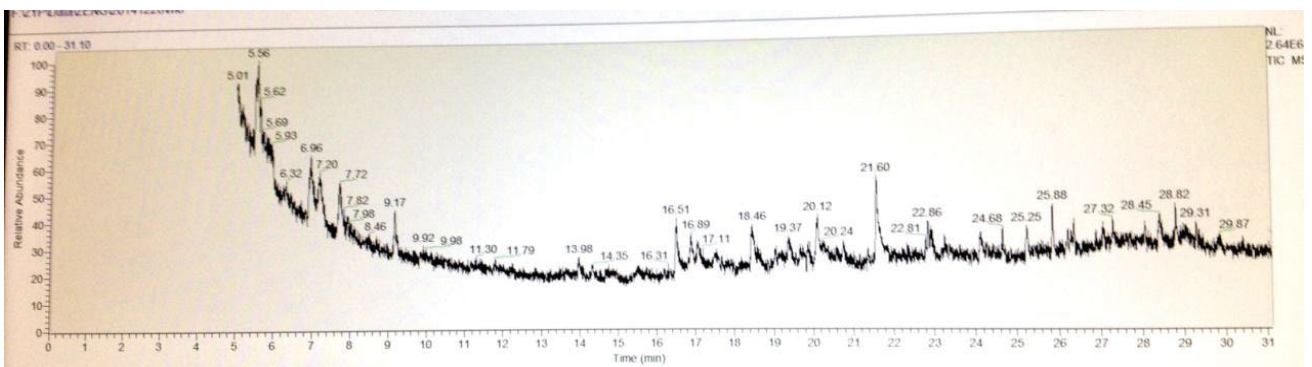


Fig. S2. Cathodic organic GC-MS resolution.