



## **PTFE PDMS/PVDF composite membrane preparation and pervaporation properties**

Organic wastewater containing halogen is difficult to degrade organics, the common characteristics of these pollutants is toxic, complex components, high chemical oxygen demand, the general microbial almost no degradation effect to its, if these substances without governance to environmental emissions, would seriously pollute the environment and endanger human health. Meanwhile, halogenated organic compounds are important chemical raw material; its recovery has important economic value. Process of pervaporation (PV) is a new type of membrane separation process, it is especially suitable for the separation of the small amounts of organic pollutants in wastewater, and it has obvious technical and economic advantages. Pervaporation process play a key role is the core element of film, from the point of view of literature retrieval condition, materials used in silicone rubber polydimethylsiloxane (PDMS). Chandak prepared silica zeolite modified PDMS composite pervaporation membrane , and used for separation of chlorinated organic aqueous solution; Salehi, etc were used in pervaporation PDMS - PES crosslinked composite membrane, investigated its removal from aqueous solution, toluene and chloroform pervaporation performance; Bennett preparation containing different organic functional groups such as side chain of the modified PDMS silicon rubber membrane, with chloroform solution system testing the pervaporation performance; Tadaihiro prepared PDMS-PMMA composite film by dimethyl siloxane crosslinking methyl methacrylate (mma) , studied the pervaporation separation of VOC pervaporation properties of aqueous solution. And with strong hydrophobicity, high crystallinity and stability good polytetrafluoroethylene (PTFE) modified PDMS is relatively rare, this paper was prepared with poly (vinylidene fluoride) (PVDF) ultrafiltration membrane as the basement membrane, PTFE superfine powder filling PDMS membrane for pervaporation of active cortex (PTFE - PDMS/PVDF) composite membrane, taking chloroform solution as separation system composite membrane pervaporation performance was studied.

### **Experimental part**

The preparation of PTFE-PDMS/PVDF composite membranes

According to take the right amount of silicon rubber PDMS, dissolved in hexane, in proportion to join the right amount of PTFE powder, TEOS crosslinking agent, mechanical stirring 2 h after ultrasonic dispersion of PTFE, join DBTL catalyst, fully stir until sticky solution, dumping on PVDF ultrafiltration membrane, extending into membrane, place 2 h at room temperature, vacuum drying oven crosslinking on 60 °C in the 4 h, quick PTFE - PDMS/PVDF composite films. In the process of preparation of PDMS: TEOS: DBTL, the mass ratio is 10:1:0.5. By PTFE: PDMS the mass ratio prepare the five (0:20, 1.5:20, 6:20, 10:20, 15:20) different composite membrane. SEM analyze and adopt the Japanese JMS - 5600 LV scanning electron microscope, contact Angle measurement by Shanghai Calvin JC2000D1 type of contact Angle meter.





The Pervaporation experiments of PTFE-PDMS/PVDF composite membrane Pervaporation separation experiment device see references. Sample analysis use UV spectrophotometer. Membrane separation factor alpha, permeate flux J and separation index PSI is the main parameter that characterization of pervaporation membrane separation performance, respectively defined as:

$$\alpha = \frac{Y_C / Y_W}{X_C / X_W} \quad (1)$$

$$J_i = \frac{G_i}{A \times t} \quad (2)$$

$$\text{PSI} = (\alpha - 1) \cdot J \quad (3)$$

Mass transfer model

Pervaporation series of low concentration organic solution mass transfer process is generally used resistance model, the component i and flux  $J_i$  are proportional to across the membrane mass transfer driving force:

$$J_i = K_{i,t} (c_i^f - c_i^p) \quad (4)$$

$$\frac{1}{K_{i,t}} = \frac{1}{K_{i,b}} + \frac{1}{K_{i,m}} \quad (5)$$

$$R_{i,t} = R_{i,b} + R_{i,m} \quad (6)$$

## The results and discussion

SEM analysis

From figure 1 (a) can be seen, no modified silicone rubber membrane surface showed very good flatness, and no found holes and cracks. But after joining PTFE composite membrane surface is uneven structure, and a large number of PTFE particles distribution in PDMS surface, the edge between PDMS and no phase separation phenomenon, the rough surface morphology significantly increased the membrane surface and the surface hydrophobicity enhanced composite membrane (water contact Angle change as shown in figure 2), to strengthen the pervaporation performance, as shown in figure 1 (b - c). From figure 1 (c),





ultrafiltration membrane surface is about 25 microns thickness of PTFE filled with PDMS active cortex.

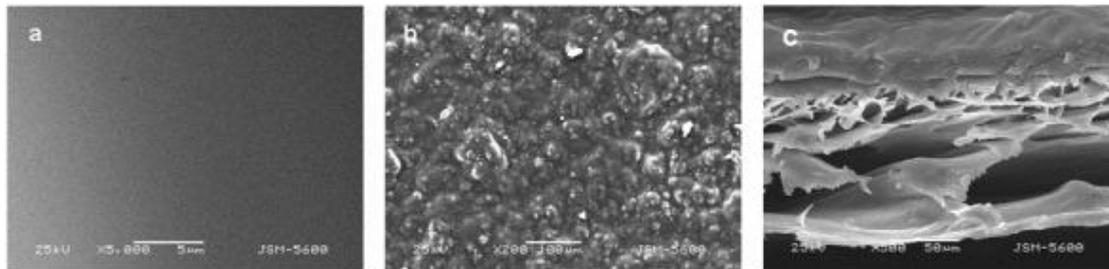


Figure 1 SEM. a-PDMS membrane surface (magnification:  $\times 5000$ ) ; b-PTFE-PDMS/PVDF membrane surface (magnification:  $\times 200$ ) ; c-PTFE-PDMS/PVDF membrane section (magnification:  $\times 500$ )

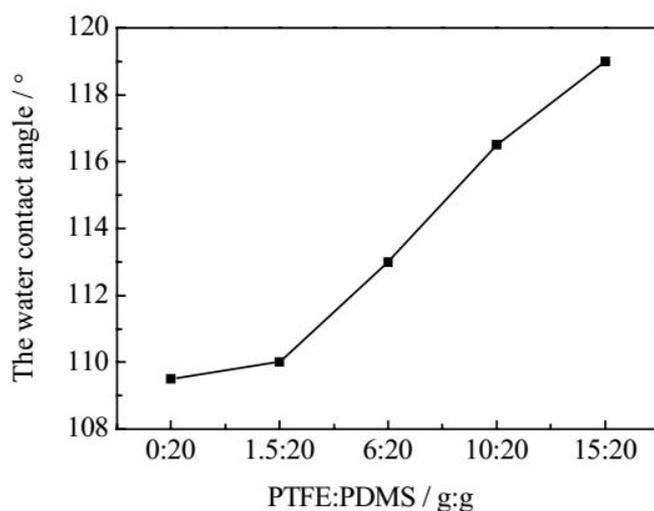


Figure 2 The impact of PTFE content on contact angle of composite membrane

The impact of PTFE content on the composite membrane pervaporation performance

The figure 3 and figure 4 shows that filling amount of PTFE film 15:20, and to explain hydrophobic nano PTFE and PDMS compatibility are good, and the addition of PTFE significantly improves the pervaporation properties of PDMS composite membrane. Water flux showed a trend of increase gradually and far greater than chloroform; Chloroform flux, the separation factor and separate index showed a trend of decrease after the first increase. Shingjiang Jessie thought the aggregation particle filling PDMS membrane help water flux to improve. By section 3.1, PTFE particles are the state of aggregation. So its content is increased, the water flux increased, chloroform adsorption quantity increases, the flux increases; and, because of the large





water impetus the chloroform water flux is greater than chloroform. when the content of PTFE more than 10:20, and get a lot of PTFE will add destroy the PDMS membrane structure of continuous phase, lead to water at this time spread more likely , the water flux increases with chloroform flux decline and separation factor decrease.

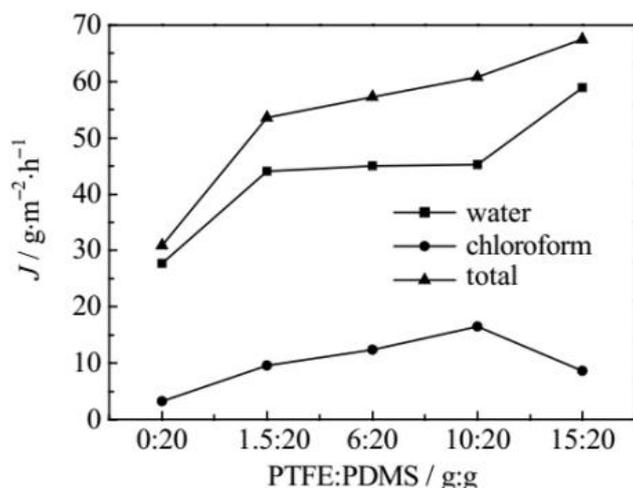


Figure 3 The impact of PTFE content on the composite membrane flux, water flux and the flux of chloroform (feed liquid temperature 60 °C and permeate side pressure 2.2 mmHg, slurry concentration 660 mg L<sup>-1</sup>, the material liquid flow 400 mL min<sup>-1</sup>)

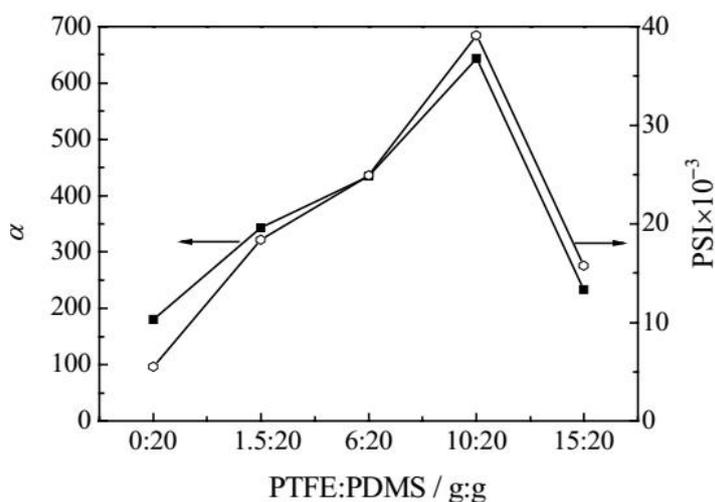


Figure 4 The impact of PTFE content on the composite membrane separation factor and the separation index (feed liquid temperature 60 °C, permeate side pressure 2.2 mmHg, slurry concentration 660 mg L<sup>-1</sup>, the material liquid flow 400 mL min<sup>-1</sup>)





### The impact of material liquid flow rate on pervaporation performance

The mass ratio is 10:20 PTFE PDMS/PVDF composite membrane pervaporation performance results under different flow rate as shown in figure 5, and 6. With the increase of feed liquid velocity, total flux, chloroform, water fluxes and separation factor increased rapidly, while less than 200 mL min<sup>-1</sup> when the flow rate is greater than 200 mL min<sup>-1</sup> change is steady, the experimental results and Park using PDMS composite membrane pervaporation VOC aqueous solution, the conclusion is very similar. Due to the effect of dissolve of the composite membrane of chloroform strong, easily happened under the condition of low velocity phenomenon of concentration polarization, but with the increase of flow velocity and boundary layer thinning, concentration polarization effect weakened and is beneficial to chloroform and mass transfer process, so when the flow rate is less than 200 mL min<sup>-1</sup> flux and separation factor are increased with the increase of flow velocity; And when the flow rate is greater than 200 mL min<sup>-1</sup> flux and separation factor change steady, shows that the boundary layer and mass transfer resistance is small, the mass transfer resistance is controlled by membrane resistance.

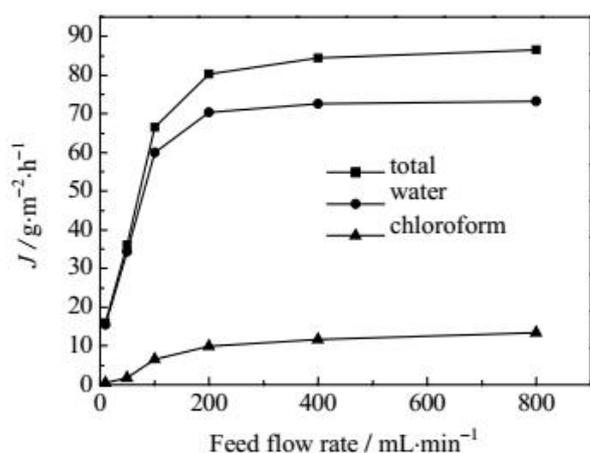


Figure 5 The impact of material liquid on the composite membrane material total flow flux, the water flux and flux chloroform (150 mg L<sup>-1</sup> material liquid concentration, feed liquid temperature 50 °C, permeate side pressure 2.2 mmHg)



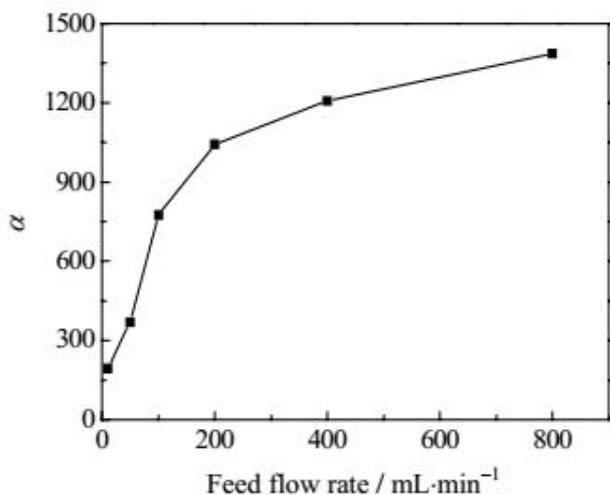


Figure 6 The impact of material liquid flow on the composite membrane separation factor (150 mg · L<sup>-1</sup> material liquid concentration, feed liquid temperature 50 °C, permeate side pressure 2.2 mmHg)

#### The impact of material liquid concentration on the pervaporation performance

PTFE material liquid concentration on the mass ratio 10:20, and get - PDMS/PVDF composite membrane pervaporation performance impact is shown in figure 7, 8. With the increase of the concentration of slurry, the total flux and chloroform flux linear increase slowly, and the water flux changes smaller; Separation factor with the increase of the concentration of material liquid drop sharply. The material liquid flow 400 mL min<sup>-1</sup> eliminate the influence of concentration polarization (see section 3.3), the type, the water mass transfer driving force changes with the increase of concentration of chloroform, so the water flux change is very small and chloroform flux linear increase. When chloroform concentrations greater than 200 PPM, film inside a large amount of dissolved chloroform by membrane of the groups in law of organic affinity effect and make the transfer resistance increases, chloroform molecules of mass transfer rate is reduced, the separation factor is on the decline.



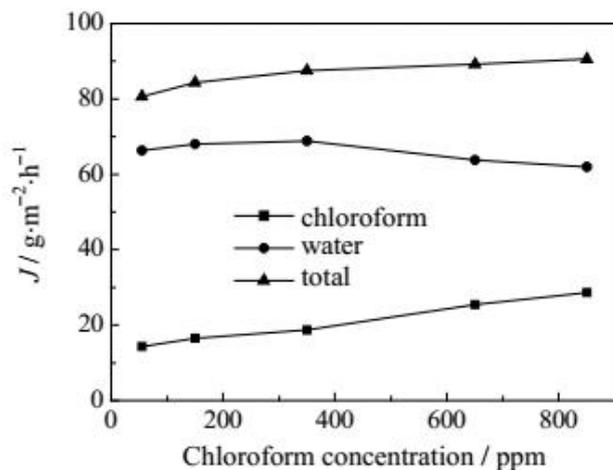


Figure 7 The impact of feed concentration on the composite membrane flux , water flux and the flux of chloroform (feed temperature 50 °C, permeate side pressure 2.2 mmHg, material liquid flow rate, 400 ml min<sup>-1</sup>)

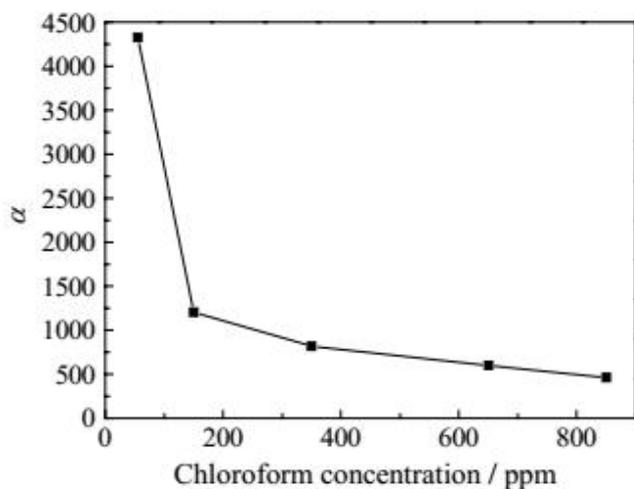


Figure 8 The impact of feed concentration of composite membrane separation factor (feed temperature 50 °C, permeate side pressure 2.2 mmHg, material liquid flow rate, 400 ml min<sup>-1</sup>)

### Process analysis of mass transfer

From figure 9, 10, with the increase of feed liquid velocity, boundary layer thickness gradually thinning,  $K_b$  increase gradually,  $R_b$  gradually decreased; When the flow rate is greater than 200 mL min<sup>-1</sup>,  $K_t$  gradually close to  $K_m$ ,  $R_t$  gradually close to the  $R_m$ , illustrate the  $R_b$ , chloroform and mass transfer process is controlled by the  $R_m$ . When the flow is 10 mL min<sup>-1</sup>,  $R_b$  is  $R_m$  29 times, chloroform and mass transfer process is controlled by  $R_b$ , thus, phenomenon of





concentration polarization in chloroform plays a considerable role in the process of mass transfer, so the pervaporation chloroform solution should be carried out under high flow velocity, in order to overcome the influence of the concentration polarization. From figure 10, flow under the condition of  $400 \text{ mL min}^{-1}$   $K_t$  basic equal to  $K_m$ , so in figure 11, with the increase of the concentration of chloroform in the material liquid, the chloroform  $K_t$  increases linearly, and water  $K_t$  has linear decreasing trend, namely chloroform  $K_m$  linear increase, and the water  $K_m$  linear decrease. This suggests that a greater influence on the concentration of chloroform in the material liquid  $K_m$ , this is mainly due to the strong hydrophilic organic composite film features generated by the results.

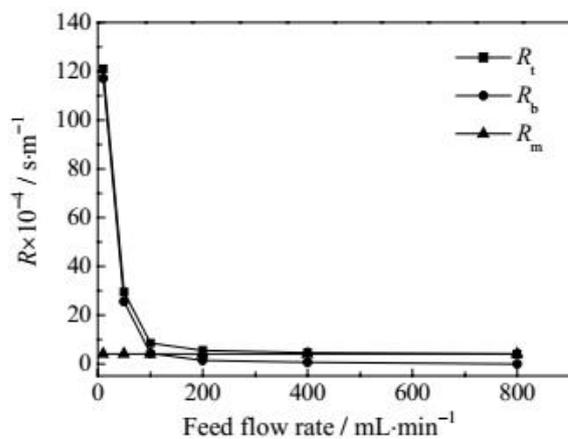


Figure 9 The impact of material liquid velocity of chloroform and total mass transfer coefficient, boundary layer and mass transfer coefficient and the membrane mass transfer coefficient (150  $\text{mg} \cdot \text{L}^{-1}$  material liquid concentration, feed liquid temperature  $50 \text{ }^\circ\text{C}$ , permeate side pressure 2.2 mmHg)

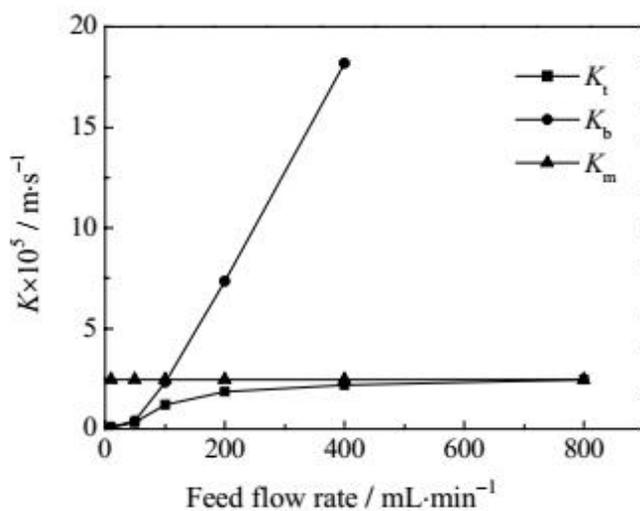




Figure 10 The impact of material liquid velocity on mass transfer resistance of chloroform (150 mg · L<sup>-1</sup> material liquid concentration, feed liquid temperature 50 °C, permeate side pressure 2.2 mmHg)

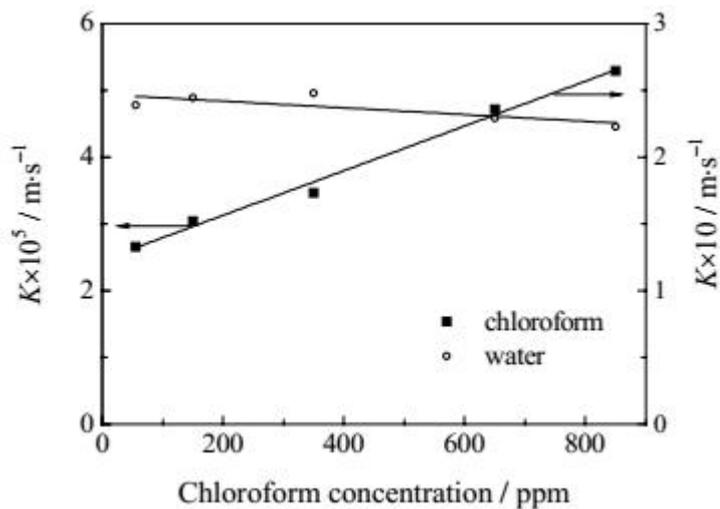


Figure 11 The impact of concentration of materials on total mass transfer coefficient of chloroform and water (feed temperature 50 °C, permeate side pressure 2.2 mmHg, material liquid flow rate, 400 ml min<sup>-1</sup>)

## Conclusion

PTFE PDMS/PVDF composite membrane was prepared, and in chloroform solution system study of pervaporation properties of the composite membrane. Increased, PTFE filler in PDMS membrane showed a trend of increasing total flux and water flux, flux and chloroform, the separation factor and separate index showed a trend of decrease after the first increase, when PTFE: PDMS is 10:20 for mass ratio, PTFE PDMS/PVDF composite membrane pervaporation performance was the best; With the increase of feed liquid velocity, total flux, chloroform, water fluxes and separation factor in increased rapidly, while less than 200 mL min<sup>-1</sup> when the flow rate is greater than 200 mL min<sup>-1</sup> change to level off; With the increase of the concentration of slurry, the total permeation flux and chloroform flux increase slowly, and the water flux changes smaller; Separation factor dramatically reduced with the increase of concentration of feed solution.

Chloroform and mass transfer process was analyzed, when the flow is 10 mL min<sup>-1</sup>, the boundary layer resistance  $R_b$  is 29 times the  $R_m$  of the membrane resistance and mass transfer process is controlled by boundary layer resistance; And when the flow rate is greater than 200 mL min<sup>-1</sup>, chloroform and mass transfer process is controlled by the membrane mass transfer resistance, thus, phenomenon of concentration polarization in chloroform plays a considerable role





in the process of mass transfer, so the pervaporation chloroform solution should be carried out under high flow velocity, in order to overcome the influence of the concentration polarization.

**Symbol explanation:**

- A The effective area of membrane,  $m^2$
- C Molarity,  $mol L^{-1}$
- G Quality, g
- J Permeate flux,  $g m^{-2} h^{-1}$
- K Mass transfer coefficient,  $m s^{-1}$
- R Mass transfer resistance,  $s m^{-1}$  t Operating time, h
- X Raw material liquid component mole fraction
- Y Penetrating fluid component mole fraction Superscript
- f Raw material liquid
- p penetrating fluid Subscript
- b boundary layer
- i component
- m membrane
- t total
- C chloroform
- W water

