Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.926649

52 (2014) 5158–5164
July

Taylor & Francis
Taylor & Francis Group

Vacuum membrane distillation to remove ethyl acetate from aqueous solutions

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Received 7 May 2013; Accepted 30 March 2014

ABSTRACT

Water pollution of volatile organic compounds (VOCs) was a serious environment problem. Vacuum membrane distillation (VMD) was an environmental friendly membrane separation technology to treat VOCs wastewater. Aqueous binary mixtures of ethyl acetate were treated by VMD process. Comparisons were made between different membrane modules for investigating the influence of channel on the membrane separation performance. Three kinds of channel presented different useful area, shape, width, and depth. The arc flow channel was more easier to reduce resistance than square flow channel. Operation parameters influencing flux and separation performance were examined: feed-flow rate, feed concentration, vacuum degree, and feed temperature. Vacuum degree and feed temperature had more significant influence on membrane flux and separation factor than other parameters. The effect of membrane type on separation properties was also investigated, the smaller pore membrane was better for increasing the separation factor. Three membrane modules with various channels were used for experiments. VMD is very suitable for low concentration of aqueous solution VOC separation and better experimental separation performance could be obtained.

Keywords: Vacuum membrane distillation; Membrane module; Operation parameters; Ethyl acetate solution

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1. Introduction

With the rapid development of industry, water contamination becomes increasingly serious, especially water pollutions of volatile organic compounds (VOCs), which are dangerous to human survival and health [1].

The traditional methods to remove VOCs are distillation, extraction, and active carbon adsorption. In general, distillation and extraction are used when VOCs content is high, and adsorption method is used when VOCs content is low in wastewater. Many by-products produced in these traditional methods bring post-treatment problems, which can be avoided by vacuum membrane distillation (VMD) method. VMD is an energy saving, efficient, and environmental friendly membrane separation technology. VMD is a separation process with lower operating temperatures and pressures. Boiling point temperature is not

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Presented at the Conference on Water Resources and Urbanization Development, 26–27 September 2012, Tianjin, China

necessary, operating pressure is just kept at differential pressure on both sides of the membrane surface, and higher mechanical properties are not demanded [2–9]. The treatment of wastewater-containing VOCs by VMD is not only recovering VOCs, but also avoiding secondary pollution.

In recent years, a lot of researches have been done in removing VOCs from wastewater. Urtiaga [10] separated chloroform from aqueous solutions by the use of VMD process, investigated the influence of initial concentration, feeding velocity in laminar flow and turbulent flow, feeding temperature, and vacuum degree in cold side. In the range of 278 and 323 K, the phase diffusion coefficient was obtained. Izquierdo-Gil and Jonsson [11] investigated the effect of operation parameters on separating isopropyl alcohol–water mixture by the use of VMD method. When operation temperature was from 20 to 50˚C, the selectivity of isopropyl alcohol reached 10–25. Izquierdo-Gil et al. [3] separated water and ethanol binary mixtures through VMD process. The result suggested that membrane flux increased with the increase of temperature. Membrane flux was affected by membrane material. The separation factor of aqueous solution was not affected by feed temperature. The research work of Bing [4] indicated that VMD process could remove trichloroethane (TCA) from wastewater effectively. When the cold side pressure was 60–80 mmHg, feed temperature was 50˚C and feed velocity was 0.001 m^3/h, the removal rate of TCA was 97%.

Ethyl acetate is an important group of environmental contaminants, which is widely used in large volumes of industrial solvents, adhesives, extraction agents, and perfume material. In ethyl acetate production process, the discharge of wastewater containing a lot of ethyl acetate, which is a damage to the human health, causes environment pollution and extreme waste resources. It is urgent to find an economic and feasible method to deal with this wastewater. VMD process is used to remove ethyl acetate from aqueous solutions, and the operation condition is investigated for the effect of removing ethyl acetate from aqueous solutions by the use of VMD process.

2. Experimental

2.1. Experiment method and materials

The experimental set-up is shown in Fig. 1. Heating and circulation system includes thermostatic bath (Shanghai Boxun Company Ltd), magnetic driving pump (Shanghai Xinxishan Pump Company Ltd) and flowmeter (Suzhou Chemical Instrument Company Ltd). Condensing system includes a condenser and a vacuum pump (Zhengzhou Great Wall Industry and Trade Company Ltd). Numerical display system includes pressure sensor (Beijing Kunlun Haian Company Ltd. Sensing Technology Center) and temperature sensor (Xiamen Yudian Automation Technology Company Ltd). The membrane used in experiments is polyvinylidene fluoride (PVDF) hydrophobic membrane, which is manufactured by Millipore Company. The liquid entry pressure of the membrane is 2.0 bar [12].

For reducing the loss of volatile ethyl acetate, a certain amount of distilled water was firstly added into the feed reservoir, and the distilled water was heated and pumped into membrane module. When the temperature, flow rate, and vacuum degree were constant, the corresponding quality ethyl acetate was added into the feed reservoir and a set of percentage content of ethyl acetate solution was prepared. The feed solution was heated in the heating circulation system and pumped into the membrane module. The vapor crossed over the other side of the membrane and was collected in the condenser pipe. The membrane flux and separation factor were calculated according to the quality of the collection of distillation liquid and absorbency value of distillation liquid. Three membrane modules with various channels were used for the experiments and the schematic diagram is shown in Fig. 2. The active area of module 1 was 20 cm^2 and the shape of channel 1 was curved surface. The dimensions of cold and hot side channel were 100 mm long, 20 mm wide, and 2 and 3 mm deep, respectively, the cross-section is shown in Fig. 2(a). The active area of module 2 was 15 cm^2, and the cross-section of the channel was semicircular, the shape of channel 2 was curved surface, the cross-section of the channel is shown in Fig. 2(b). The dimensions of cold and hot side channel were 150 mm long, 10 mm wide, and 5 mm deep. The channel of the membrane 3 was a rectangular cross-section. The channel is 100 mm long, 20 mm wide, and 2.5 mm deep, the active area of the membrane was 20 cm^2, and the cross-section of the channel is shown in Fig. 2(c).

2.2. Permeation measurements

In the process of VMD, the separation properties were evaluated by water flux and the separation factor. Membrane flux referred to the solution quality through unit time and unit area of the membrane. The equation is as follows:

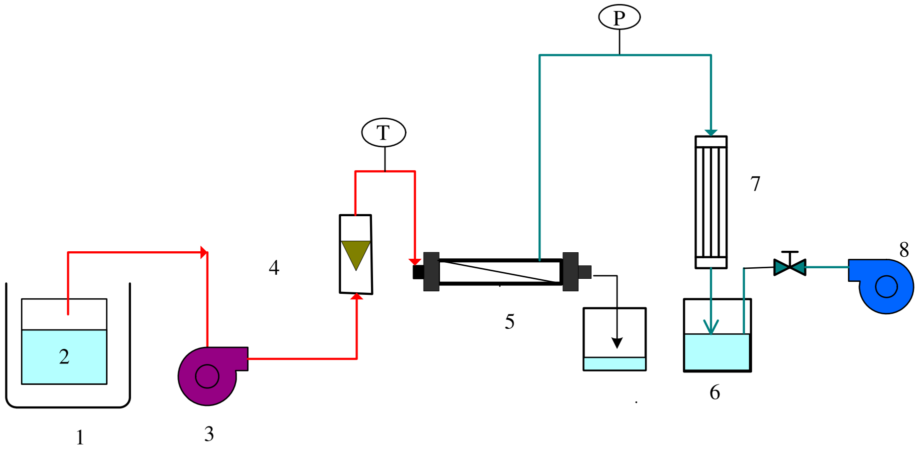


Fig. 1. Experimental set-up for VMD. 1–thermostatic bath; 2–feed tank; 3–magnetic driving pump; 4–rotameter; 5–membrane module; 6–distillate receiving flask; 7–condenser; and 8–vacuum pump.

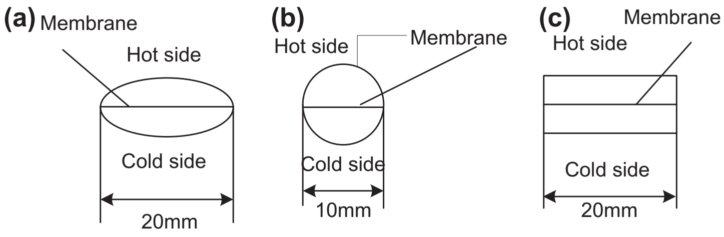


Fig. 2. The cross-sections of channels.

$$J = m/t \times s \qquad (1)$$

where J was membrane flux, kg/m^2 h; m was quality, kg; t for time, h; s was the effective membrane area, m^2.

The separation factor was indicated as α, α affects the selective permeability of the membrane, which is defined by the ratio of the proportion component A and component B in the permeation solution and the proportion component A and component B in the feed solution. It can be explained as follows:

$$\alpha = (Y_A/Y_B)/(X_A/X_B) \qquad (2)$$

where A, B component; X feed solution proportion; Y feed solution proportion.

3. Result and discussion

Ethyl acetate aqueous solution was treated by VMD process, the effect of vacuum degree, feed temperature, feed solution concentration, and feed flow rate was investigated. Three membrane modules with different channels were used for experiments and the influence of channel structure was also investigated.

3.1. The effect of temperature

As shown in Fig. 3, membrane flux increased quickly when temperature went up. Separation factor increased when temperature increased from 45 to 55℃, then the separation factor reduced gradually. When the temperature increased, the saturated vapor pressure in the hot side increased, the driving force of mass transfer increased and the viscosity of the feed solution decreased, which was useful for increasing the membrane flux. At the same temperature, the saturated vapor pressure of VOCs was higher than that of water, VOCs through the microporous membrane into the cold side were more than water, which led to the increase of the separation factor at a certain temperature range. A major part of the feed solution was water. When the temperature continued to rise, the water flux exponent increased with the temperature increase, increment of water flux was more than ethyl acetate flux, and then the separation factor decreased. The range of the temperature was from 45 to 60℃, the

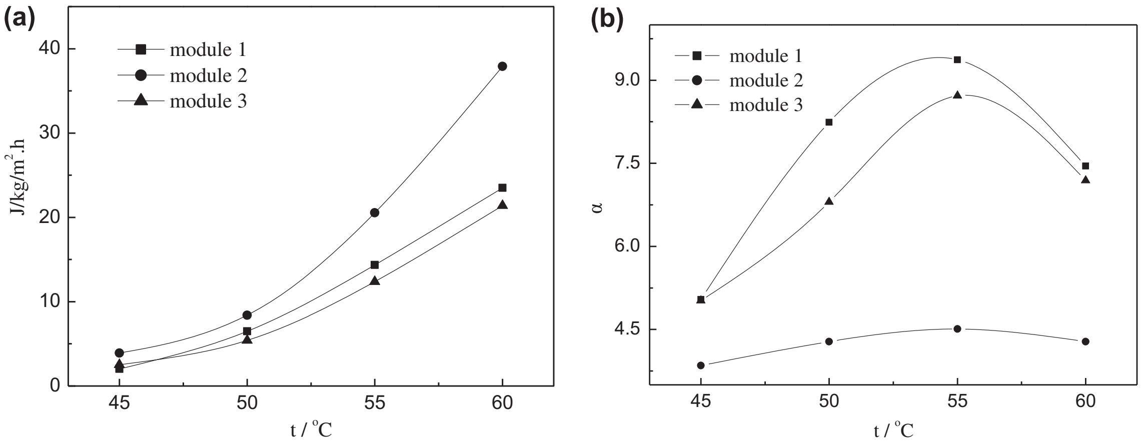


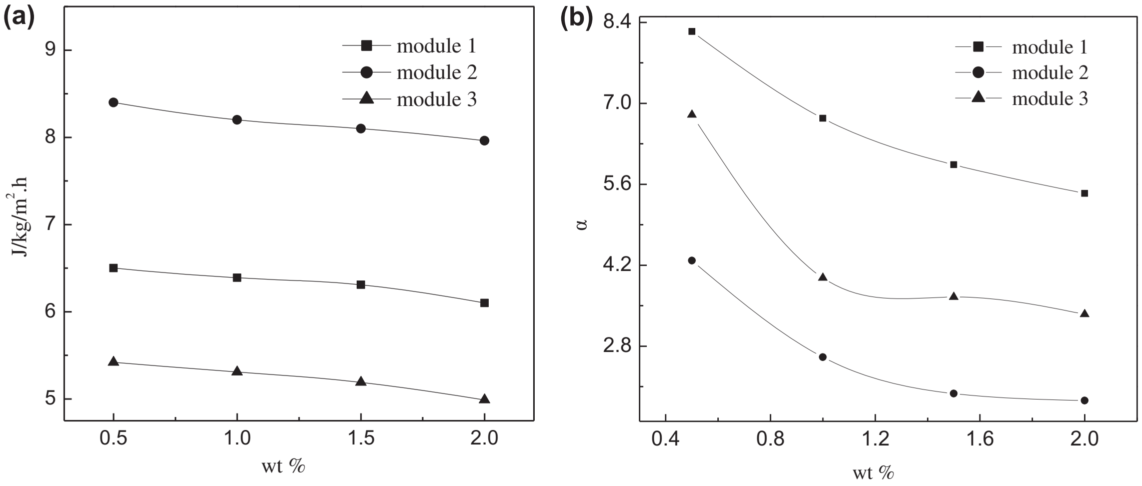
Fig. 3. The influence of temperature on the permeation performance (operating conditions: the feed solution concentration was 0.5 wt%, vacuum degree of the cold side was 89 kPa, and the flow of feed solution was 76 L/h). (a) Membrane flux and (b) Separation factor.

maximum flux was 23.49 kg/m^2 h in module 1, 37.90 kg/m^2 h in module 2, and 21.39 kg/m^2 h in module 3. The separation factor occurred at 55℃ and the highest separation factor was 9.37, which was obtained in module 1.

3.2. The effect of feed concentration

Experiments were carried out when the flow of feed solution was 76 L/h, feed solution temperature was 50℃, and vacuum degree of the cold side was 89 kPa. Various concentrations of aqueous ethyl acetate were prepared for investigating the effect of feed concentration on the separation factor and flux. The results are shown in Fig. 4. The membrane flux and the separation factor decreased with the increase of the feed solution concentration.

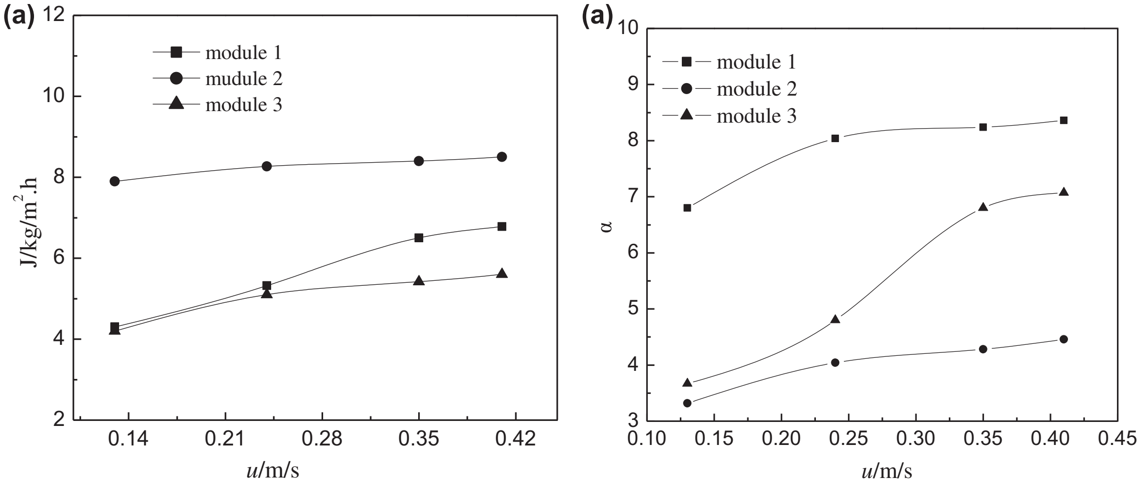
It can be deduced that saturation vapor pressure increases with the increase of concentration, which leads to the increase of the bulk driving force. However, at the same time, the increase of concentration leads to a serious concentration polarization, which blocks the mass transfer and lowers the flux. Under the effect of the pressure difference and concentration polarization, the flux decreased gently, but not obviously. With the increase of concentration, the ethyl



Membrane flux

Separation factor

Fig. 4. The influence of feed concentration on the permeation performance (operating conditions: flow of feed solution 76 L/h, feed solution temperature 50℃, and vacuum degree of the cold side 89 kPa).



Membrane flux

Separation factor

Fig. 5. The influence of feed-flow rate on the permeation performance (operating conditions: concentration of feed solution 0.5 wt%, feed solution temperature 50℃, and vacuum degree of the cold side 89 kPa).

acetate concentration in the cold side increased, the partial pressure difference of ethyl acetate decreased, as a result, the separation factor decreased. The result at the same operation parameters showed that module 1 was the best one. It could be concluded that the channel of the cold side should not be too deep, and the channel was unfavorably designed to square form. Less mass transfer resistance lied in the arc channel. The depth and width of the hot side channel should be proportional to guarantee sufficient equivalent diameter, which was helpful for mass transfer process and improvement of the separation performance.

3.3. The effect of feed velocity

Experiments were carried out when the concentration of feed solution was 0.5 wt%, feed solution temperature was 50℃, and vacuum degree of the cold side was 89 kPa. The influence of feed solution on separation performance was investigated. As shown in Fig. 5, the membrane flux and separation factor increased with the increase of average velocity. The increase of average velocity can lead to a lower residence time and polarization. Lower residence probably decreases the flux, however, lower polarization can increase the flux. As a result, the increase of average velocity led to a slow sweep in flux. At a determined operation condition, the flux order of three sets membrane flux was module 2, module 1, and module 3. The sequence of three sets separation factor was module 1, module 3, and module 2. Along with the increase of velocity, the separation factor of module 3 changed more than the other two modules. The separation factor of module 3 changed from 7.07 to 3.67, while for other two modules it changed more gently. The main differences of the three modules were form, size, and cross-section. The net cross-section of module 3 is the largest one. Module 2 with a smaller net cross-section probably presented stronger turbulent motion, which improved mass transfer. The form and depth of the cold side also affected membrane separation performance. The vapor entered into the cold side from the hot side through the microporous membrane, and then it was pumped into the cooler condenser under negative pressure. The vapor in the deeper cold side channel cannot be extracted from the condenser in time. The vapor accumulation on the membrane surface in the cold side affected the separation performance.

3.4. Influence of the membrane type

Two kinds of membranes were used for investigating the influence of the membrane pore diameters, which were named PVDF1$^{\#}$ and PVDF2$^{\#}$. The pore diameter of the two membranes was 0.225 and 0.463 μm, respectively. As shown in Fig. 6, the results were that membrane fluxes and separation factor reduced with the increase of the feed concentration. The flux of membrane PVDF2$^{\#}$ was about two times higher than that of membrane PVDF1$^{\#}$, and the separation factor of membrane PVDF1$^{\#}$ was higher than that of membrane PVDF1$^{\#}$. It also showed that the bigger pore diameter was good for increasing the flux,

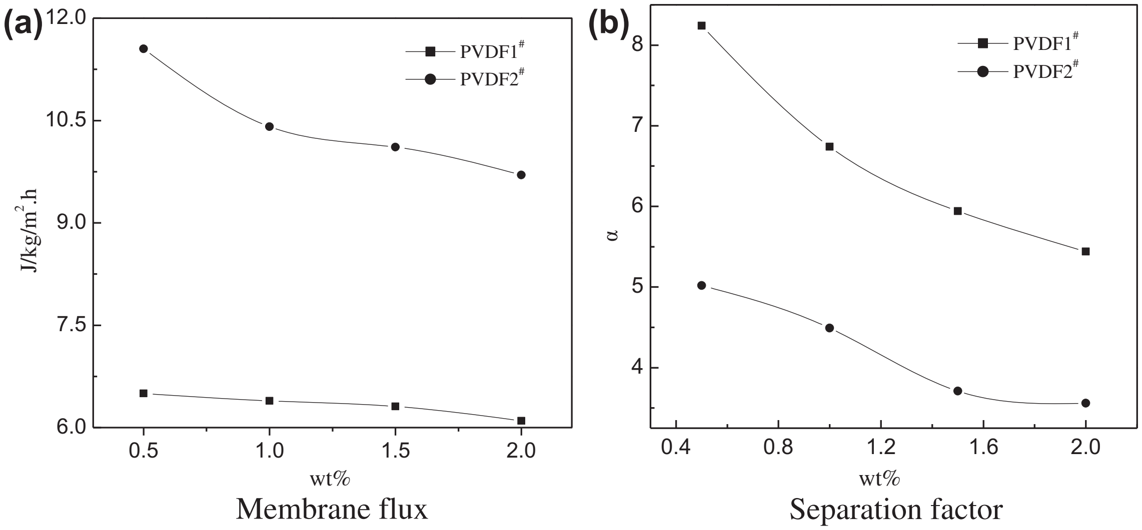


Fig. 6. Influence of the membrane type on the permeation performance (operating conditions: feed solution temperature 50℃, vacuum degree of the cold side 89 kPa, and flow of feed solution 76 L/h).

but the change of ethyl acetate flux was little. So in the membrane of the cold side, with the increase of the membrane pore diameter, the volatile concentration was low. In the VMD process, the appropriate membrane was chosen according to the composition of the feed solution.

4. Conclusions

Experiments were made for investigating the effect of removing ethyl acetate from aqueous solutions by VMD. It was shown that the feed flow rate and concentration had slight effects on the membrane flux, but significant influence on ethyl acetate flux, the separation factor enhanced with the increase of feed flow rate. The increase of feed concentration led to the decrease of the separation factor. Vacuum degree had an important influence on the membrane flux and separation factor. With the increase of the vacuum degree, the flux increased sharply, and the separation factor decreased. When the feed temperature was lower than 55℃, the higher temperature led to the higher separation factor, and the maximum value was 9.37. The larger diameter brought higher flux, but lower separation factor. The mass flow resistance of the membrane module with the quadrate channel was higher than the membrane module with the arc channel. As a result, the flux of the membrane module with the quadrate channel was lower. The larger equivalent diameter of the hot side in the membrane module could gain a higher permeate flux. The shallower cold side in the membrane module could obtain the higher separation factor.

Acknowledgments

This study was supported by the National Nature Science Foundation of China (No. 20806008) and the National Nature Science Foundation of China (21111120074).

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