Electronic Supplementary Material

Preparation and properties of hollow fibre nanofiltration membrane with continuous coffee-ring structure

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1. Effect of TMC concentration on PA/GO NF membrane performance

TMC concentration will affect the crosslinking degree of the selective layer and directly affect the separation performance of the NF membrane. The effect of TMC concentration on NF membrane performance was studied, and the results are shown in Fig. S1. The PIP concentration was 0.6 wt%, the GO concentration was 0.01 wt%, the heat treatment temperature was 60°C and the treatment time was 10 minutes. The rejection rate of the NF membrane for $MgSO_4$ first increased with increasing TMC concentration and then decreased. When the TMC concentration was 0.3 wt%, the salt rejection reached the maximum value. At the same time, the flux decreased with increasing TMC concentration. When the PIP concentration remained stable, the functional layer gradually became denser as the TMC concentration increased, which led the selective layer to become increasingly compact and the flux to decrease slowly. When the TMC concentration was 0.5 wt%, it was largely excessive. The permeation flux increased, and the salt rejection clearly decreased. This was due to the interfacial polymerization reaction rate being accelerated when the TMC amounts were clearly in

excess. The PIP molecules were consumed quickly, and the functional layer that formed was relatively loose. At the same time, the hydrophilicity of NF membranes improved due to the hydrolysis of many unreacted acyl chloride groups to carboxyl groups, which made water molecules permeate the membrane more easily. Therefore, the permeate flux increased and salt rejection decreased when the TMC concentration reached 0.5 wt%. In the following studies, 0.3 wt% was chosen as the optimum concentration of TMC.

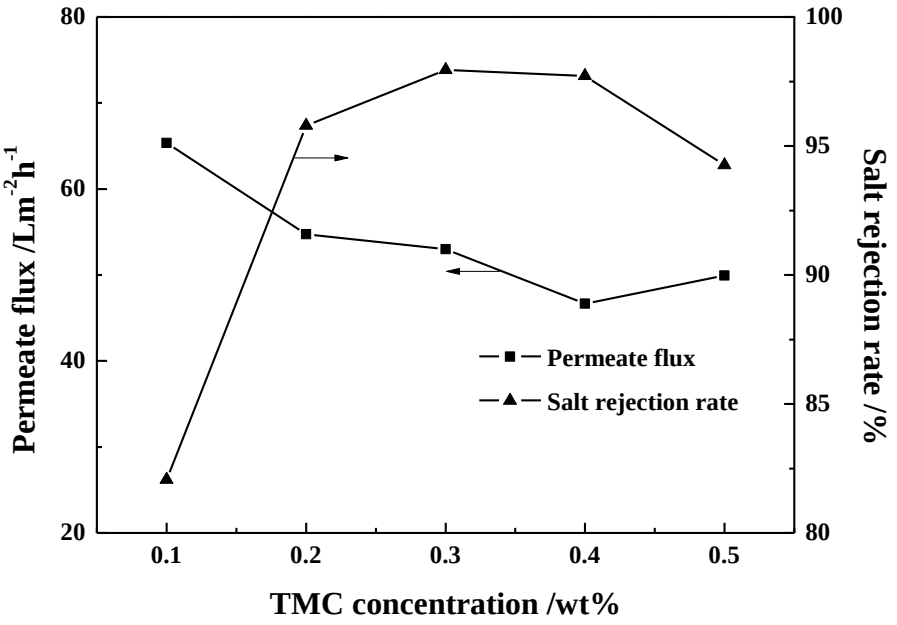

Fig. S1. Effect of TMC concentration on PA/GO NF membrane performance

2. Effect of PIP concentration on PA/GO NF membrane performance

The PIP concentration can affect the thickness of the selective layer. Therefore, the effect of PIP concentration on PA/GO NF membrane performance was explored when the GO concentration was kept at 0.01 wt%. As shown in Fig. S2, the rejection rate of the PA/GO NF membrane for $MgSO_4$ first increased with increasing PIP concentration and then reached a relatively stable state. When the PIP concentration was 0.4 wt%, the salt rejection rate reached 97%. However, the permeation flux declined gradually as the PIP concentration increased. If the TMC concentration

remained unchanged, the active selective layer of the NF membrane gradually became thicker as the PIP concentration increased. As a result, the permeate flux decreased and the rejection rate increased with increasing PIP concentration. Combining the results of permeation flux and rejection rate, the optimum concentration of PIP was adopted as 0.4 wt%.

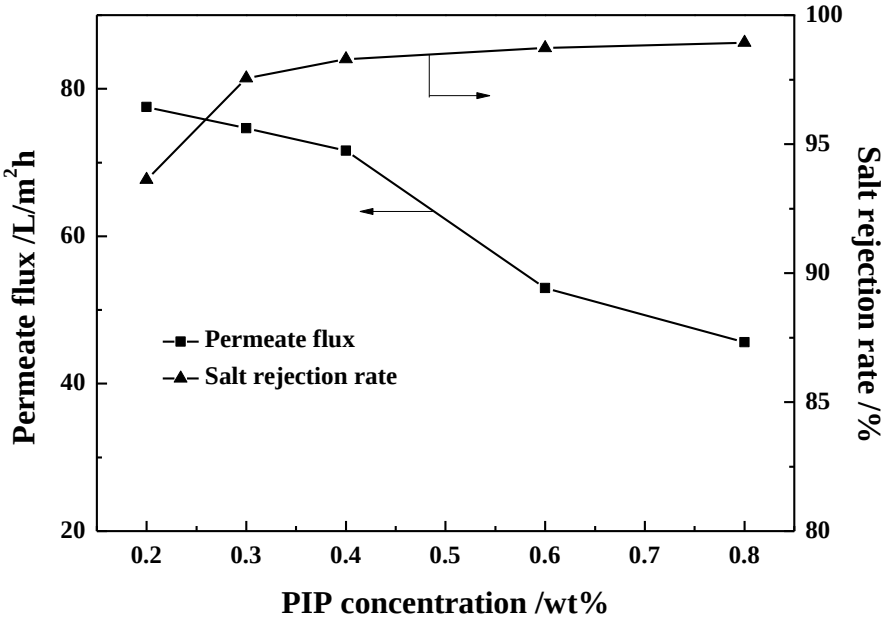

Fig. S2. Effect of PIP concentration on PA/GO NF membrane performance

3. The cross-sectional structure of the coffee ring

The enlarged cross-sectional SEM image of the NF membrane upper part is shown in Fig. S3. As shown in Fig. S3, the wall thickness of the coffee ring is about 60 nm. And the coffee ring was not only The circular ring structure not only exists in the surface morphology of the NF membrane, but also runs through the entire cross-sectional selection layer of the NF membrane.

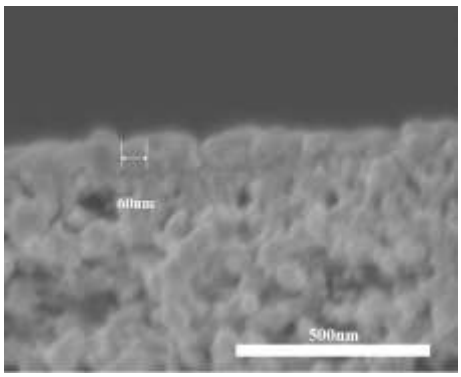

Fig. S3. The enlarged cross-sectional SEM image of the NF membrane upper part

4. Effect of GO on diffusion of PIP in organic phase

During interfacial polymerization process, the reactive monomer PIP in aqueous phase would diffuse into organic phase and react with TMC. However, it is very difficult to directly measure the diffusion coefficient of PIP in organic phase. Thus, the preparation process was simulated and UV spectroscopy was used to monitor the concentration change of amine functional groups (from PIP) in organic phase to predict the diffusion coefficient change of PIP. The Polysulfone (PSF) ultrafiltration (UF) membrane was cut into suitable length and fixed in the cuvette. The UF membrane was immersed into aqueous phase for the first. Then, the UF membrane was dried with nitrogen gas. Finally, the UF membrane was immersed into n-hexane and characterized by UV spectroscopy. The illustration process was showed as Fig. S4. Pure n-hexane was used as detection background and the detection wavelength was kept at 228 cm (maximum absorption peak of amino group). After n-hexane was added, the measurement would be started immediately. The change of absorbance was recorded every 1 s.

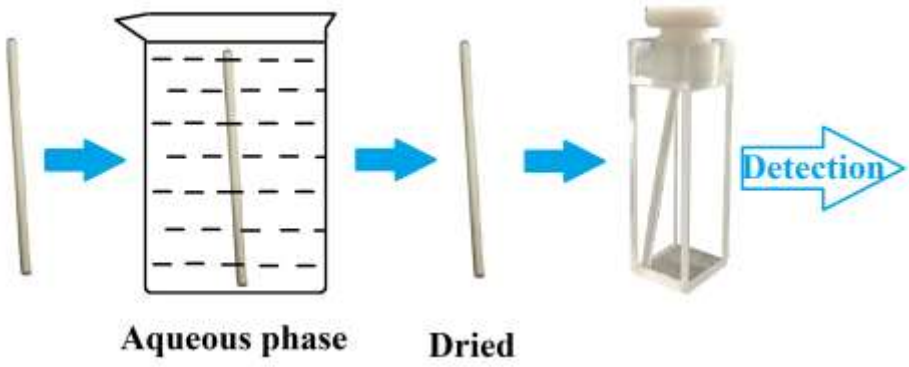

Fig. S4. Illustration of diffusion coefficient characterization process

The absorbance changed with immersion time for functional groups of different aqueous phases, shown as in Fig. S5. The results showed that the absorbance of amine functional group increased with immerse time prolonging for all groups, indicating that more PIP molecules diffused into n-hexane. However, when GO was added into aqueous phase, the absorbance increase rate was relative slower than that the aqueous phase without GO. Additionally, the absorbance increased rate decrease with the increasing of GO concentration. It could be known from the results that the addition of GO indeed inhibited the diffusion of PIP from water phase into the organic phase. This was attributed to hydrogen bond, which was formed between the carboxyl group, hydroxyl group of GO and the amino group of PIP.

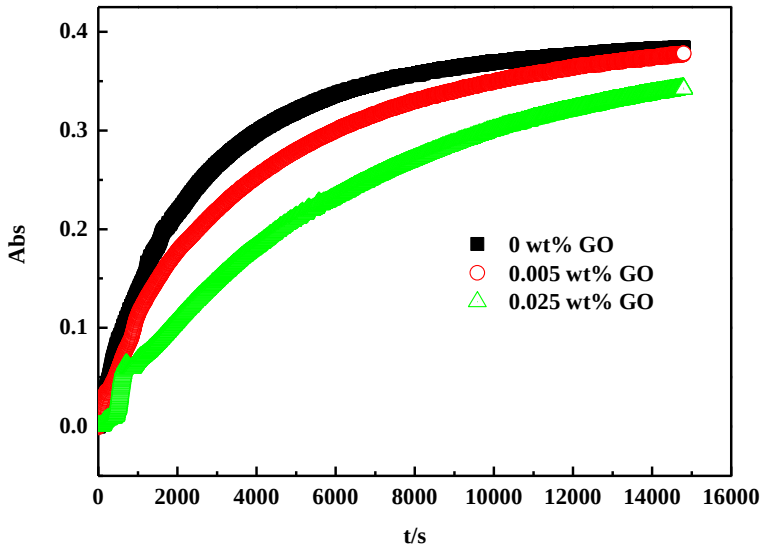

Fig. S5. PIP diffusion change of different membrane with immersion time