

Effect of Swelling on Performance of Surface-Imprinted Composite Membranes

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Abstract. Molecularly imprinted composite membranes (MIMs) are developed by thermally initiated copolymerization on the surface of polyvinylidene fluoride (PVDF) hollow fiber membranes for the selective binding to levofloxacin. The prepared membranes before and after surface polymerization are characterized by SEM and FT-IR. The water flux, swelling changes and selectivity of the membranes are evaluated. The highest specific separation factor of about 1.27 is achieved for MIMs to separate levofloxacin and ofloxacin. The results show that imprinted polymerization has obvious influence on the performance of membranes and swelling results in the decrease of specific recognition.

1.Introduction

Molecularly imprinted membranes (MIMs) have gained increasing attention in the last few years and been developed for some technically challenging separations, including the separation of chiral drugs or biomolecules, owing to the advantages of the highly specific identification to molecules and membrane separation. At present, MIMs are always prepared as free-standing membranes either from conventional molecularly imprinted polymers (MIPs) or from simultaneous formation of imprinted structure and membrane morphology and surface imprinting polymerization on support membranes [1]. Comparing to the simultaneous preparations, surface imprinted polymerization can optimize MIPs recognition and membrane transport properties at the same time. Generally the approaches for synthesis of MIMs are heterogeneous plasma polymerization[2], photografting[3] and thermal initiated copolymerization[4] on the surface of membranes in different solvents. Usually support membranes and MIPs have different degrees of swelling in solvents, which will bring the changes of permeability and selectivity of MIMs.

Levofloxacin, as an important quinolone, is well tolerated and displays impressive pharmacokinetics attributed to excellent bioavailability and widespread tissue penetration. Asymmetrical synthesis to produce levofloxacin is always reported has very low yield and difficult purification [5]. In China, the



throughput of ofloxacin occupies 98% of yield of fluoroquinolones together with norfloxacin, ciprofloxacin [6]. Therefore, it has huge potential to separate ofloxacin for levofloxacin in industrial application.

In this study, levofloxacin-imprinted composite membranes by thermal initiated copolymerization are developed on PVDF hollow fiber membranes. We aim to provide an alternative technique for obtaining levofloxacin and study the effect of swelling on selectivity of MIMs.

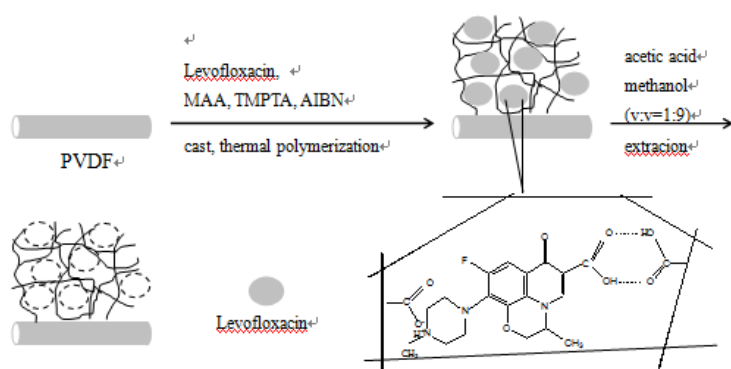
2.Experimental

2.1 Materials and instruments. PVDF hollow-fiber membranes (self-made; porosity=70%, MWCO with BSA67000 as a standard solution=94.7%). Ofloxacin and levofloxacin were from Kunshan Double-crane Pharmaceutical Co. LTD. Trimethylolpropanetria- crylate (TMPTA) was from Shanghai Kewang Chemical Co. LTD. 2, 2'-Azobis-(isobutyronitrile) (AIBN), Methacrylic acid (MAA), Glacial acetic acid, chloroform, methanol and ethanol, solvents of analytical-reagent grade, were all obtained from Shanghai Sinopharm Chemical Reagent Co. Ltd. MAA was further purified by using active carbon.

A UV762 spectrophotometer (Shanghai Precision & Scientific Instruments Co., Ltd), JSM-6360 LV scanning electron microscope (JEOL, Japan) and V70 Fourier transform infrared spectrometer (Bruker, German) were used in this study.

2.2 Membrane preparation. Prepolymerization solutions recipe contained 1.0 mmol of levofloxacin, 4.0 mmol of MAA, 15 mmol of TMPTA, and 0.2 mmol of AIBN in a chloroform solution. All the solutions were mixed for 30 min by ultrasonic wave before casting on the support PVDF membranes. Polymerization was performed by heating the membranes in a vacuum oven at 60°C for 24 h. Then, the membranes were rinsed with acetic/methanol (1:9 v/v) and ethanol to extract the templates and dried at room temperature. For comparison, non-imprinted polymer membranes (NIMs, without template) were also subjected to same treatment.

Polymerization process can be described as scheme1.



Scheme1 Polymerization process of MIMs

2.3 Swelling analysis. Swelling experiments were performed as described in literature [7]. The definite mass of dry membranes (m_0) were soaking in methanol at atmospheric conditions. After 24h equilibration at 25°C, the excess of solvent was removed from the MIMs by applying reduced pressure for 1 min, and the weight of the swollen membrane (m_s) was measured. The swelling ratio (Sr) of the membrane was calculated from the following equation:

$$Sr = \frac{m_s - m_0}{m_0}$$

2.4 Performance evaluation of membranes. Evaluation device and separation process of membranes were referred to literature [1]. The water flux was investigated under 25 °C and 1 bar. The binding capacity of the prepared membranes to levofloxacin and ofloxacin was determined by levofloxacin/ofloxacin concentration of 0.02 mmol/L in methanol under 25 °C and 1 bar. The concentration of the solution was monitored by a UV spectrophotometer at 298 nm.

3. Results and discussion

3.1 Morphology of membranes. Fig.1 shows the SEM images of external surfaces and cross sections of membrane before and after imprinted polymerization. Seen from it, support PVDF membranes (Fig1. A, B) are completely covered by a polymer layer after surface polymerization (Fig1. C, D). The surface of modified membranes appears crosslinked network and the thickness increases, which indicated a polymer layer has anchored the surface of PVDF membranes successfully.

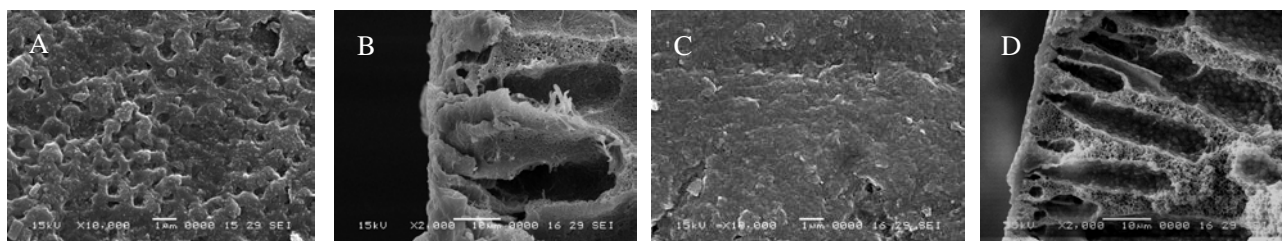


Fig.1 SEM images of PVDF membrane (A, B) and MIMs (C, D)

3.2 ATR-FTIR spectra of membranes. Fig.2 shows the ATR-FTIR spectra of support membrane and extracted MIMs. In Fig. 2a, the absorption peaks of 1,408, 1,043, 878 and 835 cm^{-1} are the typical absorption peaks of PVDF. The peak at 2,930 cm^{-1} are corresponding to dissymmetry stretching vibration of $-\text{CH}_2-$. Seen from Fig. 2b, the absorption peak 1,722 cm^{-1} should correspond to absorption bands of $-\text{C}=\text{O}$ stretching vibration. It is concluded that the surface of the support PVDF membrane has appeared imprinted polymer layer.

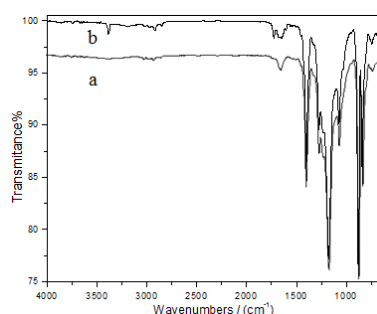


Fig.2 ATR-FTIR spectrograms of PVDF membrane (a) and MIMs (b)

3.3 Parameters of membranes. Pure water flux measurements (L_p , at 1bar and 25°C) and swelling changes in methanol of PVDF membranes, MIMs and NIMs are listed in Table 1. The results shows that surface polymerization causes a decreasing water permeability due to the block of some cavities. At the same time, the decreasing L_p of NIMs than MIMs can be due to the formation of new cavities after removal of the template. A higher S_r of MIMs and NIMs than PVDF membrane indicated the polymer layers are infinite to methanol. Often unreacted double bonds remains in the polymer will

lead to the change of pore volume, surface areas, and swelling properties [7]. It is clear that surface polymerization has a significant effect on the performance of the membranes and there remain many unreacted double bonds under the experiment conditions in this study.

Table1 Changes in character of membrane after and before surface polymerization

Sample	L_p (L/m ² · h · bar)	Sr in methanol
PVDF membrane	12.00	0.4556
MIMs	6.14	0.7764
NIMs	3.87	0.6044

3.4 Membrane adsorption binding studies. The binding capacity of PVDF membranes, MIMs and NIMs to levofloxacin and ofloxacin was evaluated. Seen from Table2, MIMs and NIMs have a higher binding capacity compared to the support PVDF membranes, which shows both imprinting polymerization and swelling play the roles on recognition. Active polymer layer contained imprinted recognition sites and channel after swelling attributed to the sorption of levofloxacin. Owing to ofloxacin is racemic mixture, MIMs also has the adsorption to ofloxacin, specific separation factor $\alpha_{\text{Levofloxacin/ofloxacin}}$ is 1.27.

Table2. The results for levofloxacin and ofloxacin binding to the initial and modified membranes

Sample	$C_{\text{Levofloxacin}}/\text{mmol} \cdot \text{L}^{-1}$	$C_{\text{ofloxacin}}/\text{mmol} \cdot \text{L}^{-1}$
PVDF membrane	0.0009	0.0012
MIMs	0.0202	0.0156
NIMs	0.0056	0.0041
Specific adsorption	0.0146	0.0115

4. Conclusions

In this study, levofloxacin-imprinted composite membranes by thermal initiation copolymerization are developed on PVDF hollow fiber membranes. Imprinting polymerization results in the change of morphologies, water flux, swelling ratio and binding capacity of the prepared membranes. Both imprinting polymerization and swelling play the roles on recognition. When polymerization recipe contains levofloxacin, MAA, TMPTA (at a molar ratio of 1:4:15) and chloroform as solvent, the highest separation factor of about 1.27 was achieved. Optimized experiment process may decrease swelling and increase specific binding capacity. This approach for MIMs preparation and swelling analysis offers a foundation to levofloxacin and other chiral drug separation.

5. Acknowledgements

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