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Research on the Extraction of Bromine from Seawater Using the Membrane Method

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ABSTRACT

China's Model BSF-II flat gaseous membranes with different pore diameters (0.1 μm, 0.2 μm and 0.5 μm) have been studied. Their capacities for separating bromine under various conditions (temperature, bromine concentration and velocity) were compared. The separation factor of the 0.2 μm pore diameter membrane is the best of the three kinds of membranes. The mechanical strength and separating capacities of membranes show no obvious changes when soaking in seawater (pH ≤ 3.5, bromine concentration ≥ 65 ppm) for 220–640 days, thus pointing to the possibility of applying and popularizing this method to a certain extent.

INTRODUCTION

This research project is the continuation of the "bromine extraction from seawater with hollow fibre gaseous membrane" project (Zhang et al., 1986), which aims to solve the problem of short membrane life (about 60 days) and search for a high bromine corrosion resistance membrane of Chinese manufacture. Experimental investigations of process parameters and the effects of membrane pore diameter on bromine migration have been performed using China's Model BSF-II porous membrane and the life of this membrane has been tentatively examined.

The advantages of the bromine extraction method lie in its simple technological process and low power consumption (only half that of the air blow-out bromine extraction method).

METHODS

Technological procedure of the experiment

Membrane assemblage: 7 layers of 10 x 6 cm membrane with 406 cm^2 effective area are assembled between two 12 x 10 cm plates. There are 4 feeding and discharging holes for feed stream and absorbent on 2 plates. The technological procedure is shown in Fig. 1.

Flat membrane: Model BSF-II membranes with average pore diameters of 0.1, 0.2 and 0.5 μm and porosity of 50%, 55% and 60% respectively; the thickness of the membrane is 60–80 μm.

Reagent: the experimental seawater is taken from Tanggu, Tianjin. The reagents utilized are all reagent grade except for bromine which is industrial grade.

Apparatus: 2 SYB-Z perfusion pumps, 1 Model CS 50 ultra-thermostat, 1 Model HH-S21-6 electric heating thermostatic water bath, 1 Model PHS-Z acidity meter.

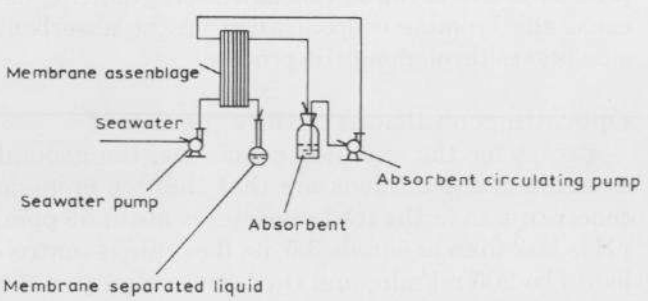


Fig. 1. Schematic diagram of the experimental process.

Migration mechanisms

A porous hydrophobic polymer membrane is placed between seawater containing free bromine and a sodium hydroxide aqueous solution. Water

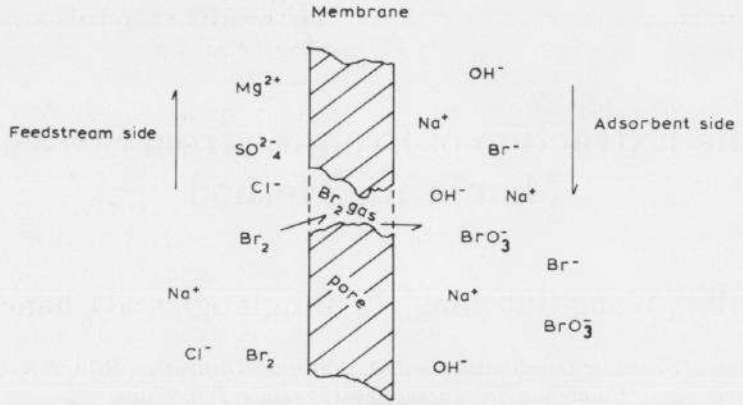


Fig. 2. Bromine migration through gaseous membrane.

and the non-volatile matters cannot soak and penetrate the membrane, and the volatile Br_2 is enriched on the right hand side of the membrane through the following process (Fig. 2).

(a) Br_2 diffuses to the membrane surface from the solution on the left hand side of membrane.

(b) Br_2 volatilizes to a gaseous state at the interface of membrane pore and solution.

(c) Gaseous Br_2 diffuses to the right in the membrane pore.

(d) Gaseous Br_2 dissolves into the aqueous solution of sodium hydroxide on the right hand side of membrane and reacts with NaOH as the following equation:

$$6NaOH + 3Br_2 \rightarrow 5NaBr + NaBrO_3 + 3H_2O$$

and forms Br^- and BrO_3^- which cannot re-diffuse to the left hand side.

(e) Br^- and BrO_3^- leave the right hand interface and diffuse towards the right into the aqueous solution.

The driving force behind the above migration process is the bromine concentration gradient, because the bromine concentration on the absorbent side is zero throughout the process.

Operating conditions of the experiment

Except for the specified conditions, the general experimental conditions are that the free bromine concentration in the feed seawater is about 65 ppm, pH is less than or equals 3.5, its flow rate is controlled to be 200 ml/min, and the linear velocity in the membrane chamber is 2.7 cm/s. The selected alkaline absorbent was a 250 ml aqueous solution of 0.2 N sodium hydroxide with a flow rate of 200 ml/min. The operating temperature is 30±0.5°C. The time taken for 250 ml seawater to discharge from the membrane separator was obtained. The analytical method is iodometric titration.

Calculation equation

The recovery ratio of bromine is

$$\eta = \left\{(C^0_{Br_2} - C^t_{Br_2}) / C^0_{Br_2}\right\} \times 100\%$$

where $C^0_{Br_2}$ is the initial bromine concentration (ppm), and $C^t_{Br_2}$ is the bromine concentration in discharging liquid (ppm).

The bromine flux is

$$J = (V_s \times C^0_{Br_2} \times \eta\ 100^{-6}) / (A \times t)$$

where J is the bromine flux ($g/cm^2 \cdot min$), V_s is the obtained discharging liquid volume (250 ml), t is the time taken to obtain V_s (min), and A is the effective area of the membrane assemblage (406 cm^2).

EXPERIMENTAL RESULTS AND ANALYSIS

The relationship between $C^0_{Br_2}$ and η and J

Figure 3 shows that: (1) $C^0_{Br_2}$ has no effect on η and J is proportional to $C^0_{Br_2}$. Therefore this method is more suitable for the high bromine concentration feed stream. (2) From the view point of the effect of membrane pore diameter on η and J, the η and J values of 0.5 μm and 0.2 μm membranes are similar, their η values are 18–20% higher than that of the 0.1 μm membrane, and their J values are 11–14% higher than that of the 0.1 μm membrane.

For a wide range of the feed pressure, not only should the high flux membrane be selected, but also the membrane high pressure at bubble point is required in application. Therefore, the 0.2 μm pore diameter membrane is considered to be better than the other membranes.

The effect of operating temperature on η

With the increase of the feed temperature, the vapour pressure of bromine and the fluid viscosity increase (Fig. 4), the thickness of laminar flow at the

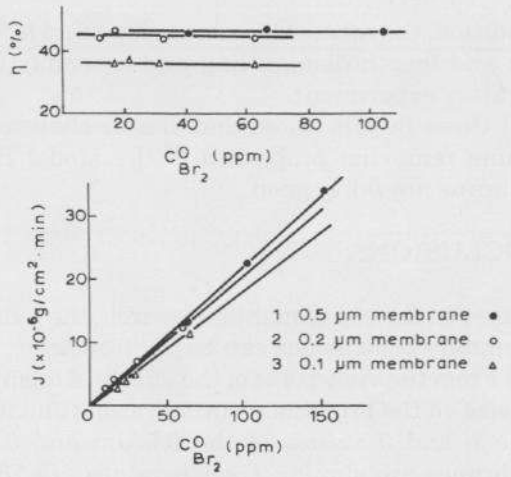


Fig. 3. The relationship between bromine recovery, bromine flux and Br_2 concentration in feedstream.

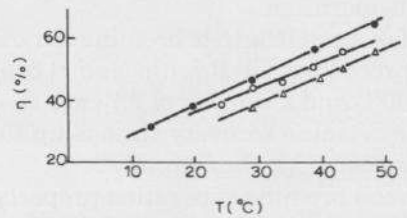


Fig. 4. The effect of temperature on bromine recovery ratio.

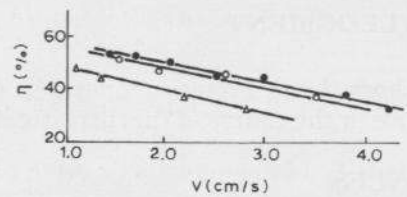


Fig. 5. The effect of seawater velocity on bromine recovery ratio.

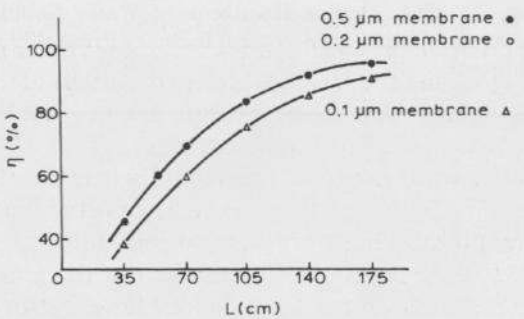


Fig. 6. The effect of process length on bromine recovery ratio.

membrane surface decreases, the concentration gradient of bromine increases, and the migration effects improve.

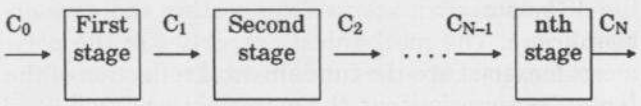
The relationship between feed seawater velocity and η

As is shown in Fig. 5, a proper increase of feed velocity results in a decrease of the bromine recovery ratio, while a higher velocity leads to a higher bromine flux. Therefore, a comprehensive balance of feed velocity and J must be made in practice. In addition, from the effects of feed velocity on the recovery of the above three membranes, the membranes of 0.5 μm and 0.2 μm pore diameter are better than the 0.1 μm membrane.

The effects of technological process length on η

Taking the 0.2 μm membrane as example, the relationship between L and η are found by the following method (Fig. 6).

Suppose that the experiment is composed of many stages in series (the first, second... and nth stage). The bromine concentration of each stage is C_0, C_1... and C_N in order (as shown in the following figure):



Notice that in the data group, $C_{Br_2}^0 = 60.64$ ppm, $C_{Br_2}^t = 33.78$ ppm, V = 2.7 cm/s, L = 35 cm, and L_1 = 35 cm, $L_2 = 2L_1$, ..., $L_N = N \cdot L_1$, therefore the feed and discharging bromine concentrations of every stage have the following approximate relationship:

$$C_0/C_1 = C_1/C_2 = C_2/C_3 = \ldots, = C_{N-1}/C_N = (C_0/C_N)^{1/N} = 1/\alpha \quad (1)$$

$$\alpha = (C_N/C_0)^{1/N} \quad (2)$$

That is

$$C_N = \alpha^N \cdot C_0 \quad (3)$$

Substituting the data in experiment number 11-7-02 into equation (2) and (3) and the calculation equation of η, Table 1 is obtained.

It can be seen from Fig. 6 that, when the stage number in the assemblage is greater than 4, i.e. the length of the technological process is greater than 140 cm, the varying tendency of the η curve becomes smoother. Therefore, 140 cm was chosen as the favoured length of the technological procedure, where the bromine recovery ratio is 90%. Point a on the curve is the measuring point.

TABLE 1
The effects of L on η and J

	Stage number					
	1	2	3	4	5	6
Length of the technological process L (cm)	35	70	105	140	175	210
Recovery ratio η (%)	44.7	69.0	82.7	90.4	94.6	97.0
Bromine flux $J \cdot 10^{-6}$ ($g/cm^2 \cdot min$)	13.2	10.3	8.2	6.7	5.7	4.8

The curve for the 0.5 μm membrane almost coincides with that for the 0.2 μm membrane. When L is 140 cm, the recovery ratios of the 0.5 μm and 0.2 μm membrane are 7% higher than that of the 0.1 μm membrane.

Examination of the life of the membrane

The life of a gaseous membrane depends on the life of polymeric materials supporting the gaseous membrane. The mechanical properties of the polymeric material are the fundamental reflection of the inner characteristics of the material itself.

Soak the Model BSF-II membrane in seawater of $C_{Br_2} > 65$ ppm and pH < 3.5 for 640 days and examine its mechanical properties along with the unsoaked membranes. The tensile strength of the former is greater than 130 kg/cm^2, its extension at break is greater than 42%. While the tensile strength of the unsoaked membrane is greater than 150 kg/cm_2, its extension at break is greater than 50%.

At the same time, the bromine separation property of the 0.5 μm membrane soaked in seawater for more than 7 months has been determined. When $C_{Br_2}^0$ is 55.04 ppm the recovery ratios of the two determinations are 44.57% and 46.04% respectively. In addition, the membranes are still perfect after the third and fourth dismantling and assembly in the laboratory experiment.

All these factors show that the mechanical and bromine removing properties of the Model BSF-II membrane are fairly good.

CONCLUSIONS

Based on the experimental research, the following preliminary conclusions can be put forward:

(1) From the view point of the effects of membrane pore size on the bromine recovery ratio η and its flux J, the η and J values of the 0.5 μm and 0.2 μm membranes are similar, their η values are 18–20% higher than that of the 0.1 μm membrane, their J values are 11–14% higher than that of the 0.1 μm membrane. The 0.2 μm membrane is best by comprehensive consideration.

(2) The favoured length of bromine removing technological procedure for 0.2 μm and 0.5 μm membranes at 30°C and a velocity of 2.7 cm/s is about 140 cm and the bromine recovery ratio is up to 90%, its average flux is $6.7 \mathfrak{Z} 10^{-6}$ $g/cm^2 \cdot min$.

(3) Both the bromine separation property and the mechanical strength of the Model BSF-II membrane as the gaseous membrane support are good and its service life is expected to be two years.

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