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Experimental study on desalination using electro-sorption technology with plate-type activated carbon fiber electrode

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ABSTRACT

The amount of blow-down water from circulation cooling water system in power plant is quite large, and it has high salinity. To achieve high desalination efficiency at low cost is vital for the reusability of blow-down water. Compared with the traditional desalination methods, the electro-sorption technology has many advantages, such as high energy efficiency, low scaling risk, no secondary pollution, and so on. Based on this, an experimental study on desalination from simulated salt solution (NaCl solution) was carried out in a self-designed electro-sorption device with plate-type activated carbon fiber (ACF) electrode. The effects of feed concentration, feed flow rate, and voltage on salt adsorption rate and system desalination rate were studied. The optimum operating conditions for this system were determined as follows: the flow rate was 40 mL/min, and the voltage was 1.5 V; the actual desalination performance and the main ions removal conditions are investigated by using the actual circulating cooling sewage under the best experimental conditions. The average conductivity of raw water was 2,270 μs/cm, and the conductivity of producing water was up to 145.6 μs/cm. The maximum desalination rate was 75.63%, and the average desalination rate was 60.66%. The average removal rate of Ca^{2+} was 50.1%, the average removal rate of Mg^{2+} was 48.5%, the average removal rate of sulfate was 51.21%, and the average removal rate of Cl^- reached 69.99%. The experimental data show that the electro-adsorption of ACF has a good application prospect for desalting treatment of circulating cooling water in power plant. This study provides basic experimental data for the application of electro-adsorption in desalination of circulating cooling blow-down water in power plants.

Keywords: Electro-adsorption; ACF; Blow-down water from circulation cooling water; Desalination

1. Introduction

"Action Plan for Prevention and Control of Water Pollution" ("Water 10") was issued by State Council of China on April 16, 2015; the governance of all kinds of water pollution problems will be strengthened [1]. The scarcity of water resources has become the main factors that restrict the development of industrial enterprises, making it urgent to explore more ways to save water and reduce efflux of sewage. The power plant is a large consumer of industrial water, whose water consumption is about 20% of the whole industrial water consumption and especially the make-up water of the circulating cooling water system accounts for 50%–80% of its total water consumption. Therefore, in order to save water and reduce blow-down, it is the primary problem that improving the concentration ratio of sewage in the circulating cooling system and reducing the blow-down flow rate and supplying freshwater [2].

To achieve sustainable development, novel water treatment technologies are urgently needed. At present, some

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methods of desalination used widely in industry at home and abroad have some drawbacks in practice. The traditional distillation method [3] has a slow evaporation rate, low water production efficiency, and high energy consumption. Ion-exchange technology is one of the most complete methods of desalination, but large amount of acid and alkali is needed in the regeneration process, and the system is complex and prone to produce the secondary pollution [4]. The application of electro-dialysis [5] and reverse osmosis [6] is limited by its high investment cost, huge energy consumption, and complicated maintenance. What is more, they are strict to the inlet water quality, and the membranes are easy to scale. Therefore, development of a low-cost technology to recover wastewater is crucial for economic and environmental benefit. Electrochemical technology has a lot of advantages and quite extensive research space. A novel adsorption/desorption technology called capacitive deionization technology, also is known as electro-adsorption technology, has been widely concerned. In capacitive deionization (CDI) process, adsorptive material is used as electrode and potential control is applied in solution [7]. CDI has received high expectation in the field of water treatment with the properties of low cost, high efficiency, environmental friendliness, and no secondary pollution [8].

The CDI community has grown exponentially over the past decade, driving tremendous advances via new cell architectures and system designs, the implementation of ion-exchange membranes, and alternative concepts such as flowable carbon electrodes and hybrid systems employing a Faradaic (battery) electrode. Also, vast improvements have been made toward unraveling the complex processes inherent to interfacial electrochemistry, including the modeling of kinetic and equilibrium aspects of the desalination process [9]. Porada et al. [10] found that CDI performance stability CDI was operated in continuous mode using different amounts of carbon loading. After an initial run-in phase (ca. 20 min), all carbon loadings yielded a stable performance (tested for a total of 60 min) [10]. Dermentzis and Wessner [11] presented a new continuous capacitive deionization system with intermediate bipolar rotating film electrodes. Various initial concentrations of 1–3 g/L NaCl solutions were separated in a desalinated and a concentrated water stream. Its electrical energy consumption was over 60% lower than that reported with the prior art capacitive deionization devices, whose system was achieved by applying current densities of 4.45–32.6 A/m^2 and flow rates of 1.5–7.5 mL/min. Zhou et al. [12] used graphite and activated carbon fiber (ACF) composite materials as electrodes to treat the refined cotton black liquor and sodium copper chlorophyll high salt wastewater. The experimental results showed that the removal effects of wastewater conductivity and chemical oxygen demand (COD) were excellent. X. Yue et al. [13] applied ACF carbon electrode to make continuous flow electric adsorption device to deal with uranium-containing (VI) wastewater. The mass concentration of uranium (VI) in effluent was 100 g/L, and the treatment effect was better [13]. CDT systems made use of carbon aerogel as electrode material to dispose the industrial circulating cooling water with total dissolved solids (TDS) of 1,000 mg/L, the effluent TDS of 10 mg/L, the energy consumption of 0.1 kWh/t, and the energy available for regeneration was about 50%–70%. There were few reports on the electro-sorption of circulating cooling water in power plants. Researches on the influencing factors of desalting effect and the changing rules of desalination rate were lacking.

In this experiment, aiming at the characteristics of high salinity and large amount of wastewater in circulating cooling system in power plant, ACF was utilized as electrode self-made adsorption test bench. Under different feed concentration, liquid flow rate, and different voltage condition, the electrochemical adsorption experiments were carried out. The combinations of single-factor experiment and orthogonal experiment were used to explore the influencing factor of desalination efficiency and desalination rate, and to determine the optimal operating conditions. In addition, the actual circulating cooling water samples collected in the field were conducted by electro-adsorption experiments to explore the main influences of ion and desalting effects. This research aims to offer basic experimental data for the treatment of wastewater that comes from circulating cooling blow-down water in power plants through using ACF electrode electro-sorption technology (EST).

2. The principle of electro-adsorption

The surface of charged electrode can absorb ions and charged particles in water, thus the electrode can be used in water purification and desalination by concentrating the dissolved salts and other charged substances on its surface. That is the principle of electro-adsorption technology [14].

Due to the existence of electric field, the anions and cations in the solution are gradually migrated to the plates with the opposite polarity and are enriched in the electric double layer formed between the plates, making the salt dissolved [15], and removing the colloidal partials and charged substances [16]. The desalination process of electro-absorption is shown in Fig. 1.With the process of reaction, the ions adsorbed on the electrode surface gradually become saturated. At this point, the electrode is charged and the polarity of the bipolar plate changes. The ions adsorbed in the dielectric layer are released into the solution through the repulsive action of the electric field. Meanwhile, the concentrated water is discharged, and the electrode is regenerated (the schematic diagram of electrode regenerated is illustrated in Fig. 2).

According to the electrochemical theory, for a solid electrode immersed in an electrolyte solution, when a voltage below the decomposition voltage of the solution is applied, charges are redistributed and arranged within a very short distance between different phases of the electrode and the solution. As compensation, the positively charged electrode will attract the negative ions in the solution (on the

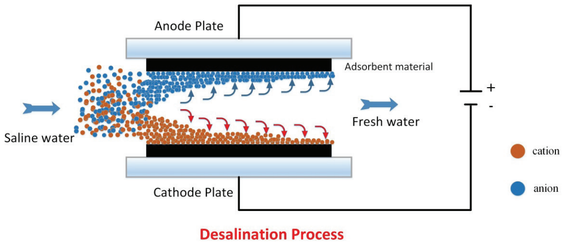

Fig. 1. Electro-adsorption.

contrary, the negative electrode will attract the positive ions). The change of residual charge in the interface will cause the variation of potential difference of the interface double layer, which will form a compact electric double layer at the electrode and electrolyte interface. It can be seen that electro-adsorption means the adsorption process of bioelectric layer under the electric field.

The development of the theoretical model of the double layer has gone through three important stages. The earliest parallel plate capacitor model proposed by Helmhotz [17]; the Gouy–Chapman–Stern modification model [18] was presented by Gouy and Chapman who modified the model of the Helmhtz model, and later Stern further refined the theory. This model can more effectively reflect the real structure of the electric double layer [19]. At present, the widely applied and generally accepted theoretical model is the BDM (Bockris–Devanathan–Muller) [20]. It states that the compact layer is composed of inner Helmholtz plane and outer Helmholtz plane. A dispersion layer is constituted between the outer compact layer and the bulk of the solution (Fig. 3), thereby generally improving the principle of ion migrant and adsorption in the double layer [21]. During the process of electro-adsorption, the structure of the electric double layer will take some changes [22]. Of course, different electrode materials also have large differences; a more in-depth process needs to be explored in future.

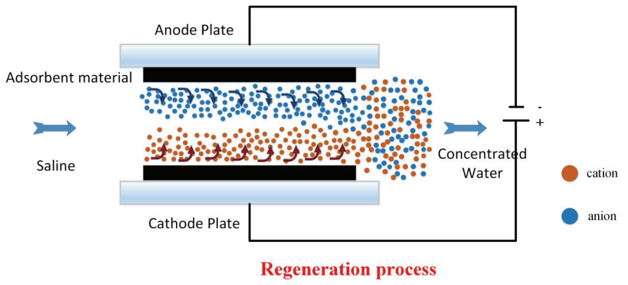

Fig. 2. Electro-absorption regeneration process diagram.

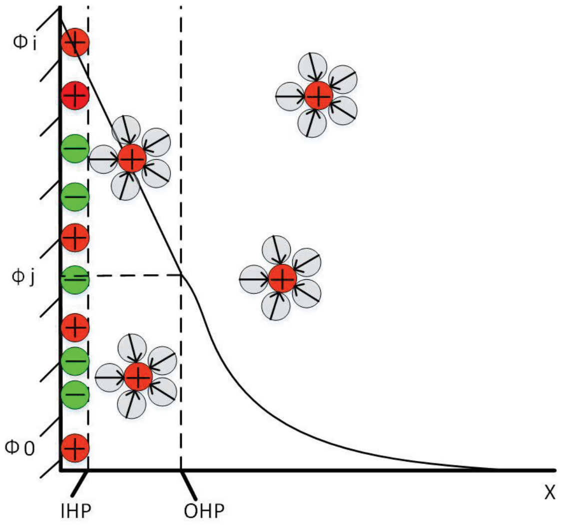

Fig. 3. BDM model diagram.

3. Experiment

3.1. Material

The drugs of this experiment are as follows: the analysis of sodium chloride solid was purchased from the Beichen Fangzheng reagents factory of Tianjin. Deionized water is produced by reverse osmosis (RO) high-purity water machine (RO high-purity water is made by Baoding Xin Jia Environment Protection Special Equipment Manufacturing Co., Ltd). ACF was bought from Jiangsu Zhi Kang Carbon Technology Co., Ltd (Jiangsu, China). The main parameters of indicators are presented in Table 1. DB2011 copper conductive adhesive was brought from Wuhan Double Bond Kim Sealed Material Co., Ltd. (Hubei, China); the 316 L stainless steel plate with a thickness of 1 mm was from the steel joint stainless steel Zhongbin Sales Company of Tianjin; polyethylene fiber was purchased online from Yanli Industrial and Trade Co., Ltd.

3.2. The system of experiment

The experiment system adopted a self-designed test bench to research the adsorption of ions in brine. The experiment system diagram is shown in Fig. 4, the test table is revealed in Fig. 5. The whole electro-adsorption experiment was conducted by utilizing sodium chloride solution prepared by a certain concentration to stimulate the electro-adsorption desalination experiment. This experiment was making self-made electric adsorption module, a pair of electrodes was used as the experimental electrode.

Table 1
Parameters of activated carbon fiber

Type	SY-1500
Specific surface area (m^2/g)	1,400
Benzene absorption amount static (wt%)	45–50
Benzene absorption amount dynamic (wt%)	≥40
Iodine absorption value (mg/g)	1,300–1,400
Methylene blue value (mL/g)	220
Hole volume (mL/g)	0.8–1.2
Average pore size (A)	17–20
pH	5–7
Fire point (°C)	>500

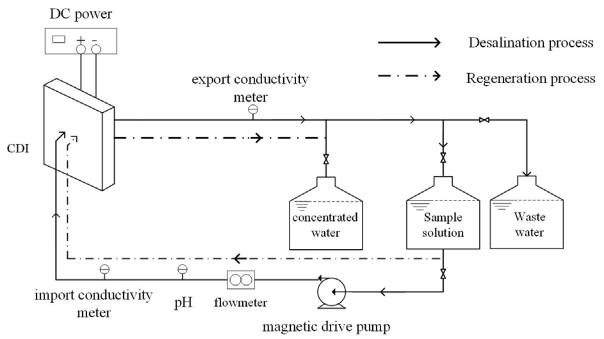

Fig. 4. ACF electro-adsorption experimental system diagram.

The internal structure of the membrane pile is shown in Fig. 6: plexiglass as the end plate used to fix the membrane stack internal components, while reserving external ports, as the entrance of the flow; 1 mm rubber pad for sealing. Rubber ring used to fix the ACF electrode, while sealing the electrode plate; 316 L stainless steel plate, as a current collector. ACF, the adsorption carrier of anion and cation ions in saline solution, is insulated diaphragm (polyethylene fiber mesh) as water channel.

In this experiment, 79-1 thermostatic magnetic stirrer (Tianjin Gongxing Electric Application Factory, Tianjin, China) was used to prepare the stimulated feed solution (NaCl solution). MP-20RM magnetic drive circulating pump (Shanghai Xianshan Industrial Co., Ltd., Shanghai, China) for salt water flow. LZB-3W rotor flow meter (Changzhou Ruiming Instrument Factory, Jiangsu, China) was used to control the influent flow. During the process of electrical adsorption, the electric conductivity was measured real time by adopting the CCT-3300 type conductivity meter (Hebei Co., Polytron Technologies Inc., Hebei, China). OP-160-type industrial online pH meter (Tianjin Equipment Firm, Tianjin, China) was taken to measure the pH value of the solution. Utilizing DHD15010 DC switching power supply (Beijing Dahua Radio Instrument Factory, Beijing, China) to provide the constant voltage and current of electro-adsorption; the conductivity value of the sample solution was measured by CT-3030 conductivity test probe (Shenzhen Cordida Electrics Co., Ltd., Shenzhen, China).

3.3. The method of experiment

At first, ACF was cut into rectangular pieces (two sides): 500 mm × 200 mm, tiled in SHA-82A Digital Water Bath Thermostatic Oscillator (Guangzhou Putian Instrument Manufacturing Firm, Gangdong, China), boiled for 2 h at 100°C to remove volatile impurities in ACF, then immersed in deionized water for 24 h, and finally placed in DHG-9076A-type electric constant temperature drying oven (Shanghai Jinghong Experimental Equipment Co., Ltd., Shanghai, China) at 120°C for 24 h. The 316 L stainless steel plate was cut into rectangular (two pieces) of 500 mm × 200 mm in length, welded to a wire post at one end of the steel plate, ground with a draw cotton to coarseness, rinsed with deionized water. The DB2011-type conductivity adhesive was evenly spread on the stainless steel plate; and ACF was slowly laid on the stainless steel plate, during the bonding period, it is strictly avoided to cause damage to ACF, otherwise, it would affect the adsorption effect on the electrode, the next step is compacting the ACF and curing for 24 h at the room temperature. A 1 mm rubber pad was cut (the following rubber products was washed with deionized water and removed the excess moisture with air blower) the length and width were beyond the ACF 200 mm; Cutting the 1 mm thick rubber ring to make its internal size equal to the size of the ACF electrode; tailoring polyethylene web whose length and width is 500 mm × 200 mm, then the two layers of polyethylene mesh were superposed, next using a caliper measured the thickness of 1 mm and equal to the positive and negative electrode spacing, which were the manufactory processes of the anode plate and the manufactory process of cathode was same with above.

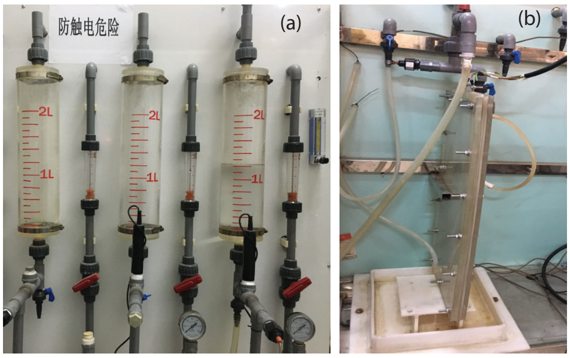

Fig. 5. Experimental device picture: (a) front and (b) back.

The assembly was arranged in order from left to right, and the CDI module was obtained by fixing the anticorrosion bolt. The wiring post welded on the electrode plate led the wire to connect the DC switch power supply, and the modules at the left and right ends were connected to the water and effluent conduit, the conductivity meter and pH meter were installed on the entrance side, and the conductivity meter was fixed at the outlet side. The CDI module was installed on the bench and the entire experimental system was completed.

In this experiment, non-cyclic injection method was adopted, and the treated saline was directly entered into the freshwater tank for further research. The NaCl solution was first configured in the sample tank, then keeping the freshwater value was open, opening the pump switch, adjusting the water flow, opening the DC switching power supply and monitoring the voltage between the two plate size, finally recording the initial entry conductivities and pH values.

And the export conductivities were recorded at every other 10 s, the desalting process was not over, until the export conductivity value dropped to the lowest point and the conductivity value began to increase subsequently. The DC power was reversed, but the original concentration sample

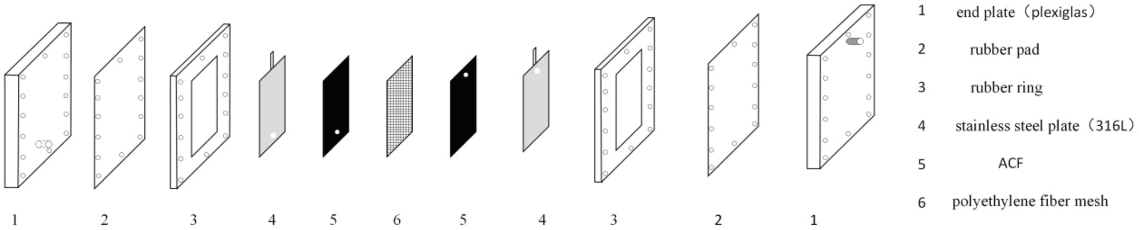

Fig. 6. CDI internal structure diagram.

was continued to be used, and monitoring the export conductivity value. Due to the reversed power, the direction of electrostatic force would have a change, and the ions that adsorbed on the surface of the plate would desorb from the plate. Meanwhile, the export conductivity values would raise consistently, which was the discharge stage of concentrated water. At this time, the conductivities continued growth to the greater than the entrance conductivity values. If the conductivity values began to descend, turning off the DC switch power supply, so the regeneration process was end and what we needed to do next was to wash the module stack. When the conductivity values of outlet and inlet was reduced to less than 5 μs/cm, the cleaning process was completed, then adjusting the sample tank flow regulator to the appropriate flow rate for the next experiment, finally closing the overall experiment system until the next experiment. Electrical conductivity could characterize the amount of salt in solution [23], and there was a good linear relationship between the concentration and conductivity of solution. In this experiment, the removal rate of electrical conductivity was utilized to determine the desalination ability of electrical adsorption.

The calculation parameters used in this experiment are defined as follows:

$$\eta = \frac{\int_0^t (C_0 - C)dt}{\int_0^t C_0 dt} \times 100\% \qquad (1)$$

where η—conductivity removal rate, %; when the outlet conductivity and inlet conductivity is equal, then the t is the most corresponding time (i.e., electrode adsorption saturation time), at this time, the η is the average desalination rate; C_0—the inlet conductivity value, which is a constant, is the value of the injection sample, μs/cm; C—the value of export conductivity changed with time, μs/cm; This is, $C = f(t)$, the time interval of t is 10 s.

4. The results and analysis of experiment

The desalination performance of electro-adsorption equipment is affected by many factors. The concentrations of sample, voltages, and flow rates are the main influence parameters. ACF was made as electrode and sodium chloride solutions with concentration of 300–800 mg/L were taken as samples. In this experiment, in order to achieve desalination rapidly and efficiently, reduced the experiment times, shorten the experiment time, and avoided the repetition of experiment, the single-factor experiment and orthogonal experiment were used to study the influence of various parameters. The optimal operation parameters were obtained through comparing the desalination efficiency of the different working conditions.

4.1. The repeatability of experiment

To verify the accuracy and reliability of the experiment system, multiple repeated experiments were performed under the same experiment conditions. The experimental conditions for the repeatability of electro-adsorption were performed as follows: the NaCl concentration of 2 L was 0.5 mol/L, the flow rate of the repeated all three times experiment were 30 mL/min, the experiment working voltage was constant pressure at 2 V, and the electrical conductivity value was recorded once every 10 s. The results were shown in Fig. 7. Because the time of the start time is slightly different, the three groups of electro-adsorption experiment data curves were shifted marginally along with the reaction time axis. The outlet conductivity values of three sets of experiments were falling sharply in the initial stage, and then decreased slowly. In other words, before 200 s, the effectiveness was declining; after 200 s, the values were almost stable; finally, the electrical conductivity plummeted to an all-time low at 350 s. On the whole, the output conductivity of the three experiments could be overlapped with the reaction time curve, indicating the adsorption experiment could be repeated and the consequences were reliable.

4.2. The influence of the concentration of feed liquid

The electro-adsorption reactor designed in this experiment is a laboratory scale different from the actual production and industrial application. Limited by the objective environment and economic conditions of the laboratory, one pair of electrodes is adopted in the electro-adsorption reactor. In view of the limited adsorption capacity by limited electrodes, 2 L, 300, 500, and 800 mg/L NaCl solution was, respectively, used, the voltage was 1.5 V, and the flow rate was 40 mL/min. And the experiment was tested at room temperature and atmospheric pressure. The results of specific experiment are shown in Figs. 8 and 9.

It can be seen from Fig. 8, the output electrical conductivity of the three kinds of sample dramatically fell with time at the beginning, followed by slow decline, and eventually stabilizing. Obviously, at the beginning, the electrode in a blank state has stronger adsorption ability.

However, after a period of desalination treatment, both surfaces of the electrode would be enriched with a certain number of charged particles. At this time, due to the ions of same charge adsorbed on one side plate, there would be a certain degree of repulsion between each other the ions or particles, they entered into flow channel but could not be adsorbed, so the desalination capability of the electro-absorption device was declined.

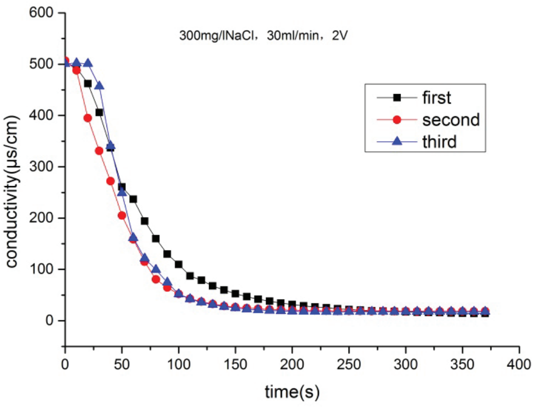

Fig. 7. Repeatability verification of the electro-adsorption experiment system.

Therefore, the outlet conductivity would decrease slowly. When the electrode adsorption reached saturation, the electrode of adsorption capacity was forfeit; the export conductivity value dropped to a minimum, then remained unchanged.

As can be seen from Fig. 8, the higher the concentration of NaCl solution in the influent, the greater the drop gradient of the conductivity of the effluent, and shorter the time to reach the adsorption equilibrium. Because at the same velocity, time, and solution volume, the higher the concentration, the greater the amount of ions contained in the same volume of solution, and greater the amount of Na^+ and Cl^- that participate in the reaction; which means at the same time, per unit area of the electrode have more chances to absorb the ions in the solution, thus the process of electro-adsorption would reach saturation more quickly. On the contrary, the lower the concentration of the solution, the lesser the total number of ions in the unit volume solution, and time to reach the adsorption saturation will also be extended, so it would affect the adsorption efficiency.

It can be seen from Fig. 9 that the desalination rate of NaCl solution at different concentrations can be observed with the time change curve. As the concentration increased at the beginning of the reaction, the desalination rate enhanced, but as the reaction time lengthened, the desalination rate reached its peak and then began to drop down slowly. At the concentration of 800 mg/L, the highest desalination rate at 600 s was up to 90.17%, which was 5.57% higher than the sample of 500 mg/L. Because the concentration of ions or charged particles will affect the adsorption capacity of the material, when the concentration increases the adsorption capacity will be increased accordingly. From the above picture, the higher the concentration, the lower the desalination rate, and the final desalination rates of the three concentrations from low to high were 62.26%, 51.27%, and 48.71% respectively. With the increase of influent concentration, the increase of electrode adsorption cannot keep up with the increase of concentration. Under the same volume, the higher the concentration of the sample solution required, the lower the total desalination rate. Hence, according to the different concentration of sample solution, the electrode device of corresponding scale will be selected to achieve the desired desalination effect.

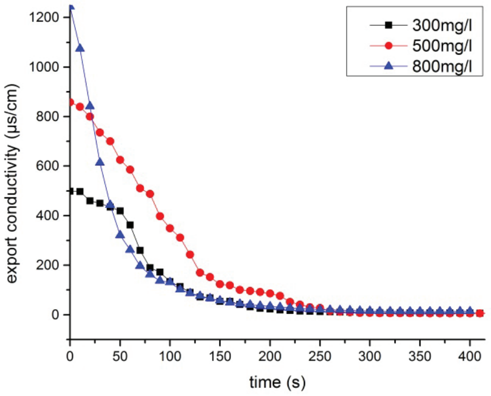

Fig. 8. Desalination effect of different liquid concentration.

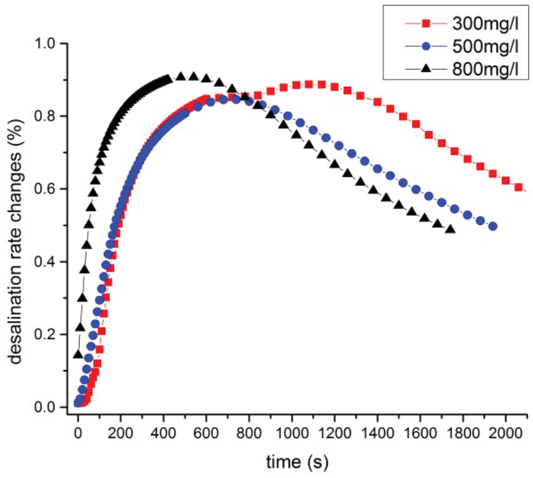

Fig. 9. Desalination rate of different liquid concentration.

4.3. Effect of the flow rate of feed liquid

According to the specific conditions of the experimental system, the flow rates of material were selected at 20, 40, and 60 mL/min, respectively, the influence of the flow rate on the adsorption process was investigated under normal pressure at room temperature. The voltage was 1.5 V, and the sample was selected as 500 mg/L of NaCl solution. The results of specific experiment are shown in Figs. 10 and 11.

According to Fig. 10, as time gone by, the overall change trend of electrical conductivity was as follows: rapidly drop, steadily decline, gradually stable, and dramatically improve. The three velocity curves were basically consistent. The smaller the flow rate, the greater the conductivity removal time; the larger the flow rate was, the more obvious was the change of conductivity curve, and the shorter time that reached the minimum value, the shorter time that maintained the adsorption equilibrium and the electrical conductivity of the second half of the curve increased significantly. This means that a large number of ions are still not adsorbed

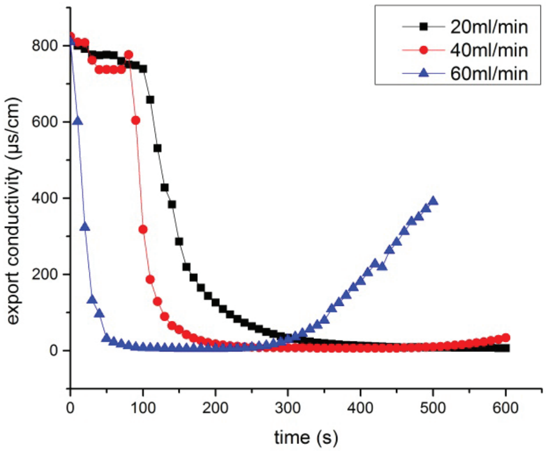

Fig. 10. Desalination at different flow rates.

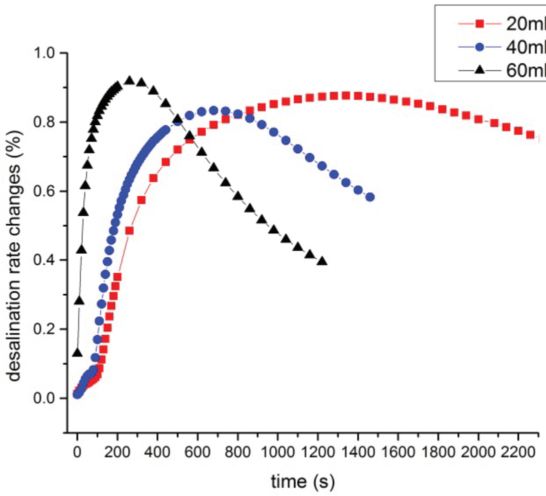

Fig. 11. Rate of desalination at different flow rates.

by the electrode and are discharged with the water, causing a rapid rise in electrical conductivity.

It can be seen from Fig. 11, under the same conditions of the inlet voltage and sample conductivity, the flow rates were 20, 40, and 60 mL/min, respectively, and the corresponding maximum conductivity removal time points were 1,340, 680, and 320 s, respectively. Rates were 69.74%, 58.28%, and 39.46%, correspondingly. As the inflow velocity decreased, the time of the sample solution in the electro-adsorption reactor increased, and the hydraulic disturbance was smaller. This allowed the double layer to have more sufficient time to adsorb charged ions in the solution; thus, the amount of ions that were carried away by the water decreased and the effect of desalination would be better.

However, if the flow rate is too slow, the amount of water processed per unit time will also decrease, the desalination efficiency will be greatly affected, the energy consumption will enhance, and the processing cost will rise.

4.4. The impact of voltage

Considering that the voltage exceeds the limit voltage of the adsorption device, NaCl solution can be electrolytic, which affects the effect of desalting. Therefore, in this experiment, the three voltages of 1.5, 2, and 2.5 V were selected to conduct the experiment of electro-sorption at normal temperature and pressure. At the same time, in order to explore the influence of self-adsorption of electrodes on the effect of desalination, a group of control experiments with no voltage were done. The concentrations of the feed solution of this experimental were 500 mg/L for 2 L, flow rate of 40 mL/min, and the number of plates for a pair. The experimental results were shown in Figs. 12 and 13.

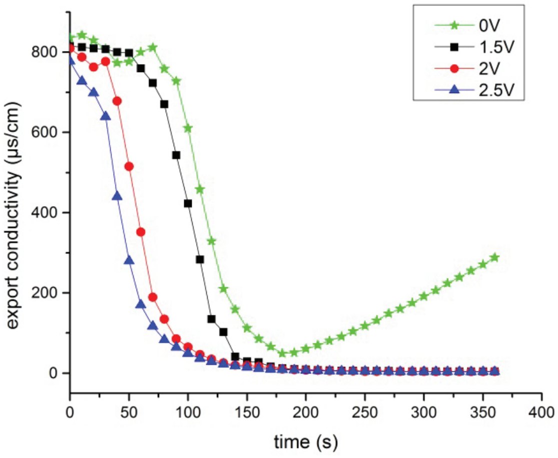

Fig. 12. Desalination effect at different voltages.

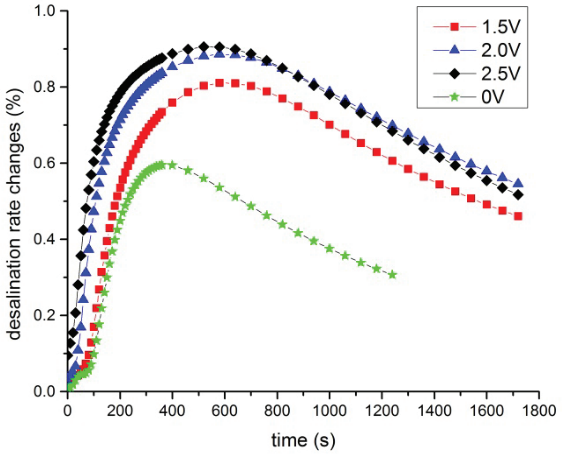

Fig. 13. Change rate of desalination at different voltages.

From Fig. 12, what we can obtain was that part of the electrical conductivities can be removed through self-adsorption by ACF electrode without voltage and reached the adsorption equilibrium at about 180. The equilibrium time cannot be sustained. The conductivity of the outlet rapidly increased with time, but the outlet conductance rates were significantly higher than the case of voltage, the results of this experiment had a worse effect on the adsorption of ions. Under the condition of different voltage applied, the conductivity of the outlet dropped sharply within the first 150 s of operation. The higher the voltage, the more obvious is the declining trend, at last, which reached the plateau after about 150 s. The durations of steady phase were 210, 350, and 290 s, respectively, and the rising time points were 270, 460, and 400 s, respectively, and the lowest value of outlet conductivity was almost the same. According to the above data, it could be seen that as the voltage increases, the stationary phase would last longer, but when the voltage continued to rise to 2.5 V, the steady phase duration can no longer extend, and fell slightly instead. This is because the electric field is the main motivation for ion transport in the electro-sorption device. According to the electrochemical theories, the electric field force enhances with the rising of the voltage under certain conditions of the plate spacing. Under the same conditions, the faster the migrations rate of ions, the greater the drop in outlet conductivity at the same time. When the voltage continued to go up to 2.5 V, there was a small amount of air bubbles in the water, which indicated that the electrolysis of the part of the sodium chloride solution, causing the corrosion of the metal plate and also increases the loss of the energy of the module, and it had a serious effect on the removal of the salts, so that the rate of electrical conductivity was not decreasing.

As can be seen from Fig. 13, in the absence of voltage, the desalination rate was significantly lower than the ratio of applying voltage; the final desalination rate could reach 30.6% only, which showed that the voltage was the main driving force of ion migration during the process of desalting. With the aggrandizement of voltage, the rate of desalination increased gradually, and the corresponding instantaneous cumulative maximum desalination rates were 81.11%, 88.63%, and 90.54%, respectively; the desalting rates were 60.6%, 69.8%, and 68.4% (no-voltage, the saturation time of electrode adsorption). With the enlargement of the voltage, the time required to reach the maximum desalination rate diminished. This is because the greater the voltage applied between the plates, the thicker is the electric double layer formed on the plate surface, the total amount of charge stored on the plate manifold, resulting in an increase in the residual charge density on the electrode surface. The dispersed layers in the layers become more compact, which makes it easier to adsorb ions in the water. The enhancement of electrostatic force accelerated the migration of ions in the solution, and the ion-enrichment effects in the double-layer ACF surface were also stronger and faster, which manifested that the desalination efficiency was improved, and the time to reach the adsorption equilibrium was shortened.

4.5. Orthogonal experiment

In order to explore the main factors affecting desalination rate, so as to determine the optimal adsorption conditions. In this experiment, the effects of feed concentration, flow rate, and voltage on the electro-adsorption were studied by orthogonal experiments of three factors and five levels. The sample concentrations were 200, 300, 500, 600, and 800 mg/L. Flow rates were 10, 20, 30, 40, and 60 mL/min, respectively. The voltages were 1.5, 2, 2.5, 3, and 4 V, respectively. Total 25 experiments, the precise experimental datum are shown in Table 2.

According to the calculation method of orthogonal experiment, the data in Table 2 are analyzed by orthogonal analysis. The calculation results are shown in Table 3.

In Table 2, instantaneous maximum desalination rate is defined as follows:

$$P_{\max} = \frac{\int_0^t (C_0 - C_{\min})dt}{\int_0^t C_0 dt} \times 100\% \tag{2}$$

where $P_{\max}$ is instantaneous maximum desalination rate (%); $C_{\min}$ is the minimum value of outlet conductivity over time (μs/cm); and C_0 is the initial value of inlet conductivity (μs/cm).

In Table 3, the sum of the desalination rates for every five experiments is defined as follows:

$$K_x = \sum_{i=1}^{5} P_i (x = 1{\sim}5) \tag{3}$$

Table 2
Orthogonal analysis data sheet

Order	Concentration (mg/L)	Voltage (V)	Flow rate (mL/min)	$P_{\max}$ %
1	200	1.5	10	95.83
2	200	2.0	20	84.71
3	200	2.5	30	85.26
4	200	3.0	40	93.41
5	200	4.0	60	82.21
6	300	1.5	10	88.18
7	300	2.0	20	77.89
8	300	2.5	30	90.96
9	300	3.0	40	86.47
10	300	4.0	60	86.07
11	500	1.5	10	89.93
12	500	2.0	20	86.06
13	500	2.5	30	92.94
14	500	3.0	40	88.24
15	500	4.0	60	76.62
16	600	1.5	10	86.03
17	600	2.0	20	88.12
18	600	2.5	30	83.62
19	600	3.0	40	80.96
20	600	4.0	60	91.87
21	800	1.5	10	91.23
22	800	2.0	20	90.01
23	800	2.5	30	87.97
24	800	3.0	40	86.68
25	800	4.0	60	94.04

Table 3
Orthogonal analysis calculation results

Consequence	Concentration	Voltage	Flow rate
K_1	441.42%	451.20%	443.77%
K_2	429.56%	426.79%	418.43%
K_3	433.80%	440.75%	431.64%
K_4	430.60%	435.76%	450.50%
K_5	449.93%	430.81%	440.98%
k_1	88.28%	90.24%	88.75%
k_2	85.91%	85.36%	83.69%
k_3	86.76%	88.15%	86.33%
k_4	86.12%	87.15%	90.10%
k_5	89.99%	86.16%	88.20%
R	4.08	4.88	6.41

where x is experiment number and K is the sum of the desalination rates for every five experiments.

In Table 3, k_x is the average value of K_x;

$$k_x = \frac{K_x}{5} \quad (x = 1,2,3,4,5) \tag{4}$$

In Table 3, R_x is the result of range analysis. When the range value is large; the range has great influences on the index, which is the main factor; while the range value is small and the influence of the index is small, it is the secondary factor. The formula of R_x can been as follows:

$$R_x = \max(k_x) - \min(k_x) \quad (x = 1,2,3,4,5) \tag{5}$$

Experimental data can be obtained by range sequence: *R* (velocity) > *R* (voltage) > *R* (concentration), so the velocity is the main factor, followed by voltage, concentration, owing to the ranges value of concentration and voltage are close, they have the same effect on the desalination effect. In view of that experimental result and the experimental setup of the experiment, the best run conditions of the experiment were as follows: when the spacing of plates was 1 mm, the flow rate was 40 mL/min, the voltage 1.5 V, and the concentration of 800 mg/L. It should also be pointed out that the initial current of the system is 0.034 A under these conditions, and current of the stack tends to stabilize and remains at 0.02 A as the electro-sorption process progresses. Li et al. [24] used ACF electrode for electro-adsorption and desalination experiment, through the single-factor experiment analysis, the optimal voltage was 2.0 V, the electric plate spacing was 1 mm, and the inlet rate was 10 mL/min, the water inlet conductivity was 1,000 µs/cm, and the conductivity removal rate above 40% could be achieved. Ma et al. [25] carried out the similar experiments, the best conditions were the optimal voltage 2 V, spacing 1 mm, flow velocity 0.56 m/min, and the process length 330 cm, the desalination rate of 90% could be reached. The results of this experiment are consistent with the existing research results, and reveal that the ACF electrode has better application prospects in the aspect of adsorption and desalination.

4.6. Electro-adsorption experiment of actual circulating water sample

Considering the use of synthetic wastewater does not achieve proof of concept for real wastewaters, the circulating cooling wastewater from a thermal power plant in the local city was collected. The experiment was performed under the optimum conditions by using the simulated electro-adsorption test bed obtained above. Firstly, a full analysis of the water quality was performed on the water samples. The results of the analysis are shown in Table 4. During the experiment, the outlet conductivity was recorded and the desalination rate was calculated. The results are shown in Fig. 14. At the same time, during the entire experiment process, seven samples were taken at the exit of the membrane stack every 100 s. A titration test was performed on the main ions of calcium, magnesium, chloride, and sulfate in the seven samples, respectively, and the specific results are shown in Fig. 15.

Color is one of the important indicators reflecting the appearance of water. The actual circulating water is yellow and tasteless transparent liquid. After treated by EST module, the effluent was colorless and clarified liquid. It shows that the removal of color can reach the standard of reuse of "Code for design of industrial recirculation cooling water treatment (GB/T 50050-2017)". Before the experiment, the conductivity of the actual water sample was 2,270 µs/cm. In Fig. 14, the electrical conductivity of the export coincided with the simulated sodium chloride solution, and all of which declined rapidly at the beginning stage and then gradually increased steadily.

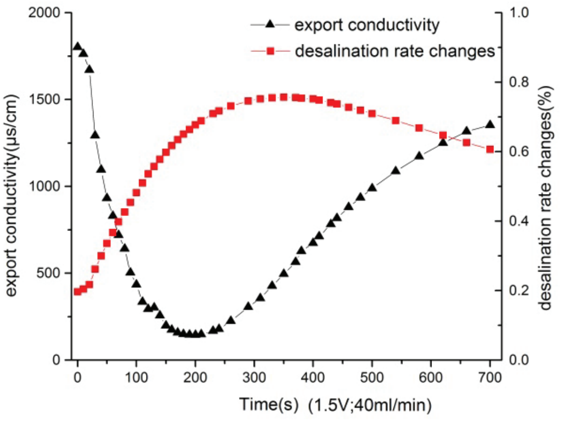

Fig. 14. Desalination effects of actual circulating cooling water.

Table 4
Water quality analysis of actual circulating cooling water sample

Cation (mg/L)	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cu^{2+}	Fe^{2+}
	335.77	130.81	174.75	174.75	0.01	0.003
Anion (mg/L)	F^-	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	NO_3^-
	2.85	452.01	384.24	613.86	50.7	194.90
Hardness/acidity and alkalinity (mmol/L)	Total hardness	Non-carbonate hardness	Carbonate hardness	Methyl orange alkalinity	Phenolphthalein alkalinity	pH
	15.45	5.39	10.06	10.06	1.69	8.91
Others (mg/L)	COD_{Mn}	Dissolving solids	Suspended substance	Total silica	Conductivity	Turbidity (NTU)
	6.89	2,350.8	20.2	57.75	2,824	7.59

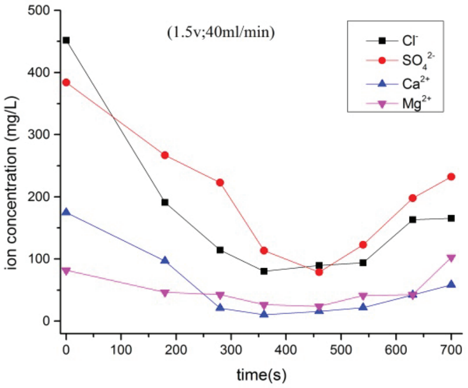

Fig. 15. The removal effect of each ion in the actual circulating cooling water.

The export conductivity could be as low as 145.6 μs/cm in 190 s. At the 350th s, the desalination rate was 75.63%, which was the best for desalination. The average desalination rate of the whole process was 60.66%. The data show that the device has good desalination effect on the actual circulating water. However, the time of conductivity reaching the lowest point was much earlier than that of the analog liquid outlet, the electric conductivity remained stable for a short time. This can be explained by the fact that the conductivity of the actual recirculation water sample is high and the ion components are complex. Meanwhile, the size of the membrane stack is small and the adsorption capacity is limited, so the time to reach adsorption saturation will also be advanced. In the same desalination standard, in the same desalination standard, the water volume that membrane stack handling also decreases. Therefore, to further explore the electrical adsorption performance of the actual circulating water, it is necessary to increase the logarithm of the electrode and the size of the electrode, and design a more reasonable scale to meet the requirements of recycling.

SO_4^{2-} is an important factor for the scaling and blocking of pipes. The corrosion of metal pipes increases with the increase of concentration. SO_4^{2-} ion is very difficult to remove in the sewage water. It will cause adverse effects on the environment and human health. As can be seen from Fig. 15, the concentration of SO_4^{2-} in the influent was 384.24 mg/L, and the concentration of sulfate in the effluent reached a minimum of 78.77. The average removal rate of sulfate could reach 51.21%.

Both Ca^{2+} and Mg^{2+} are hardness-related indicators, excessive concentration can cause severe fouling of the heat-exchange equipment. From Fig. 15, it can be seen that the lowest concentrations of calcium and magnesium ions in the effluent were 10.4 and 24 mg/L, respectively. The average removal rate of Ca^{2+} was 50.1%, and the average removal rate of Mg^{2+} was 48.5%.The removal rate of the total hardness of the electro-adsorption device was stable at about 65%, and the effluent concentration of the treated water satisfied the standard of water supply for open circulating water.

Chloride is the main component of the influent. Excessive chloride ions will corrode the steel pipe fittings. The ability removing chlorides is an important indicator of electro-adsorption. The influent Cl^- concentration was 452.01 mg/L, which had exceeded the standard of open circulating water supplementation. The Cl^- concentration of produced water could reach 80.23 mg/L, the maximum removal rate was 82.25%, and the average removal rate of Cl^- in the whole process could reach 69.99%. As we all known, electro-adsorption is the dynamic equilibrium movement of ions in the electric field. Chloride ions are obviously more active than other impurity particles in the directional movement, and the proportion of adsorbed ions is also relatively low. This shows that the experimental device is ideal for Cl^- removal in actual water samples.

5. Conclusions

The higher the concentration of influent NaCl solution is, the faster will be the declining rate of conductivity of effluent, and the fastest declining rate of conductivity was 3.42 μs/cm. In the same volume, the higher the sample liquid concentration is, the lower is the desalination rate. The average desalination rates of the three concentrations from low to high were 62.26%, 51.27%, and 48.71%, respectively. The growth of electrode adsorption capacity cannot keep up with the improvement of concentration, and the electrode device of corresponding scale should be selected to achieve the desired desalination effect, according to the different concentration of treatment sample.

The smaller the flow rate is, the slower is the desalination rate, but the effect on desalination will be better. The desalination rate of the flow rate at 20 mL/min is 30.28% higher than that at 60 mL/min. The time spent on dealing with the same fluid in the flow rate at 20 mL/min is 3.1 times more than that at 60 mL/min. When the flow rate is too low, the desalination efficiency is greatly affected, and the energy consumption is aggrandized, which is not economical enough. With the gradual increase of the voltage, the decline degree of outlet conductivity will go up, the faster the desalination rate, the longer the plateau time, the higher the final desalination rate. The desalination rate with voltage was increased by 30%–37.8% compared with no-voltage. When the voltage rose from 1.5 to 2 V, the maximum salt removal rate increased by 7.5%. However, when the voltage continued to go up to 2.5 V, the solution was electrolyzed, and the desalination rate of the solution went down.

Based on the results of the comprehensive orthogonal experiment and single-factor experiment, the optimal electro-adsorption operation conditions of the device in the selection of a pair of ACF electrode were as follows: flow rate 40 mL/min; voltage 1.5 V. Under these conditions, the electro-adsorption experiments of actual water samples in power plants were carried out. The following conclusions were drawn: the average conductivity of raw water was 2,270 μs/cm, and the conductivity of water production could reach 145.6 μs/cm. The maximum desalination rate was 75.63%, and the average desalination rate was 60.66%. The average removal rate of Ca^{2+} was 50.1%, the average removal rate of Mg^{2+} was 48.5%, the average removal rate of sulfate was 51.21%, and the average removal rate of Cl^- reached 69.99%. The experimental data show that the electro-adsorption of ACF has good treatment effect on circulating cooling blow-down water in power plant.

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