The effect of ion exchange membranes on the bipolar membrane electrodialysis of ammonium chloride wastewater

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Abstract. The different bipolar membranes and their configurations with monopolar ion exchange membranes from different manufacturers such as FAB-FBM-FKB, AHA-(BP-1E)-CMB, and JAM-(BMP-1)-JCM are used in the bipolar membrane electrodialysis (BMED) of simulated NH4Cl wastewater to examine the effect of membrane properties on the generation of HCl and NH3∙H2O. The results indicated that the configuration of AHA-(BP-1E)-CMB presented the promising performance among all the ion exchange membranes according to the generated acid and base concentration. And the configuration of FAB-FBM-FKB presented the expected performance on the membrane stack voltage, energy consumption, current efficiency of the BMED system. The stability of different ion exchange membranes in strong acid and base solution were investigated further by the analyses of SEM, contact angle and membrane resistance. It was found that the membranes AHA and FKB had better chemical stability than other membranes.

1. Introduction
Bipolar membrane electrodialysis (BMED) technology is a special technique to convert salt into its corresponding acid and base without addition of other reagents [1]. The BMED is based on the advantage of a bipolar membrane (BM) that can efficiently split water into H⁺ and OH⁻ under a direct electric fields [2]. BM consists of an anion exchange layer on one side and a cation exchange layer on the other side. Water splitting occurs at the BM interfacial layer when placed backward voltage on it [2-4]. Only 0.83 V applied potential on bipolar membrane could make H₂O split into H⁺ and OH⁻, which is obviously lower than the potential of water electrolysis required in a traditional electrolytic cell (2.057 V) [5].

BMED takes the advantage of bipolar membranes to generate acid and base from neutral salt under the direct electric field and shows high current efficiency and low energy consumption. At present, BMED has received increased attention due to its specific performance, particularly in the field of organic acids production and purification [6-9]. It was reported that the wastewater containing sodium formate was processed by a combined-step: traditional electrodialysis (ED) for concentration and BMED for formic acid production. The ED was carried out with the current efficiency of 90% and the formic acid concentration up to 30% was obtained by BMED with the current efficiency of 80% [10].
Moreover, the succinic acid could be produced by using BMED with the unit energy consumption below 2.3 kWh/kg and high current efficiency up to 90% [11]. With increasing environmental protection awareness and the demand of resource shortage, much attention has been paid to the application of BMED in the treatment of industrial wastewater [12-15]. For example, when effluent containing NaCl was treated by BMED, the concentrations of the NaOH and HCl produced was close to 2 mol/L [16]. It has been reported that the wastewater produced from a metal washing step was treated by BMED technology for the generation of corresponding inorganic acid and base with the concentration of acid up to 1.76 mol/L and base to 2.41 mol/L [17]. BMED could also be used to treat high concentration of NH₄Cl wastewater to reach desalination and with products of HCl and NH₃·H₂O [13]. For reasons of economics and environment protection, a sustainable solution should be explored. The wastewater may be considered a ‘renewable resource’ that can be reused or recovered. BMED is a promising process to control wastewater pollution and achieve economical sustainable development [18-19]. There are many reports on the application of BMED in treating industrial effluent because of the many superior properties of BMED such as no gas produced following the water splitting, low running costs, space-saving and no undesirable products generated [20]. Current efficiency (CE), energy consumption (EC) and the yield of acid or base are generally taken as the important criterion of the BMED performance, while the operation conditions could make influence on those criterion by improving the properties of BMED [13-14, 16-17, 21-22]. The influences of conditions on the properties of BMED system are listed on Table 1.

### Table 1. The influences of conditions on the properties of BMED.

| Limitations                      | Influences                                                                 | Reference        |
|---------------------------------|---------------------------------------------------------------------------|------------------|
| Concentration of salt solution  | High salt concentration can produce high concentration of acid and base, reduce EC and increase CE. | [13], [17]       |
| Concentration of acid or base solution | High initial concentration of acid or base can increase final yield of acid or base while reduce production rate. | [13]             |
| Current density                 | Had an important influence on the EC of BMED.                             | [13], [17], [23] |
| Membrane stack                  | Three compartments produce both pure acid and base, two compartments only produce pure acid or base, while it has lower EC. | [13], [23]       |

Optimizing the operating conditions of BMED system could lead to improve the properties of it to some extent. While the performances of bipolar membranes and monopolar membranes are the fundamental factors of BMED system, studies about the influences of different bipolar membranes and membrane configurations are rare, and the stability of ion exchange membranes in strong acid or base solution has not been reported.

Rare earth, electroplating, fertilizer and other industries will produce ammonium chloride wastewater. The direct discharge of ammonium chloride wastewater will lead to eutrophication of water bodies. Using the BMED technology to produce HCl and NH₃·H₂O from ammonium chloride wastewater has great research value.

In this study, simulated wastewater consisting of ammonium chloride was treated by BMED for the generation of HCl and NH₃·H₂O with different membranes. The influences of bipolar membranes and different membranes configurations on acid and base generation, current efficiency and energy consumption were investigated. As a key goal to produce high concentration acid and base in the BMED process, the study of the stability of anion exchange membrane in strong acid solution and cation exchange membrane in strong base solution is very necessary. The acid and base generation performance and chemical stability of the different membranes from different manufactures were evaluated systematically and the basis for the selection and preparation of ion exchange membranes was provided. This study could provide the basis of membrane screening for the industrial application of BMED technology of ammonium chloride wastewater in metallurgical industry.
2. Experimental

2.1. Reagents and ion exchange membranes

All the reagents used in the experiments were analytical reagents. The solutions containing ammonium chloride (60 g/L), hydrochloric acid (36%-38%) and ammonia solution (25%-28%) were used to prepare the initial solutions of salt, acid and base compartments, respectively. The solution containing 0.5 mol/L sodium sulfate was used as electrode rinse solution. It’s volume was 700 mL.

Sodium hydroxide (0.5 mol/L) and hydrochloric acid (0.5 mol/L) were used as the titration agents in acid-base titration analysis, in which methyl orange and phenolphthalein were used as the indicators, respectively. All the reagents were provided by Xilong Chemical Co. Ltd.

In order to examine the effect of different membranes on the treatment of NH\(_4\)Cl wastewater by BMED, the mono-polar ion exchange membranes and bipolar membranes from different manufacturers were used in the experiments. The membranes from three representative manufacturers (FuMa Tech, Astom and Tingrun) were chosen. The main properties of membranes used in the experiments are showed in Table 2 and Table 3, which were provided by the manufacturers.

| Membrane       | Thickness (mm) | Ion exchange capacity (meq/g) | Area resistance (Ω cm\(^2\)) | Transport number (%) | Manufacturer |
|----------------|----------------|------------------------------|------------------------------|----------------------|--------------|
| Cation exchange membrane | FKB 0.1-0.13 | 1.2-1.3                      | 4-6                          | 98-99                | FuMa Tech    |
|                 | CMB 0.18-0.25 | 1.5-1.7                      | 2.5-6.0                      | 97-98                | Astom        |
|                 | JCM 0.16-0.23 | 1.8-2.2                      | 2-5                          | 95-99                | Tingrun      |
| Anion exchange membrane | FAB 0.1-0.13 | 1.0-1.1                      | 4-7                          | 94-97                | FuMa Tech    |
|                 | AHA 0.15-0.24 | 1.5-1.7                      | 2.6-6.0                      | 95-98                | Astom        |
|                 | JAM 0.16-0.23 | 1.8-2.0                      | 5-9                          | 90-95                | Tingrun      |

Table 3. The main properties of the bipolar membranes applied in this study.

| Membrane | Thickness (mm) | Water splitting voltage (V) | Burst strength (10\(^3\) Pa) | Manufacturer |
|----------|----------------|----------------------------|------------------------------|--------------|
| Bipolar membrane | FBM 0.20-0.25 | < 1.2                      | 2.5                          | FuMa Tech    |
|           | BP-1E 0.22     | 1.2 V                      | > 4.0                        | Astom        |
|           | BPM-1 0.16-0.23| 1.25 V                     | > 2.5                        | Tingrun      |

2.2. Experimental procedure

The lab-scale experimental set-up of BMED was provided by Sanyuanbada Technology Development Co. Ltd, China. It was composed of salt-, acid- and base-compartments in the BMED experiments. The membrane stack of the BMED system consisted of a cathode, an anode, cation exchange membranes, anion exchange membranes and bipolar membranes. Four solutions including acid, salt, base and electrode rinse solutions circulated through the different compartments driven by magnetic pumps, respectively. The experimental conditions were given in Table 4. Soak the membrane in pure water for 2 h before using.

| Comparator | Initial concentration | Volume of initial solution (mL) | Current density (mA/cm\(^2\)) | Flow rate (L/h) | Membrane configuration | Surface area (cm\(^2\)) |
|------------|-----------------------|---------------------------------|-----------------------------|----------------|------------------------|--------------------------|
| Acid       | 0.05 mol/L HCl        | 500                             | 48                          | 45             | 1) FAB-FBM-FKB         | 5×10                     |
| Base       | 0.05 mol/L NH\(_3\)H\(_2\)O | 500                         |                              |                | 2) AHA-(BP-1E)-CMB     |                          |
| Salt       | 60 g/L NH\(_4\)Cl     | 700                             |                              |                | 3) JAM-(BPM-1)-JCM     |                          |
| Electrode  | 0.5 mol/L Na\(_2\)SO\(_4\) | 700                           |                              |                | 4) JAM-FBM-JCM         |                          |
|            |                       |                                 |                              |                | 5) JAM-(BP-1E)-JCM     |                          |

(Note: There were two flows of electrode rinse solution from the same electrode compartment, so the flow rate of them were the half of the other flows such as acid, base and salt solution)
The schematic diagram of the BMED system used in the experiments was showed in Figure 1. The NH₄Cl wastewater, HCl, NH₃·H₂O and electrode rinse (Na₂SO₄) solutions were recirculated in the BMED system in batch mode, and driven by four magnetic pumps. The bipolar membranes (BM), anion exchange membranes (AM) and cation exchange membranes (CM) were arranged alternately with the configuration of BM-AM-CM-BM in a membrane stack. The number of membrane triples was five in a stack. The effective surface area of each membrane was 50 cm². The spacer thickness between two membranes was 0.8 mm. When applying a direct electric field on the BMED system, the NH₄⁺ in the salt solution would transport into base compartment through cation exchange membrane and Cl⁻ into acid compartment through anion exchange membrane, respectively, and then combine with the OH⁻ and H⁺ generated by water splitting in the interface of the BM to generate NH₃·H₂O and HCl.

![Figure 1. Schematic diagram of the BMED system used in the experiments.](image)

2.3. Analytical methods
The samples of acid and base compartments were collected every 20 min of operation for analysis of hydrochloric acid and ammonia concentrations. The electrical conductivity and pH were measured by conductivity-meter (S230 SevenCompact conductivity, Mettler Toledo) and pH-meter (S220 SevenCompact pH/ion, Mettler Toledo). Surface appearance, contact angle, and membrane resistance of different membranes were analyzed by field emission scanning electron microscope (JSM-6700F), contact angle measuring instrument (OCA-20, Dataphysics) and LCR Meter (ZM2353, NF).

2.4. Data analysis
The performance of BMED process for treating NH₄Cl effluent to generate HCl and NH₃·H₂O was evaluated in terms of energy consumption (EC) and average current efficiency (ACE). The energy consumption EC (kWh/kg) was calculated as Equation 1 [17],

\[
EC = \frac{\int U \cdot I \cdot t}{60 \cdot M \cdot (C_0 - C_t)}
\]  

(1)

where \( U \) was the membrane stack voltage (V) at time \( t \) (min), \( I \) was the current (A), \( t \) was the time (min), \( M \) (g/mol) was the molar mass of base or acid, \( C_0 \) (mol/L) and \( C_t \) (mol/L) were the concentration of acid (or base) in the acid (or base) compartment at time 0 and \( t \), respectively, and \( V_0 \) (L) and \( V_t \) (L) were the volumes of acid (or base) solution at time 0 and time \( t \).

The average current efficiency (ACE) was calculated as Equation 2 [17],
where \( z \) was the ionic charge, \( t \) was the time (min), \( F \) was the Faraday constant (96485 C/mol), \( C_0 \) (mol/L) and \( C_t \) (mol/L) were the concentrations of acid (or base) in the acid (or base) compartment at time 0 and \( t \), respectively, \( V_0 \) (L) and \( V_t \) (L) were the volumes of acid (or base) solution at time 0 and time \( t \), \( N \) was the number of cell triples in a membrane stack \((N = 5)\), and \( I \) was the current (A) for time period \( \Delta t \).

3. Results and discussions

3.1. The influence of bipolar membrane on BMED

In order to examine the effect of different bipolar membranes on the performance of BMED process for the treatment of NH\(_4\)Cl wastewater, two ion exchange membranes JAM and JCM were used as anion and cation exchange membranes, in all the experiments. The bipolar membranes including FBM, BP-1E and BPM-1 were used to constitute the membrane stack configurations such as JAM-FBM-JCM, JAM-(BP-1E)-JCM, JAM-(BPM-1)-JCM. The experiment conditions were showed in Table 4.

It may be seen from Figure 2 that the electrical conductivity of salt solution decreased from 124 mS/cm to about 10 mS/cm during the BMED process with different bipolar membranes. The removal ratio of NH\(_4\)Cl were all above 90% and roughly equivalent. The conductivity of salt solution with bipolar membrane BPM-1 decreased somewhat more slowly than the other two systems at the end of the experiment. As observed in Figure 3, the concentration of the generated acid and base increased slowly with the BPM-1 at the end of the experiment which was consistent with Figure 2. Although the theoretical potential of water splitting in bipolar membrane was 0.83 V, for practical application, the potential of water splitting was usually slightly larger than 0.83 V, as seen in manufacturer’s data shown in Table 3, which was closely related to the properties of bipolar membrane. Compared with other two bipolar membranes, the poorer ability of BPM-1 to split water leaded to the reduce of H\(^+\) and OH\(^-\) splitting from water by BPM-1 in the acid and base compartments. In order to maintain the charge balance in acid and base compartments, the transfer number of Cl\(^-\) and NH\(_4\)^+ from the salt compartment to the acid and base compartments would be reduced, which leads to reduced acid and base production.

The voltages of all the membrane stacks had the same trends in constant current Figure 4. The membrane stack voltages dropped rapidly at the beginning period, and then reduced slowly at the end of experiments. The reason was that the low initial concentrations of acid and base in the acid and base compartments led to the high solution resistance, which resulted to the high voltages of the membrane stack at the beginning of the experiment. Along with the increase of the concentrations of acid and
base, the resistance of acid and base solutions decreased, which resulted in the rapidly drop of the membrane stack voltages. At the end of the experiment, the ion concentration in the salt compartment was depleted and led to increased resistance of the membrane stack, thus all the membrane stack voltages of the BMED systems with different bipolar membranes gained to increase.

At the beginning of the experiment, the voltage of membrane stacks with different bipolar membranes had different values under the same current density, i.e., $U_{\text{BPM-1}} > U_{\text{BP-1E}} > U_{\text{FBM}}$, which means that the potential of water splitting with the bipolar membranes had an order: BPM-1 > BP-1E > FBM.

After a period of BMED process, the voltage order of membrane stacks had changed to $U_{\text{FBM}} > U_{\text{BP-1E}} > U_{\text{BPM}}$. The reason was that the conductivity of salt solution with the bipolar membrane BPM-1 reduced more slowly than the other two BMED systems, and the acid and base concentration with BPM-1 also increased slower than the other two. That made the ions concentration difference of Cl⁻ (or NH₄⁺) between acid (or base) compartments and salt compartments with BPM-1 system lower than those with FBM and BP-1E systems at the end of the experiments, which could reduce the solution resistance of BPM-1 system. Therefore, the voltage of the membrane stack JAM-(BPM-1)-JCM was lower than the other two membrane stacks at the end of experiment.

The current efficiency and energy consumption of acid and base generated from NH₄Cl by BMED with the three different bipolar membranes were shown in Figure 5, which indicated that the three bipolar membranes configurations had different unit energy consumptions, i.e., $EC_{\text{BPM-1}} > EC_{\text{BP-1E}} > EC_{\text{FBM}}$, and different current efficiency, i.e. $ACE_{\text{FBM}} > ACE_{\text{BP-1E}} > ACE_{\text{BPM-1}}$. The range of the $EC$ in this study was 7~9 kWh/kg HCl and 8~10 kWh/kg NH₃H₂O. the range of $ACE$ in this study was 50%~90%. The water splitting potential of BPM-1 was higher than the other two bipolar membranes, thus the membrane stack voltage of JAM-(BPM-1)-JCM was higher at the beginning of experiment which leaded to the unit energy consumption of acid and base with JAM-(BPM-1)-JCM higher than the other two configurations. Although the voltage of the membrane stack with JAM-(BPM-1)-JCM was lower at the end of the experiment, the lower concentrations of the acid and base also lead to the higher unit energy consumption. From Equation 2, the current efficiency was closely related to the concentration of acid and base generated from NH₄Cl. As seen from Figure 3, the concentration of acid and base, $C_{\text{FBM}} > C_{\text{BP-1E}} > C_{\text{BPM-1}}$. Therefore, the current efficiency with different bipolar membranes presented the same trend as the concentrations of acid and base.

![Figure 5](image_url1) **Figure 5.** The effect of bipolar membranes on the current efficiency and unit energy consumption of acid and base with the BMED treating NH₄Cl wastewater.

![Figure 6](image_url2) **Figure 6.** The effect of membrane stacks from different companies on the conductivity of salt solution.

![Figure 7](image_url3) **Figure 7.** The concentration of acid and base in the acid and base compartments in the BMED system with different membrane configurations.
Considering the influences of three bipolar membranes on BMED of NH₄Cl in the matter of acid and base concentrations, current efficiency and energy consumption, the performance of bipolar membrane FBM was the best, and the BPM-1 was the worst among the three bipolar membranes.

3.2. Combination of different membranes

In order to examine the performance of different membranes combination from different manufacturers, three kinds configurations such as FAB-FBM-FKB, AHA-(BP-1E)-CMB and JAM-(BPM-1)-JCM were used in the treatment of NH₄Cl wastewater by BMED. The operating conditions of the experiments were shown in Table 3.

From Figure 6(a), the conductivity of solution in salt compartment with the membrane configuration of AHA-(BP-1E)-CMB decreased more quickly than that of JAM-(BP-1E)-JCM. Figure 6(b) showed that the electrical conductivity of solution in salt compartment of FAB-FBM-FKB decreased more quickly than that of JAM-FBM-JCM. Thus, it may be inferred that the anion membranes FAB and AHA, and cation membranes FKB and CMB had better ion selective permeability for Cl⁻ and NH₄⁺ ions, and lower permeability for H⁺ and OH⁻ ions than JAM and JCM. It also means that the anion membranes FAB and AHA had less resistance for the transmembrane migration of Cl⁻ ions and cation membranes FKB and CMB had less resistance for the transmembrane migration of NH₄⁺ ions.

The electrical conductivity of the solution in salt compartment with membrane configuration FAB-FBM-FKB decreased more quickly than that with the other two membrane configurations (Figure 6(c)). The results were connected with the water splitting potential of bipolar membranes and the selective permeability of ion exchange membranes. The results from section 3.1 showed that the water splitting potential of bipolar membrane FBM was the lowest of the three bipolar membranes. It means that it was easier to reach the water splitting potential of FBM and led the lower voltage of membrane stack FAB-FBM-FKB. The low voltage of membrane stack could reduce the splitting of H₂O to produce H⁺ and OH⁻ ions on the surface of anion and cation exchange membrane, thus avoid H⁺ and OH⁻ ions to replace NH₄⁺ and Cl⁻ ions from salt compartment into base or acid compartments when applying the high membrane stack voltage. So the solution conductivity of salt compartment with FAB-FBM-FKB reduced quickly. The other reason was that the conductivity change of the solution in the salt compartment was dependent on the removal of NH₄⁺ and Cl⁻ ions and on the migration of H⁺ and OH⁻ ions through the cation and anion exchange membranes.

In Figure 7, the increase rates of acid and base concentrations with different configurations were almost the same at the beginning of the experiments. After a period of BMED process, the increase rates of acid and base concentrations of FAB-FBM-FKB were higher than the other two: FAB-FBM-FKB > AHA-(BP-1E)-CMB > JAM-(BPM-1)-JCM. The higher acid and base concentrations of FAB-FBM-FKB were also related closely to the selective permeability of ion exchange membranes FAB and FKB, which meant that the membranes FAB and FKB had better ion selective permeability for NH₄⁺ and Cl⁻ ions, respectively, compared with the other mono-polar membranes. The higher acid and base concentrations in the acid and base compartments were consistent with the lower conductivity of the salt solution, shown in Figure 6. Therefore, it may be concluded that the membrane configurations of FAB-FBM-FKB presented the better performance in the treatment of NH₄Cl wastewater by BMED, due to the better perm-selectivity and lower leakage of H⁺ and OH⁻ of FAB and FKB membranes over the other mono-polar membranes.

It could be seen clearly from Figure 8 that the voltage of the three configurations showed an order that: $U_{[JAM-(BPM-1)-JCM]} > U_{[FAB-FBM-FKB]} > U_{[AHA-(BP-1E)-CMB]}$ at the prior period of experiment. With the same initial solution concentrations and current density, the higher the voltage was, the higher the membrane stack resistance was. Therefore, the resistance of the membrane configurations was: $R_{[AHA-(BP-1E)-CMB]} > R_{[JAM-(BPM-1)-JCM]} > R_{[FAB-FBM-FKB]}$. Because of the higher H₂O splitting potential of BPM-1, the voltage of membrane stack with the membrane configuration of JAM-(BPM-1)-JCM was lower than those with the other two configurations at the later period of experiment. So the concentration of acid and base in acid and base compartments with the membrane configuration of JAM-(BPM-1)-JCM
increased slower than the other two membrane configurations. Meanwhile, the conductivity of salt solution in salt compartment also reduced slower than the other two membrane configurations. Therefore, the resistance of acid, base and salt solution with the JAM-(BPM-1)-JCM was lower than the other two configurations, which led to the lower voltage of membrane stack and higher concentration of NH₄Cl in the salt compartment compared with the other two cases.

Figure 8. The voltages of membranes stack in the BMED system with different membrane configurations.

Figure 9. The current efficiency and energy consumption of acid and base generated from NH₄Cl in the BMED system with different membrane configurations.

The current efficiency and energy consumption of acid and base generated by BMED with the three membrane configurations were shown in Figure 9, which indicated that the three membrane configurations had the different unit energy consumption, i.e. $EC_{[\text{AHA-(BP-1E)-CMB}]} < EC_{[\text{FAB-FBM-FKB}]} < EC_{[\text{JAM-(BPM-1)-JCM}]}$. The unit energy consumption of acid and base generated in the BMED system with the membrane configuration of AHA-(BP-1E)-CMB were the lowest among the three membrane configurations. The result was related closely to the better perm-selectivity of AHA and CMB membranes, and the lower membrane stack resistance, which was favorable to increase the acid and base concentrations in the BMED system and reduce their unit energy consumption.

The $ACE$ of acid and base with the membrane configuration of AHA-(BP-1E)-CMB was almost the same with FAB-FBM-FKB, which was higher than that with JAM-(BPM-1)-JCM (Figure 9). The average current efficiency was related to the concentration difference of acid and base at the same time period. The concentrations of acid and base with the membrane configurations of AHA-(BP-1E)-CMB and FAB-FBM-FKB increased quicker than those of JAM-(BPM-1)-JCM. Therefore, the concentrations of acid and base with the membrane configurations of AHA-(BP-1E)-CMB and FAB-FBM-FKB were higher than those with JAM-(BPM-1)-JCM. The concentrations of acid and base with different membrane configurations presented the same trends as that of their $ACE$.

The high $ACE$, low $EC$ and high yield of acid and base meant the positive performance of BMED system could reduce the running cost of the process. The membrane configuration of FAB-FBM-FKB showed good performance in the generation of acid and base by BMED, while the membrane configuration of AHA-(BP-1E)-CMB had highest average current efficiency and lowest unit energy consumption among the three configurations. So the membrane configuration of FAB-FBM-FKB and AHA-(BP-1E)-CMB could be selected for the BMED treatment of NH₄Cl wastewater for their high productive rate of HCl and NH₃·H₂O, due to the advantages such as low leakage of H⁺ and OH⁻, low resistance of membrane stack, high current efficiency and low energy consumption.

3.3. The stability of ion exchange membranes
The anion exchange membrane was directly contacted with the acid produced in acid compartment, while the cation exchange membrane was directly contacted with the base produced in base compartment in the BMED system. In order to investigate the chemical stability of cation and anion exchange membranes in strong base and acid solutions, three kinds of cation exchange membranes FKB, CMB, JCM and anion exchange membranes FAB, AHA, JAM were soaked in 3 mol/L NaOH
solution or 3 mol/L HCl solution for a week, respectively. And then the fresh membranes and soaked membranes were analyzed by the measurement of contact angle, membrane resistance and scanning electron microscopy (SEM) to examine the chemical stability of them.

The SEM images of the fresh membranes and soaked ones were shown in Figure 10, which indicated that the membranes of FAB and FKB had no obvious change after soaking in the strong acid or base for a week. The granular compositions on the surface of fresh FAB and FKB membranes disappeared after soaking in 3 mol/L HCl and NaOH, respectively, and their surface became smoother. The reason might be that the fresh membranes are usually stored in salt solutions such as NaCl, and some salt crystallization formed on the membrane surface after drying. The salt crystallization on the membranes could be dissolved in the solutions when the membranes were soaked in the HCl or NaOH solution.

For AHA, there were some large cracks appeared on the membrane surface after soaking in 3 mol/L HCl for a week. For JAM, many flaws appeared on the membrane surface, which could be caused by the generation of the cracks on the surface of the membrane. After soaked in 3 mol/L NaOH solution for a week, the surface of CMB and JCM membranes also changed obviously, which indicated that the NaOH solution could seriously damage the two cation exchange membranes. The different changes occurred in the surface of different membranes meant that the ion exchange membranes had different chemical stability in the strong acid and base solutions. It was shown that the ion exchange membranes FAB and FKB had the better chemical stability in the strong acid and base solutions, which were more suitable to be used in the treatment of NH₄Cl wastewater by BMED.

![Figure 10. SEM images of fresh membranes and the membranes soaked in 3 mol/L HCl or NaOH solution for a week (in which ‘1’ indicates the fresh membranes, ‘2’ indicates the soaked membranes).](image)

The hydrophilicity and hydrophobicity of ion exchange membranes before and after soaked in the strong acid or base solutions for a week were further examined. The changes of contact angle are shown in Figure 11. According to the changes of contact angle after soaked in 3 mol/L HCl solution, the stability of anion exchange membranes had an order: AHA > FAB > JAM. Generally, the active group of the ion exchange membrane was hydrophilic. When the active group was damaged, the hydrophilicity of the membrane would change. From the SEM picture in Figure 10, it could be found that the surface of JAM presented obvious changes after soaked in 3 mol/L HCl for a week, which could infer that the active groups and membrane structure of JAM were seriously damaged. Thus the anion exchange membrane JAM presented a poor stability in strong acid. In contrast, the AHA and FAB showed the better stability in strong acid solution.
The stability of cation exchange membranes according to the changes of contact angle in 3 mol/L NaOH solution had an order: FKB > JCM > CMB. The SEM images in Figure 8 showed that the surface of CMB and JCM were seriously damaged after soaked in 3 mol/L NaOH for a week. The changes of the membranes surface led to the changes of hydrophilicity. The cation exchange membrane FKB showed the better stability in the strong base solution.

Figure 11. The contact angle of fresh membranes and the membranes soaked in 3 mol/L HCl or NaOH solution for a week.

The resistances of the fresh membranes and the membranes soaked in 3 mol/L HCl or NaOH for a week were measured to evaluate the stability of the membranes, shown in Table 5. In terms of the membrane resistance, the anion membranes FAB changed considerably and the AHA changed little. It was inferred that the structure of FAB after soaking in strong acid might become more compact and led to the increase of membrane resistance. In contrast, some large cracks appeared on the surface of AHA and JAM, which led to ions could passing easily through the membrane with big cracks, therefore the membrane resistance of AHA and JAM reduced compared with the fresh ones.

The electrical resistance of cation exchange membrane JCM increased obviously after soaked in strong base solution for a week. According to the SEM images of JCM in Figure 10, the original drape on the surface disappeared and the membrane structure was damaged. That might be the reason for the big change of membrane resistance, which could lead the membrane resistances of FKB and CMB obviously reduced. The surface morphology and contact angel of FKB changed little, so the membrane resistance of FKB changed little, which meant the FKB had a promising stability in strong base solution. The serious damage on the surface of the CMB lead to the poor ion selective ability, which might be the reason for the reduce of membrane resistance of CMB.

Table 5. The electrical resistances of fresh membranes and membranes soaked in 3 mol/L HCl or NaOH for a week.

| Membrane type | Membrane resistance (Ω·cm²) | Percentage change | Membrane type | Membrane resistance (Ω·cm²) | Percentage change |
|---------------|---------------------------|-------------------|---------------|---------------------------|-------------------|
|               | fresh | Soaked   | fresh | Soaked   |                         |                   |
| FAB           | 6.1   | 8.2      | +34.4% | FKB       | 9.2   | 5.2      | -43.5%          |
| AHA           | 4.6   | 4.3      | -6.5%  | CMB       | 4.5   | 3.6      | -20%            |
| JAM           | 3.4   | 2.9      | -14.7% | JCM       | 4.6   | 8.5      | +84.8%          |

(Membrane resistance: Measured in 0.5 mol/L NaCl under the condition of 25 °C, 100 kHz)

4. Conclusions
In this study, wastewater simulated as ammonium chloride was treated by BMED for the generation of HCl and NH₃·H₂O with different membranes to investigate the influences of membrane properties on acid and base generation, voltage of membrane stack, current efficiency and unit energy consumption. The stability of anion exchange membrane in strong acid solution and cation exchange membrane in strong base solution were also studied in this work. The results showed that the bipolar membranes BP-1E and FBM presented promising performances. Moreover, the membrane configuration of FAB-
FBM-FKB showed prospects in treating NH$_4$Cl wastewater by BMED than others. The surface morphology, contact angle and membrane resistance of anion exchange membranes FAB, JAM, AHA and cation exchange membranes FKB, JCM, CMB could cause a certain amount of changes after being soaked in 3 mol/L HCl or NaOH solution for a week, respectively. Compared with the fresh membranes, the SEM images indicated that the surface morphologies of FAB and FKB had no obvious change after soaking in strong acid or base for a week. The measurement contact angles and membrane resistances showed that the anion exchange membrane AHA and the cation exchange membrane FKB presented better chemical stability.

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