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Study of the bubble membrane crystallization process for zero-brine discharge

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ABSTRACT

Zero-brine discharge technology is being closely followed because it can help address water scarcity. Crystallizers show the promise of zero discharge because of their ability to recover resources from concentrated brine. However, traditional industrial metal crystallizers corrode easily and are bulky. Membrane distillation is favored because of its large evaporation area and high efficiency. However, membrane fouling is an inevitable problem in membrane distillation. To address these issues, this study designed a new type of membrane crystallization process, namely bubble membrane crystallization (BMC). In this process, a hollow fiber hydrophobic membrane was used to aerate a feed solution to accelerate the evaporation of the feed solution, which helped crystallize the concentrated brine, and avoided corrosion and membrane fouling. In this study, NaCl crystals with uniform distribution (80.0–110.0 μm) were produced. The results showed that the membrane aeration treatment made BMC possesses excellent anti-pollution and long-term stability. This process advances all-plastic crystallizer technology to achieve zero-brine discharge.

1. Introduction

Zero-brine discharge technology has been proposed to address global water shortages. Industrial crystallization technology is an important chemical process that can be used for the separation and purification of chemical products. Therefore, industrial crystallization technology can be applied to recycle concentrated brine without brine discharge [1,2]. Nowadays, various industrial evaporative crystallizers have been developed, such as forced circulation evaporative crystallizers, draft tube baffle evaporative crystallizers, Oslo evaporative crystallizers, and GaLiCos cryogenic crystallizers. However, the main parts of these crystallizers are composed of metal, and their service life will likely be compromised due to metal's poor corrosion resistance and severe operating conditions [1–4]. To reduce the operational costs of crystallization technology and to improve its production efficiency, researchers have focused on developing high-quality and long-life evaporative crystallizers.

Membrane distillation (MD) is a promising alternative process for hypersaline water desalination and wastewater treatment [5,6]. This process separates the volatile solutes from an aqueous solution by passing vapor across a hydrophobic membrane. Not only can MD obtain high-purity water on the permeate side of the membrane, but it also produces highly concentrated water with a high salt content at or near saturation on the feed side [7–9].

Membrane distillation crystallization (MDC) is the coupling of MD and crystallization technology, and it has become an important MD research area. The process removes the solvent from the feed solution by MD technology, which can form a near saturated solution; an external crystallizer is then used for crystallization. MDC possesses the advantages of corrosion resistance, large evaporation area and high efficiency [10–12]. In addition, since both the hydrophobic membrane and the membrane module shell are polymer materials, MDC can resist chloride ion corrosion. Therefore, this is an effective way to avoid the deficiency of traditional metal evaporation crystallizer.

In recent 20 years, membrane distillation crystallization (or membrane crystallization) technology has received more and more attention [13]. Curcio et al. [14] first used direct contact membrane distillation (DCMD) for the concentration of NaCl solutions, and obtained NaCl crystals. Then Curcio et al. [15,16] utilized MDC to treat biological polymer solutions. Similarly, Gryta [17] used DCMD to treat brackish water and NaCl solutions for crystallization. Julian et al. [18] used submerged vacuum membrane distillation (VMD) to treat inland

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brackish water. Lu et al. [19] used VMD to separate NaCl crystal particles (with a uniform size distribution and smooth surface) from the NaCl-H_2O-EG three element system.

Although there has been continuous progress in MD and crystallization technology, there are still many technical difficulties to be overcome, such as hydrophilization of hydrophobic membrane and membrane fouling [19–22]. Therefore, developing a membrane crystallization process that can be operated stably for a long time is not only a requirement for the progress of chemical crystallization, but is also significant for the zero discharge of high-salinity wastewater.

Traditional metal crystallizers can be affected by severe operating conditions, corrode easily, and have high material requirements, all of which weaken their process performance and cause operational complexity. In this paper, a new type of membrane crystallization process, namely bubble membrane crystallization process has been designed. In this design, hydrophobic micro-porous hollow fiber membrane was used for high-density micro-bubble aeration. Theoretically, the moisture absorption ability of air differs with temperature (i.e., the higher the temperature, the higher the moisture absorption) [22–26], thus bubbles can absorb water vapor from hot feed. Applying bubbles to disturb the internal and liquid surface of the feed solution can increase evaporation area and then accelerate evaporation rate, thus the feed solution can be concentrated to super-saturation and produce crystals. Moreover, since the membrane pores are continuously blown, membrane fouling can be avoided.

The bubbles generated by aeration can cause disturbance to the feed solution, so that crystal particles in the feed can grow continuously. After reaching a certain particle size, the crystals settle under gravity and can be collected [27,28]. It is expected to achieve production of high-purity water at the same time as crystallization. The effect of membrane aeration on the evaporation and crystallization, the effect of membrane area on water production, and the effect of gas-liquid separation distance on produced water quality were experimentally studied. On the other hand, a long-term test was conducted to compare the pollution resistance performance of the BMC process and a VMD process.

2. Experimental

2.1. Materials and instruments

The hydrophobic polyvinylidene fluoride (PVDF) hollow fiber membranes were produced by our research group via the non-solvent induced phase separation (NIPS) method (PVDF: SOLEF6010) [29,30]. The mean pore size, porosity, inner/outer diameters, and bubble point of the membrane are 0.16 μm, 85.0%, 0.016 MPa and 0.8/1.1 mm, respectively. The feed solution was a NaCl solution with a salinity of 20.0 wt%. Three transverse curtain-type membrane module were used, and the effective membrane areas were $2.41{\cdot}10^{-3}$ m^2, $4.82{\cdot}10^{-3}$ m^2 and $8.44{\cdot}10^{-3}$ m^2, respectively.

2.2. Experimental apparatus

The structure of the bubble membrane crystallizer is shown in Fig. 1. The crystallization pot was made of chlorinated polyvinyl chloride (CPVC). The cross-sectional area of the pot was 0.02 m^2, and the volume was approximately 3.8 L. The membrane module was placed at the bottom of the pot as an aeration unit. The gas-liquid separation distance (h) is the distance between the liquid surface and the geometric center of the metal condenser.

The schematic of the BMC process is depicted in Fig. 2. The BMC process consisted of four parts, namely the bubble membrane crystallizer, cooling circulation system, aeration system, and water production system.

In the membrane aeration process, as the air bubbles rose up, they absorbed water vapor and some feed (in the form of droplets). After the air bubbles left the liquid surface, they rose into the gas-liquid separation space. In the gas-liquid separation space, the feed droplets were separated from the bubbles by gravity and fell back into the feed solution. Therefore, the purpose of gas-liquid separation was realized. Finally, the air bubbles carrying water vapor reached the cover condenser and the water vapor condensed to pure water.

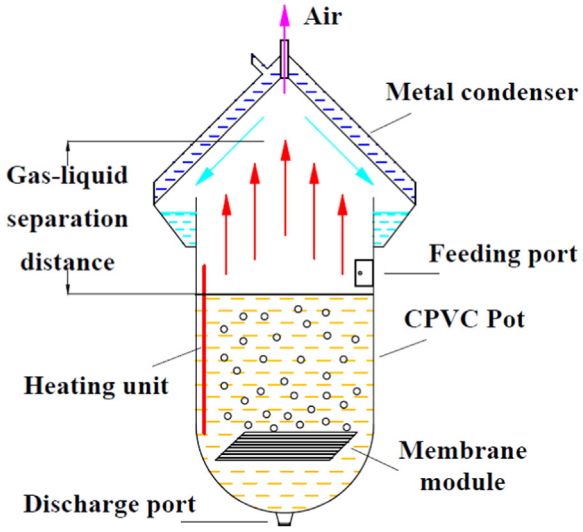

Fig. 1. Structure of the bubble membrane crystallizer.

The water production system was divided into two parts. First, the water vapor entrained by the bubbles and the naturally evaporated vapor were condensed at the metal condenser (on top of the crystallizer) to produce freshwater. Second, rest of the water vapor was condensed in an external condenser connected at the top of the metal condenser. This ensured that the water vapor was completely condensed and collected in the produced water tank. During the concentration of the feed solution, the supply feed flow was controlled to regulate the amount of water in the crystallization pot. When the feed was super-saturated, it formed tiny crystal particles, which were used as crystal nuclei. The rising bubbles exerted an upward force on the crystals, causing the crystals to sink slowly and grow continuously. After reaching a certain particle size, the crystals settled to the bottom of the pot under gravity. And the crystals were collected from the discharge port. The produced water tank was weighed every 10 min, and crystals were collected after 2 h crystallization.

2.3. Pollution resistance experiment

In this experiment, the BMC process and a VMD process were conducted to compare pollution resistance. The feed solution was a NaCl solution with a salinity of 20.0 wt%. The BMC operating conditions: the feed temperature was 80.0 °C, the cooling water temperature was 23.0 °C, the air temperature was 20.0 °C, the aeration intensity was 1.02 $Nm^3/(m^2\ h)$, the membrane area was $4.82{\cdot}10^{-3}$ m^2, and the gas-liquid separation distance was 200.0 mm. The VMD process is depicted in Fig. 3. The VMD experimental conditions: the feed inlet temperature was 70.0 °C, the cooling water temperature was 23.0 °C, the vacuum degree was 0.082 MPa, and the feed flow velocity was 0.67 m/s. The VMD module was a plastic shell-and-tube hollow fiber membrane module (23.0 cm length), and the membrane area was 0.029 m^2. The PVDF membranes that used in the curtain module and the shell-and-tube module were the same.

2.4. Performance of the BMC process

2.4.1. Aeration intensity

The aeration intensity is the air flow rate per unit liquid surface