STUDY ON EXTRACTION OF BROMINE FROM SEAWATER WITH PVDF HOLLOW FIBER GAS MEMBRANE

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Abstract: In this paper, the extraction of bromine from seawater and brine was studied with new type macromolecule polyvinylidene fluoride (PVDF) hollow fiber gas membrane. The results showed that increased pressure difference between two sides of the membrane can not improve flux J, so the impetus of this mass transfer process was not pressure difference, but concentration difference. Mass transfer coefficient k increased weakly with the increased pressure difference. Efficiencyη, mass transfer coefficient k and flux J were proportional to temperature.$\eta$and k were more obvious than J, J increased greatly with the increased concentration of seawater. The influence on η, k and J caused by velocity of seawater was neglected with cycling method.

Key words: hollow fiber; extraction of bromine; gas membrane; PVDF

1.Introduction

Membrane separation technology, owing to its low energy consumption, high separation efficiency, and operational simplicity and pollution-free, has been developed quickly for the last 30 years. And its application field has already spread from desalination to chemistry, food and medicine. Further more, as one of the important novel technologies of solving energy problems, resource shortage and environment pollution in the 21st century, membrane separation technology will particularly impressed on the technological innovations of these fields. Until now, various kinds of membrane modules such as sheet frame, hollow fiber, capillary [1] have been developed. Among these, hollow fiber membrane modules had been widely used in the application filed of membrane separation technology because of high packing density, large surface per volume and good repeatability[2]. The reported hollow-fiber membrane materials include polybenzeneamide, polybenzeneamide-hydrazide reverse osmosis membrane; polysulfone, polyacrylonitrile ultrafiltration membrane and micro-filtration membrane, polytetrafluoroethylene, polyvinylidene fluoride (PVDF), and so on. As a novel functional polymer material, Polyvinylidene fluoride (PVDF) has good stability for climate, chemistry and radiation and has the ability of erosion free from acid, base and oxidizing agent at room temperature[3]. In the mid-1980s, PVDF was marketed first by American. Subsequently, a considerable amount of research on PVDF has been performed by scientists and technologists. Du Qiyun et al. [4] had investigated the progress of membrane distillation with the PVDF hollow-fiber membrane. Lv Xiaolong et al. [5] had studied the application of the PVDF hollow-fiber membrane for purification treatment of the injection water in oil field. Wu Yonglie et al. had discussed the recovery of taurine from waste water with PVDF hollow fiber membrane modified by LiCl. Moreover, all of these had been shown to be consistently effective.

Bromine is an important raw chemical, which has shown many applications in industry. With the development of science and technology, its use will become more widespread. Bromine has an abundant reserve in seawater and the content of bromine in seawater is 99% of the total reserves in the earth. It is significant and economical to make use of membrane separation technology on extracting bromine from seawater. So, seeking the effective means to extract bromine from seawater was an important researching subject. E.L.Cussler [6] studied the process of bromine extraction from seawater using flat polypropylene membrane. Author [7] investigated the extraction approach from seawater using the flat poly(tetrafluoroethylene) membrane and evaluated the service life of the flat poly(tetrafluoroethylene) membrane. Zhang Qi et al. [9] analyzed the parameter of the extraction bromine from seawater using polypropylene hollow fiber membrane. However, the research about the extracting technology using PVDF hollow fiber membrane hadn't been reported. Combining the advantages of PVDF with those of hollow fiber materials, the extraction of bromine from seawater by using of PVDF hollow fiber membrane is discussed in this paper.

2.EXPERIMENT

2.1. Materials and instruments

The outer and inner diameters of macromolecule polyvinylidene fluoride (PVDF) hollow fiber membrane, with a porosity of 80% and an average pore diameter of 0.1μm, are 0.9 and 0.6mm respectively. There are 423 hollow fibers in a module. Its useful length is 17cm. The seawater or brine with different concentrations of bromine was used and sodium formate (AC) was bought from Tianjin chemical reagent Co., Ltd.

The bath to keep constant temperature was obtained from Tianjin Zhouhuan experiment oven Co., Ltd., The type of ZXZ-0.5 sliding vane rotary vacuum pump was purchased from Zhejiang Huangyan vacuum air pump Co., Ltd and the infusion pump from the institute of membrane separation of Tianjin University of Technology.

2.2.Parameters of separation process

$$\eta = 1 - C_{Br_2}^{t} \big/ C_{Br_2}^{0}$$

$$J = \frac{W}{S \cdot t}$$

$$k = -\frac{du}{4l} Ln[1 - \frac{4V}{\pi d^2 uNt} Ln\frac{C_{Br_2}^{0}}{C_{Br_2}^{t}}]$$

Where η is efficiency of the extraction, %; $C_{Br_2}^{0}$ and $C_{Br_2}^{t}$ denote the concentrations of the Br2 in the feed solution at 0 and t time, mg/kg, respectively; J is the permeating flux of bromine, kg/m2·h; W is the quantity of the Br2 which permeates the membrane, kg; S and t refer to the useful area, m^2 and reaction time, h, respectively; k is the mass transfer coefficient, cm/s; d is the inner diameters of the hollow fiber membrane, cm; l is the useful length, cm; N is the number of the hollow fiber; u is the linear velocity of the feed in the hollow fiber, cm/s; V stands for the volume of the feed, cm^3.

2.3. Experimental setup

The Experimental setup is shown in Figure 1.

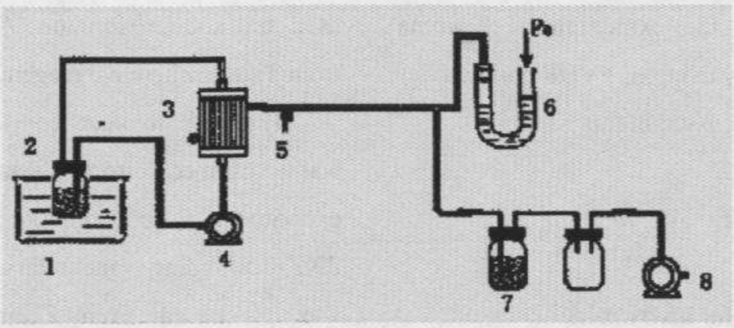

Figure 1. Schematic diagram of the experimental setup of extraction of bromine from seawater with PVDF hollow fiber membrane

1. Water bath 2. feed tank 3.PVDF hollow fiber membrane module 4. feed pump 5. atmospheric valve 6. mercury manometer 7. surge flask 8. vacuum air pump

2.4. Method and procedures

The equipment setup was showed in Figure 1, in which the feed solution was heated to the desired temperature with a bath and the outside of the membrane was connected with a vacuum air pump, keeping a certain vacuity through an atmospheric valve. The feed solution circulated by the pump at a certain flow rate, measuring the $C_{Br_2}^{0}$. The $C_{Br_2}^{t}$ was obtained after a certain time from the initial of the pump, and then calculating the valves of k, J and η.

3. RESULTS AND DISCUSSION

3.1. Relationship between vacuum and separation ability

Figure 2 showed the relations between vacuum out side the fibers with η, k, and J. Feed solution maintained velocity at 7.81cm/s, bromine concentration at 190mg/kg and 25℃ when experimental time was 15 minutes. Cartridge was full of sodium formate solution when vacuum is zero. It can be concluded from picture 2 that no matter how vacuum changed, there is little affection on η, k, and J. Generally, Gas membrane includes membrane distillation, absorption, and separation progress of volatiles in waters. Vacuum distillation is a progress made by changing the pressure on cartage and liquid side of membrane. This experiment can be looked as vacuum distillation. But J didn't improved, May be this phenomena relates to properties, structures of membrane. It also relates to molecular size of bromine. Therefore, power to promote the separation progress depends on bromine concentration difference but pressure difference between cartridge and liquid sides. Yu Boshan et al. [8] applied hollow fiber membrane to separate ammonia, and concluded: Mass transfer coefficient is proportional to Pressure difference. In this experiment, mass transfer coefficient was growing with pressure grew, but the range was weak.

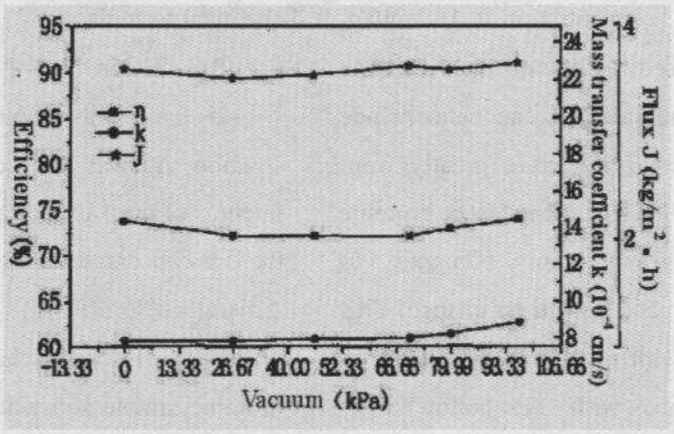

Figure 2. curve about relationship of Vacuum with k, J and η

3.2. Relationship between temperatures of seawater with the separation ability

Figure 3 showed the relations about temperatures with η, k, and J when maintained the velocity of seawater was 7.81cm/s and bromine concentration was about 190mg/kg when experimental time was 15 minute. It could be concluded from this picture that the η, k, and J were growing with temperature grew, coinciding with literature [9]. η and k were creasing greatly from 73.65% and 8.82×10^{-4} at 25℃ to 93.58% and 24.23×10^{-4} in 48℃ respectively, and Flux J increasing range was smaller than that of η and k. These increase due to the movement of Br2 increase, and active Br_2 grew, so the bromine gas increased than the status at low temperature.

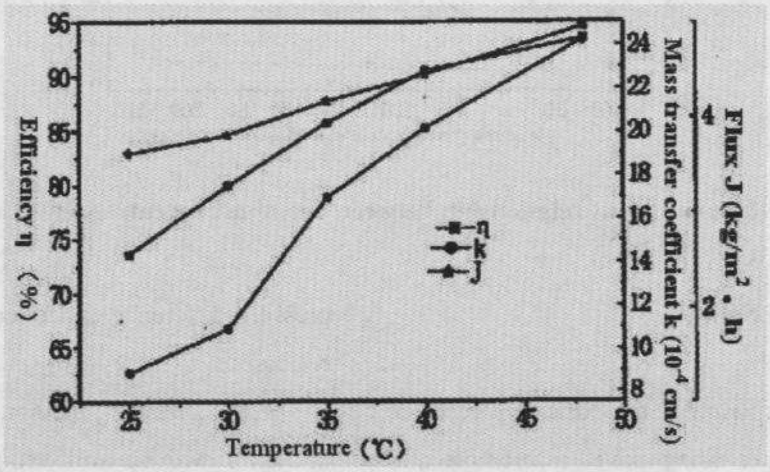

Figure 3. relationship between temperature with k, J and η

3.3. Relationship between bromine concentrations of seawater with separation ability

Figure 4 showed the curve about bromine concentration of seawater with η, k, and J, When the concentration is 190mg/kg, Velocity of feed solution is 7.81cm/s, maintained 15 minutes. It can be conclude from figure 4 as J increased greatly from 1.25×10^{-3} to 3.98×10^{-3} when feed bromine concentration grew from 60mg/kg to 210mg/kg, but η and k with no change. This was in accord with the result concluded by examination done with PP hollow fiber membrane[9]. Known as conclusion 3-1, concentration difference is the driving force to promote the separation process on both sides of the membrane. The chemical potential Δμ=μ1-μ2. Bromine gas reacts with sodium formate solution as the following chemical formula:

$$Br_2 + HCOONa \rightarrow NaBr + HBr + CO_2$$

If there was enough sodium formate solution, Δμ was still zero. In this case, the impetus of mass exchange process decided by the Br2 concentration of seawater, showing as Δμ=μ1 =μ0Br (P ,T) + RTLnXBr, which μ0Br (P ,T) was chemical potential of bromine simple substance in pressure P and temperature T. XBr is bromine mole fraction in seawater. With the concentration grew, the impetus grew, thus J grew. Velocity of seawater could be neglect as seawater recycling in the experiment.

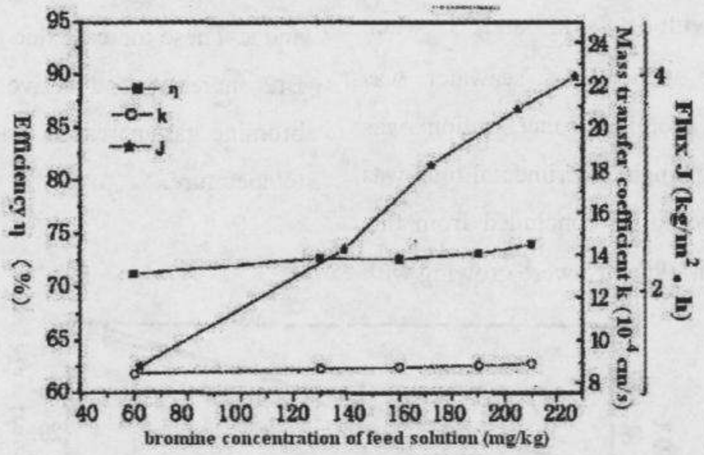

Figure 4. curve about relationship between bromine concentration with k, J and η

4. CONCLUSION

The experiment of extracting bromine from seawater using novel macromolecular Polyvinylidene fluoride (PVDF) Hollow fiber gas membrane drew the following conclusion:

(1)Pressure difference couldn't improve the Flux J. So, separation was driven by bromine concentration difference between shellside and tubeside of the module but pressure difference under these experimental conditions.

(2)Efficiency η, mass transfer coefficient k, flux J was up with temperature of feed solution increased. η and k increased greatly than J.

(3)the increase of bromine concentration of feed solution contribute a lot to J, but do little to η and k.

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