Comprehensive treatment technology of mother liquid from bromine extraction

Shujing Chai, Wei Liu, Wenyan Zhang, Xiaocui Hao, Xiaoyu Yu, Zejiang Wang, Tao Li and Qi Zhang*

Institute of Seawater Desalination and Multipurpose Utilization, MNR (Tianjin), Tianjin 300192, China

*Corresponding author e-mail: zqhaoyun@linkinfo.com.cn

Abstract. Bromine is one of the important chemical raw materials. It is widely used in flame retardants, petroleum exploitation, fungicides, pesticides, photographic materials and medicine. With the increasing pressure of environmental protection, the comprehensive treatment of mother liquid from bromine extraction becomes more and more serious. In this paper, we systematically studied the composition and concentration of mother liquid from bromine extraction, compared the effect of bromine extraction process on the change of seawater composition. The experimental study focused on pH recovery and residual chlorine reduction to provide a reference for the comprehensive treatment of mother liquid from bromine extraction.

1. Introduction
Bromine is one of the main chemicals extracted from seawater and it is an important basic raw material for fine chemical industry. Bromides are widely used in pesticide, medicine, petroleum, fuel and other industries [1]. It plays a significant role in the development of national economy and people's life. At present, there are more than 4500 kinds of bromides and more than 1800 kinds of bromides commonly used [2].

China's bromine is mainly produced from the underground brine in Laizhou Bay, Shandong Province. The industrialized bromine extraction is air blowing acid spray absorption process. In this process, the raw material solution needs to be acidified to pH=3-3.5, and excessive chlorine gas (chlorine ratio 110-130%) is added to oxidize Br⁻ into Br₂. Free bromine is carried into the absorption tower by air to react with acid spray for enrichment. After bromine extraction, the mother liquid from bromine extraction is discharged from the bottom of the blowing tower [3].

The main composition of seawater or brine is basically remained unchanged after bromine extraction. At present, the general treatment method of the mother liquid from bromine extraction is discharge into salt field for comprehensive utilization to produce magnesium hydroxide [4], calcium sulfate [5] and other inorganic chemical products. However, the mother liquid from bromine extraction has the problems of high acidity, strong corrosiveness and environmental pollution. If it is discharged directly without treatment, it will affect the surrounding environment and soil, cause water pollution, and have a huge impact on zooplankton, shellfish and other organisms, so it must be comprehensive treatment [6].
Studies have shown that the increase of acidity in the water can reduce the diversity of phytoplankton, the number of species, and the abundance of supplementary population. When the pH drops below 5, the growth of fish and shrimp will be seriously affected. Under the condition of pH 3–3.5, no fish and shrimp can survive for several hours [7]. At the same time, the acid water will cause serious corrosion to the drainage pipeline equipment[8]. Therefore, all countries in the world have relatively consistent restrictions on the pH of water discharge. Generally, the pH of water discharge is required to be controlled between 5 and 9. Japan's Water Pollution Prevention and Control Law also requires that the pH value of surrounding water change within the range of 0.2. China's current Comprehensive Wastewater Discharge Standard stipulates that all water discharge should be controlled the pH of 6–9.

Excessive chlorine gas in bromine extraction reaction will mainly exist in the form of HOCl and OCl\(^-\) in the mother liquid from bromine extraction, which is usually called residual chlorine. Under the action of residual chlorine, the concentration of chlorophyll A in phytoplankton will be reduced by 30–90\%, and the primary productivity can't completely restore until the residual chlorine is diluted to less than 0.03 mg/L [9]. When residual chlorine content is greater than 0.5mg /L, it will have a great impact on zooplankton, shellfish, fish and other ecological environment, resulting in the death of marine organisms [10, 11]. Therefore, the German Federal Water Law (WHG) was promulgated the upper limit of the industrial waste water discharge standard of residual chlorine is 0.5mg /L. China has successively issued the Marine Environmental Protection Law of the People's Republic of China, Seawater Quality Standards, and Methods for Assessment of the Impact of Wastewater Discharge from Integrated Seawater Utilization Projects, etc., but there is no mandatory standard for the control of residual chlorine discharge concentration.

In this paper, the mother liquid from bromine extraction is used as the research object, and its components are analyzed in detail. The comprehensive treatment of the mother liquid from bromine extraction was studied. The pH repair effects of neutralization methods, such as mixing seawater, sodium hydroxide and magnesium hydroxide were compared. And the residual chlorine reduction effect of natural attenuation, activated carbon adsorption and REDOX method were screened. This will provide a reference for the comprehensive treatment of the mother liquid from bromine extraction.

2. Experiment

2.1. Experimental materials and instruments
Mother liquid from bromine extraction (a bromine factory in north China), natural sea water (Bohai bay), activated carbon (Jiangsu bamboo creek activated carbon co., LTD.), other chemical reagents such as sodium hypochlorite, sodium sulfite, sodium hydroxide, magnesium hydroxide are analytical reagent, from Tianjin Jiangtian chemical industry co., LTD.

Ion chromatograph (ICS-900), multi-parameter water quality analyzer (XZ-0113).

2.2. Sampling and Analysis
In this study, four sample points were set according to the characteristics of the bromine extraction process. They are respectively the bottom of the blowing tower (marked as 1#), the transfer tank of the mother liquid from bromine extraction (marked as 2#), the main discharge outlet of the mother liquid from bromine extraction (marked as 3#) and the far end of the discharge tank (marked as 4#). The ion chromatograph was used to determine all the components in the retrieved samples, including sulfate ions, sodium ions and chloride ions.

The residual chlorine is greatly affected by water temperature, sunshine and on-site water quality. Therefore, the on-site determination requires a portable and simple method, so the residual chlorine module of the multi-parameter water quality analyzer is selected to read the residual chlorine value and pH value directly. The minimum detection limit of residual chlorine in water is 0.01mg/L.
2.3. Residual chlorine reduction method and mechanism
Due to the large variation of residual chlorine concentration, in this experiment use sodium hypochlorite to prepare the simulated mother liquid from bromine extraction with an effective chlorine concentration of 18 mg/L. Natural attenuation method, activated carbon adsorption method and REDOX method were used to study the removal effect of residual chlorine in the mother liquid. The specific experimental method and mechanism are as follows.

2.3.1. Natural attenuation method. The natural attenuation method is mainly influenced by the environment, including the temperature, pH, total organic carbon, species of bacteria, microorganisms, and light conditions. In order to characterize the influence of various factors on residual chlorine reduction, Jiang fitted the following equation through regression and statistics on the test results [12]:

$$k_v=32.460(1/\rho_0)(\rho_{TOC}+11.301/h_{pH})\exp[-27891.85/R(t+273.15)](R^2=0.906) \quad (1)$$

In the equation, $k_v$ represents the reduction rate of residual chlorine, $\rho_0$ represents the initial chlorine mass concentration, $\rho_{TOC}$ represents the mass concentration of organic matter in the water, $h_{pH}$ represents the pH in the water, and $t$ represents the temperature.

In this experiment, the simulated mother liquid was placed in an insolation device outdoor, and the concentration of residual chlorine was regularly sampled and tested until the reduction was complete.

2.3.2. Activated carbon adsorption method. It is believed that the removal of residual chlorine by activated carbon is combined action of adsorption and chemical reaction. At the initial stage, the removal of residual chlorine is mainly by physical adsorption. After the adsorption equilibrium is reached, the residual chlorine concentration continues to decline due to the action of chemical reaction [13].

In this experiment, the simulated mother liquid was placed in an insolation device, a certain amount of activated carbon was added at room temperature, and the concentration of residual chlorine was tested by regular sampling until the elimination was complete.

2.3.3. Redox method. The residual chlorine can undergo REDOX reaction with sodium sulfite and sodium bisulfite, and the specific reaction equation is as follows:

$$Na_2SO_3 + HClO \rightarrow Cl^- + SO_4^{2-} + H^+ + 2Na^+ \quad (2)$$
$$NaHSO_3 + HClO \rightarrow Cl^- + SO_4^{2-} + 2H^+ + Na^+ \quad (3)$$

In this experiment, the simulated mother liquid and sodium sulfite was added at room temperature according to the calculated molar ratio of 1:1, and the concentration of residual chlorine was regularly sampled and tested until the reduction was complete.

2.4. pH recovery method and mechanism
In this experiment, the mother liquid from bromine extraction was used as raw material, and its pH was restored to above 6, which reached the "Comprehensive Wastewater Discharge Standard". The neutralization method of mixing seawater, adding sodium hydroxide, magnesium hydroxide were used to study the removal effect of residual chlorine in the mother liquid. The specific experimental principle and scheme are as follows.

2.4.1. Mixed seawater neutralization method. The alkalinity of natural seawater is 2.0~2.8 mg/L, and the pH value is generally around 7.0~8.0. The seawater contains a lot of bicarbonate and carbonic acid, which makes it have a strong bufferability. The mixing of several times volume of natural seawater with the mother liquid can achieve the neutralization of acidity and restore the pH.

In this experiment, the mother liquid from bromine extraction and natural seawater was added with stirred, and the pH value was measured.

2.4.2. Add sodium hydroxide and magnesium hydroxide. Sodium hydroxide and magnesium hydroxide are alkaline substances, and the pH of the mother liquid from bromine extraction is recovered by using acid-base neutralization. The reaction formula is as follows.
In this experiment, the mother liquid from bromine extraction and the theoretical calculated amount of NaOH or Mg(OH)₂ was added with stirred, and the pH value was measured.

3. Results and Discussion

3.1. Composition analysis

It can be seen from Table 1 that the sample points has little influence on the content of various ions, mainly because there is no obvious physical and chemical reaction in the discharge pipeline, and the liquid in the discharge tank is updated slowly and mixed evenly. We can also see that there is little change in the concentration of cations such as Na⁺, K⁺, Ca²⁺, Mg²⁺ in the mother liquid compared with natural sea water. The concentration of Cl⁻ and SO₄²⁻ is slightly increased, which is caused by the addition of sulfuric acid in the acidification process and chlorine gas in the oxidation process. In general, the composition and content of mother liquid from bromine extraction are basically the same as that of natural seawater. After comprehensive treatment such as residual chlorine reduction and pH repair, relevant discharge requirements can be met.

| Sample points 1# | Na⁺  | Cl⁻  | K⁺  | Ca²⁺ | Mg²⁺ | SO₄²⁻ | Br⁻ |
|------------------|------|------|-----|------|------|-------|-----|
| Sample points 2# | 13156.7 | 18995.1 | 434.6 | 361.2 | 1513.7 | 3783.6 | 18  |
| Sample points 3# | 13126.0 | 19091.0 | 427.5 | 435.3 | 1498.9 | 3766.8 | 18  |
| Sample points 4# | 13136.6 | 18996.7 | 434.7 | 360.2 | 1503.7 | 3782.6 | 17  |
| Natural seawater | 12992.3 | 18960.5 | 431.1 | 357.4 | 1505.3 | 3346.8 | 57  |

Considering that the decay rate of residual chlorine is greatly affected by the temperature, in order to ensure the accuracy of the experiment, this study sampling several times at the same sample connection in winter and summer respectively to get the average value. The results are shown in Table 2.

|          | 1# | 2# | 3# | 4# |
|----------|----|----|----|----|
| Summer (26 °C) | 6.0 | 2.2 | 1  | 0.8|
| Winter (4 °C)   | 18 | 10 | 8  | 7  |

It can be seen from the Table 2 that the residual chlorine content of the mother liquid from bromine extraction is negatively correlated with the distance between the sample points and the bottom of the blowout tower. This is mainly because the residual chlorine is unstable in water, especially in water containing organic or reductive inorganic, which is easier to be reduced [14]. In different seasons the residual chlorine content in the same sample connection varies 3-10 times, which indicates that the decay rate of residual chlorine in water is greatly affected by temperature, and in higher temperature residual chlorine is more favorable to the removal.

In the process of multiple measurements, we also found that the residual chlorine value in the mother liquid after bromine extraction fluctuated to a certain extent due to the influence of the amount of chlorine added in the process (the chlorine ratio is usually 105-120%). Therefore, in order to make the research results applicable, the initial residual chlorine value of the mother liquid after bromine extraction was set at 18 mg/L in subsequent experiments.
3.2. Analysis of residual chlorine reduction capacity by different methods
It can be clearly seen from Figure 1 that the three methods of natural attenuation, activated carbon adsorption and REDOX have different removal efficiency of residual chlorine. Under almost the same temperature conditions, REDOX method has absolute advantages. It takes nearly 50 hours for the natural attenuation method to completely eliminate the residual chlorine, 65 minutes for the activated carbon adsorption method to completely eliminate the residual chlorine, and the REDOX method to completely eliminate the residual chlorine is almost instantaneous, and the time is less than 60 seconds.

Moreover, since the natural attenuation method cycle goes through day and night, we found that the reduction efficiency in the daytime was significantly higher than that in the night, which was caused by the difference in temperature and illumination between day and night, which was consistent with the results of previous studies. The comparison of attenuation efficiency is shown in Table 3.

| Method               | Eliminate 50% residual chlorine | Eliminate 90% residual chlorine |
|----------------------|---------------------------------|---------------------------------|
| Natural attenuation  | 23 h                            | 47 h                            |
| Activated carbon adsorption | 15 min                  | 55 min                          |
| REDOX                | 20 s                            | 55 s                            |

3.3. Analysis of pH repair by different methods
The relationship between the addition ratio of natural seawater and pH value of the mixed seawater neutralization method is shown in Figure 2. It can be seen from the figure, after adding 3 times the volume of natural seawater, the pH quickly rises to 7.99. Continue to add seawater, the pH rises slowly. Adding 10 times seawater, pH=8.35, close to the seawater pH. According to the experimental results, the mother liquid from bromine extraction mixed with 2~4 times seawater can restore the pH value to 6~9, and the cost is low. It is recommended to mix with 2 times seawater.

![Figure 1. Residual chlorine over time under different methods](image1)

![Figure 2. pH value over volume ratio of seawater](image2)
Using Mg(OH)$_2$ neutralization method, adding Mg(OH)$_2$ (theoretical amount) powder and stirring continuously, the pH value was 3.84 after 1h. Keep adding the Mg(OH)$_2$ (overdose one times) powder and stirring it, the pH value was 6.63 after 1h. In addition, no matter what the addition method was, the solution was opaque liquid, which was cleared after standing for a long time.

The method of NaOH neutralization, adding NaOH (theoretical amount) powder and constantly stirring, the pH value instantly increased to 7-8, and the solution was clarified.

4. Conclusion

Through the analysis of the composition and content of the mother liquid from bromine extraction provides a reference for the comprehensive utilization and discharge of the mother liquid. The residual chlorine reference value was selected according to the sampling and analysis. The residual chlorine removal effects of natural attenuation, activated carbon adsorption and REDOX methods were compared. The experimental results show that although natural attenuation method is the most commonly used in residual chlorine removal, its reduction speed is slow, greatly affected by illumination, and it occupies a large area of land. The REDOX method has the advantages of high reduction efficiency, low construction cost, small occupation area and so on. It is especially suitable for the occasions where the factory area is small and the removal rate of residual chlorine is high, so it is worth popularizing and applying.

For the pH repair of the mother liquid from bromine extraction, the effect of mixing seawater neutralization method on the marine environment is minimal, and the twofold product of bromine extraction waste solution should be mixed. However, in large-scale bromine production, the cost of water extraction and transportation is high. Although the effect of sodium hydroxide neutralization method is better, it has little influence on the system, but the operation cost is higher. The operation cost of magnesium hydroxide neutralization method is low, but the pH repair time is longer. Therefore, it is necessary to choose the appropriate treatment mode based on the actual situation.

We will further study the correlation experiment between pH repair and residual chlorine reduction, explore a more economical, efficient and green comprehensive treatment process of the mother liquid from bromine extraction.

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