Application Research on Desalination of Trona Brine by Bipolar Membrane Electrodialysis

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The salt in trona brine seriously affects the soda ash recycling in the production process of soda ash, which not only results in low quality of soda ash recycling and wastes resources. Consequently, the trona brine should be desalted. The treatment of trona brine using bipolar membrane electrodialysis can reduce the concentration of sodium chloride effectively. Desalination with two compartment of a bipolar membrane electrodialysis composed of anion exchange membrane and bipolar membrane was investigated in this study. Some parameters such as the membrane stack voltage, material flux, temperature and concentration were adjusted. The effect of the parameters on desalination rate, current efficiency and electricity consumption was researched. The optimum process conditions can be obtained through single factor experiment and orthogonal experiment when the membrane stack voltage is 24V, material flux is 5L/h, the temperature is 20 °C and the concentration is 2.0mol/L. The desalination rate can reach 97.0% while the current efficiency is 84.3%. The process is not only has low current consumption but also reach a better treatment effect.

Keywords: Bipolar membrane; Electrodialysis; Trona brine; Desalination; Orthogonal experiment

1. INTRODUCTION

The trona contains soluble non-metallic mineral of Na₂CO₃ and NaHCO₃, associated with soluble salts such as NaCl, Na₂SO₄ and a few of water insoluble and organic. The processing of trona is unique in the field of chemical industry. Typical processes for producing baking soda were carbonization process and a thermonatrite process[1-2]. Trona processing plant of inner Mongolia adopts natronite (Na₂CO₃·10H₂O) in the lake as raw material, prepared alkali halide consist of 18% sodium carbonate, 0.5% sodium bicarbonate.
According to Na$_2$CO$_3$--NaCl--NaHCO$_3$--H$_2$O quaternary solubility system principle[3], Na$_2$CO$_3$·10H$_2$O firstly reached saturation and crystallized and precipitated from solution when the temperature of evaporating and concentrating kept on the range of 35.4-109 °C [4], while NaCl still residue in the mother liquor. In order to keep solid phase point of the mixture solution staying in the Na$_2$CO$_3$·10H$_2$O crystallization area, mother liquid should be discharged properly in the process[5]. Then Na$_2$CO$_3$·10H$_2$O crystal was separated from the material liquid continuously on a certain solid-liquid ratio. Finally, bicarbonate of soda was gained after the carbonizing of Na$_2$CO$_3$.

However, the above process had two drawbacks: one is that sodium chloride residues in the mother liquor in the crystallization process, and the other is that mother liquid should be discharged timely to keep solution point staying in Na$_2$CO$_3$·10H$_2$O crystallization area, causing a lot of waste mother liquor and environmental pollution [6-7]. Recently, Qiu huibin used the phase diagram of the system to remove salt for the different solubility of salt and alkali at different temperatures [8]. But this method was limited by the solubility, leading to the low mother liquor's desalination rate and high production costs, and therefore it cannot recycling the waste liquid fundamentally.

For the purpose of rationally developing and utilizing the nature resources, a new method of desalination should be proposed which not only achieved the object of separating salt but also reduced the production costs. Ionic membrane electrodialysis technology was the combination of electrolysis and electro-adsorption [9-10], containing both of their respective advantages[11]. It has been widely used in pollution management gradually, showing a huge potential because of its cleanness, quickness and high efficiency [12-13]. Anion-exchange membrane electrolysis methods were used in this research to remove sodium chloride from mother liquid, achieving dual-purpose pollution management and resources recovery[10,14]. But it has the disadvantage of large power consumption, which makes a high cost. Bipolar membrane electrodialysis will be investigated to desalinate trona brine in this work.

2. MATERIALS AND METHODS

2.1. Reagents

Centrifugal mother liquor (contain 18% sodium carbonate, 0.5% sodium bicarbonate), Sodium chloride (analytical grade), sodium carbonate (analytical grade), sodium bicarbonate (analytical grade)

2.2 Experiment principle

Centrifugation mother liquor was added into anion membrane cathode chamber Electrolytic cell. Cl$^-$ got through anion membrane to the anode of the electrode groove, discharging electrons and generating chlorine gas on the anode surface, and then NaCl can be removed. The anion membrane electrolysis principle was shown in Figure 1:

A large amount of sodium chloride is contained in the trona brine and the quality of sodium carbonate is affected when sodium chloride is accumulated. The resources are wasted when sodium chloride is discarded [1]. In order to improve the recovery rate of sodium carbonate, the concentration
of sodium chloride need to be controlled. At present, there are many ways for industrial circulating water desalination, such as, electrodialysis [2–3], ion exchange [4–5], electrostatic shielding [6–8], and electro-adsorption [9]. The ion exchange membrane electrodialysis is clean, no pollution and low-energy, which is better than other desalting technology such as electrolysis method [10]. Among the ion exchange membrane, the bipolar membrane has a unique feature for treating salt separation [11].

Ion exchange membrane electrodialysis technology development began in 1903 and has developed slowly until Jude successfully developed the first ion exchange membrane with commercial use and high selection properties in 1949 [12-13]. In half a century, ion exchange membrane has developed from the heterogeneous phase with worse performance to the homogeneous phase which is suitable for industrial production by repeated improvements [14-17]. Up to now, electrodialysis has been extensively used in desalination, brackish water desalination, wastewater treatment and chemical separation etc [18], and recently electrodialysis in combination with bipolar membranes or with ion-exchange resins has found a large number of new interesting applications in the chemical process industry, the food and drug industry as well as in waste water treatment and the production of high quality industrial water [19].

Bipolar membranes (BPM) are composed of an anion exchange layer, a cation exchange layer and a hydrophilic interface at the junction of the two layers, and in this hydrophilic interface, water molecules are split into protons and hydroxide ions [20-21]. The bipolar membrane electrodialysis (BMED) is a novel electro-membrane process that follows the heart and soul of industrial ecology [22]. The most significant characteristic of BMED is that water can be dissociated into H\(^+\) and OH\(^-\) under a reverse current bias, and it has the advantage of economical competence and environmental benignity [23]. Improvements in stack designs and development of ion-exchange membranes with higher perm-selectivity, lower electrical resistance and better membrane stability may contribute to a significant increase of its use.

Desalination for trona brine by bipolar membrane electrodialysis is investigated, which composes of anion exchange membrane and bipolar membrane. The experiment set-up and solution to calculate desalination rate, current efficiency and energy consumption are showed in section 2. The effects of the operation parameters are researched. Finally, we conclude the feasibility of bipolar membrane electrodialysis to treat trona brine.

![Schematic diagram of the two compartment bipolar membrane electrodialysis](image)

**Figure 1.** Schematic diagram of the two compartment bipolar membrane electrodialysis
2. EXPERIMENTS

2.1 Experimental set-up

The lab-scale experimental set-up was composed of: (1) membrane stack, which is composed of six pairs of homogeneous anion exchange membrane (JAM) and bipolar membrane electrodialysis (BPM-I). The properties of homogeneous anion exchange membrane (JAM) are showed in table 1, while table 2 shows the bipolar membrane electrodialysis (BPM-I).

Table 1. The properties of homogeneous anion exchange membrane (JAM).

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Appearance</th>
<th>Thickness (mm)</th>
<th>Exchange capacity (meq g$^{-1}$)</th>
<th>Moisture content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JAM-II-07</td>
<td>yellowish</td>
<td>0.16-0.23</td>
<td>1.8-2.0</td>
<td>24-28</td>
</tr>
</tbody>
</table>

Table 2. The properties of the bipolar membrane electrodialysis (BPM-I)

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Appearance</th>
<th>Thickness (mm)</th>
<th>Exchange capacity (meq g$^{-1}$)</th>
<th>Moisture content (%)</th>
<th>Voltage drop (V)</th>
<th>Bursting strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMP-I</td>
<td>Light: sandy Shadow: pale grey</td>
<td>0.16-0.23</td>
<td>Light: 1.4-1.8 Shadow: 0.7-1.1</td>
<td>35-40</td>
<td>0.9-1.8</td>
<td>&gt;0.25</td>
</tr>
</tbody>
</table>

2.2 Technical indicators

(1) Desalination rate
Desalination rate is calculated as following Eq. 1.

$$\varphi = \frac{m_1-m_2}{m_1} \times 100\%$$ (1)

Where $m_1$ (g) is the content of sodium chloride before electrodialysis experiment; $m_2$ is the content of sodium chloride after electrodialysis experiment.

(2) Current efficiency
Current efficiency $\eta$ (%) is calculated as following Eq. 2.

$$\eta = \frac{FQ\Delta C}{nIt}$$ (2)
Where $\eta$ is current efficiency; $\Delta C$ (mol/L) is the change of the concentration of sodium chloride; $F$ is Faraday constant (96500); $Q$ (L) is the volume of base compartment; $I$ (A) is current used to the stack; $n$ is repeating unit of the stack; $t$ (s) is test time.

(3) Energy consumption

Energy consumption (kwh/kg) is calculated as following Eq. 3.

$$W = \frac{UIt}{\Delta m}$$

(3)

Where $W$ is energy consumption; $U$ (V) is the voltage drop across stack; $I$ (A) is the current applied; $\Delta m$ (kg) is the decrement of sodium chloride.

3. RESULTS AND DISCUSSION

3.1 Single factor experiment

3.1.1 Effect of membrane stack voltage

The membrane stack voltage has a direct impact on electrodialysis desalination. In the process of desalination, the current is mainly used in the bipolar membrane water dissociation when membrane stack voltage is too high, leading to the non-ideal separation effect; ion migration force of each compartment is not big enough when membrane stack voltage is too low, also leading to the non-ideal separation effect. It is important to determine the membrane stack voltage in the two compartment electrodialysis.

![Figure 2. Effect of membrane stack voltage on desalination.](image)

The effect of membrane stack voltage on desalination rate, current efficiency and energy consumption is showed in Fig. 2. Desalination rate and current efficiency increase with the membrane
stack voltage before 24 V, but they decrease after 24 V. Energy consumption increases with membrane stack voltage. The transmission of electron depends on the ions in the solution. But when the voltage is low, there is no extra current to ionization. Desalination rate and current efficiency increase with the higher voltage. This is because when the membrane stack voltage is higher, there is enough current to ionize the water in bipolar membrane, which is a favor to the transmission. However, when the membrane stack voltage is too high, the resistances become bigger, leading to the decrease of desalination rate. Because desalination rate and current efficiency is highest when the membrane stack voltage is 24 V, and power consumption is in the middle level, so it is advisable to choose 24 V of membrane stack voltage.

3.1.2 Effect of material flux

Theoretically, increasing the material flux can improve the removal rate of sodium chloride, but separation effect will not endless increase with the material flux. So the material flux must be controlled at suitable range. The effect of material flux on desalination rate, current efficiency and energy consumption is showed in Fig. 3.

![Figure 3](imageurl)

Figure 3. Effect of material flux on the desalination.

Desalination rate and energy consumption decrease with the material flux, while current efficiency increases with material flux. The brine will not enter the ion membrane when material flux increases, leading to the decrease of desalination rate. The increasing of trona brine will make the resistance become smaller, which will decrease the energy consumption. The optimum material flux is 3.5L/h from Fig. 3.
3.1.3 Effect of temperature

The effect of temperature on desalination rate, current efficiency and energy consumption is showed in Fig. 4. Fig. 4 shows that desalination rate, current efficiency and energy consumption remain steady with temperature. So room temperature can be chosen in the experiment.

![Figure 4. Effect of temperature on desalination.](image)

3.1.4 Effect of feed concentration

Feed concentration will affect the concentration difference of compartment, which will increase the ion transmittance. So it is important to choose a suitable feed concentration, resulting in a bigger desalination rate.

![Figure 5. Effect of feed concentration.](image)
The effect of feed concentration on desalination rate, current efficiency and energy consumption is showed in Fig. 5. Desalination rate and current efficiency increase with the feed concentration then lower. This is because the increase of feed concentration can lead to greater concentration difference, therefore, desalination rate and current efficiency are increased, but higher concentration of the feed concentration leads water diffusion increase, desalination rate and current efficiency is reduced when feed concentration reaches 2mol/L. The results also indicate that the energy consumption become bigger with higher concentration.

3.2 Orthogonal experiment

The result of experiment by orthogonal design is shown in table 3.

<table>
<thead>
<tr>
<th>Membrane stack voltage A (V)</th>
<th>material flux B (L/h)</th>
<th>Temperature C (°C)</th>
<th>Feed concentration D (mol/L)</th>
<th>Desalination rate (*100%)</th>
<th>Current efficiency (*100%)</th>
<th>Energy consumption (kwh/kg)</th>
<th>index</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 22 (1)</td>
<td>2 (1)</td>
<td>20 (1)</td>
<td>1.5 (1)</td>
<td>0.8911</td>
<td>0.2375</td>
<td>0.2343</td>
<td>1.8943</td>
</tr>
<tr>
<td>2 22 (1)</td>
<td>3.5 (2)</td>
<td>30 (2)</td>
<td>2 (2)</td>
<td>0.9005</td>
<td>0.5032</td>
<td>0.3532</td>
<td>2.0505</td>
</tr>
<tr>
<td>3 22(1)</td>
<td>5 (3)</td>
<td>40 (3)</td>
<td>2.5 (3)</td>
<td>0.8722</td>
<td>0.4427</td>
<td>0.2831</td>
<td>2.0318</td>
</tr>
<tr>
<td>4 24 (2)</td>
<td>2 (1)</td>
<td>30 (2)</td>
<td>2.5 (3)</td>
<td>0.9385</td>
<td>0.6812</td>
<td>0.4023</td>
<td>2.2174</td>
</tr>
<tr>
<td>5 24 (2)</td>
<td>3.5 (2)</td>
<td>40 (3)</td>
<td>1.5 (1)</td>
<td>0.9532</td>
<td>0.7682</td>
<td>0.3652</td>
<td>2.3562</td>
</tr>
<tr>
<td>6 24 (2)</td>
<td>5 (3)</td>
<td>20 (1)</td>
<td>2 (2)</td>
<td>0.9695</td>
<td>0.8429</td>
<td>0.3814</td>
<td>2.431</td>
</tr>
<tr>
<td>7 26 (3)</td>
<td>2(1)</td>
<td>40 (3)</td>
<td>2 (2)</td>
<td>0.9212</td>
<td>0.6652</td>
<td>0.4389</td>
<td>2.1475</td>
</tr>
<tr>
<td>8 26 (3)</td>
<td>3.5 (2)</td>
<td>20 (1)</td>
<td>2.5 (3)</td>
<td>0.9101</td>
<td>0.3012</td>
<td>0.4624</td>
<td>1.7489</td>
</tr>
<tr>
<td>9 26 (3)</td>
<td>5 (3)</td>
<td>30 (2)</td>
<td>1.5(1)</td>
<td>0.8813</td>
<td>0.5881</td>
<td>0.4029</td>
<td>2.0665</td>
</tr>
<tr>
<td>T1 5.9766</td>
<td>6.2592</td>
<td>6.0742</td>
<td>6.317</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T2 7.0046</td>
<td>6.1556</td>
<td>6.3344</td>
<td>6.629</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T3 5.9629</td>
<td>6.5293</td>
<td>6.5355</td>
<td>5.9981</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K1 1.9922</td>
<td>2.0864</td>
<td>2.0247</td>
<td>2.1057</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K2 2.3349</td>
<td>2.0519</td>
<td>2.1114</td>
<td>2.2097</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K3 1.9876</td>
<td>2.1764</td>
<td>2.1785</td>
<td>1.9993</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R 0.3473</td>
<td>0.1245</td>
<td>0.0671</td>
<td>0.2104</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In this orthogonal experiment, four factors were researched. Results showed that the most important factor is membrane stack voltage, while the least factor is temperature. Furthermore, the optimum process conditions of bipolar membrane electrodialysis were determined. The optimal combination was chosen by the relationship of index and factors and also the relationship of primary
and secondary of factors. For the primary factor, the best level was chosen, while both the best level and other factors benefiting the experiment may be chosen. So the best combination is A₂B₃C₁D₂.

3.3 Comparisons and discussions

Traditional phase separation methods are based on the phase diagram of system, considering the different solubility of sodium carbonate, sodium chloride and other salt components at different temperature[3-5]. These methods can separate out part of the sodium chloride from the trona brine, but are limited to the salt components solubility. The separation efficiency of sodium chloride are low with traditional phase separation methods. Meanwhile, these methods need to control strictly the temperature to realize the salt separation, which induce a high production cost[6-8]. Desalination process with bipolar membrane electrodialysis is not only clean, environment friendly, but also low energy consumption, convenient to operate and maintain, which has obvious advantages compared with the traditional separation methods.

Although anionic membrane electrolysis methods were used in this research to remove sodium chloride from mother liquid, achieving dual-purpose pollution management and resources recovery[10,14]. Because its principle is decomposition of sodium chloride by electrolysis, it has a high power consumption, and lead to a high cost. On the other hand, power consumption of bipolar membrane electrodialysis is due to ion migrations, which need less power. It can meet the demands of industrial production and save on costs.

4. CONCLUSIONS

The bipolar membrane electrodialysis technology does well in the desalination of trona brine. When the membrane stack voltage is 24V, both desalination and current efficiency is the highest and the energy consumption is modest. Desalination rate and energy consumption decrease with the material flux, and current efficiency increase with the material flux. The temperature has non-significant effect on the desalination. But the current efficiency and energy consumption are affected by the concentration, so a moderate concentration is important.

In this study, the optimum process conditions were determined. When the membrane stack voltage is 24V, the material flux is 5L/h, the temperature is 20 °C and the concentration is 2.0mol/L, high desalination rate and high current efficiency and low energy consumption are obtained. The desalination rate can reach 97.0% while the current efficiency is 84.3%. The process is not only has low current consumption but also reach a better treatment effect.

References


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