

Preparation of Evodiamine Molecularly Imprinted Composite Membrane by Sol-gel Method

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Abstract

The porous polysulfone membrane was used as the support body, and a molecularly imprinted polymer composite layer with evodiamine as the template molecule was coated on the surface of the polysulfone membrane by sol-gel method. It was found that the blending solution of methanol solution and tetrahydrofuran solution with a volume ratio of 5:1 as the solvent could satisfy the process conditions of sol-gel imprinting reaction without affecting the structure of polysulfone membrane. Infrared testing of the composite membrane and the molecularly imprinted polymer powder proved that the imprinted polymer could be attached to the supporting membrane. Then the surface morphology and structure of the prepared molecularly imprinted composite membrane were characterized by a scanning electron microscope. It can be clearly observed that the surface of the supporting membrane was covered by a layer of sol-gel molecularly imprinted polymer. The flux of evodiamine molecularly imprinted composite membrane was measured at 0.4 MPa at room temperature, and it was found that the flux reached $19.80 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$.

Keywords

Evodiamine; Molecularly Imprinted Composite Film; Sol-gel Method; Polysulfone Membrane.

1. Introduction

The preparation of molecularly imprinted composite film by sol-gel molecular imprinting technology involves introducing template molecules into the inorganic sol-gel network structure by sol-gel method [1], and then forming a layer of sol-gel imprinted polymer film on the surface of the base film with porous structure through imprinting polymerization. It combines molecular Imprinting Technology (MIT), sol-gel process, and membrane separation technology [2]. The template molecular elution is embedded in the polymer on the imprinted composite membrane through a covalent bond, non-covalent bond, hydrogen bond, and other functions, so that the composite membrane has a three-dimensional spatial structure to recognize the template molecular imprinting site, and the imprinted composite membrane can specifically recognize and adsorb template molecules through the spatial imprinting recognition site. At present, molecularly imprinted composite membranes have been widely applied in separation technology, bionic modeling, food detection, drug extraction, and other fields [3-6].

As a template molecule, evodiamine has one hydrogen bond donor and two hydrogen bond receptors, which provides a powerful condition for it to bind with functional monomer APTES through hydrogen bond and introduce the sol-gel inorganic network to generate evodiamine

molecular-imprinted polymer and attach it to the polysulfone membrane. Infrared and scanning electron microscopy were used to characterize whether the sol-gel molecular-imprinted polymer of evodiamine could attach to the polysulfone membrane and compare the membrane flux between the base membrane and the imprinted composite membrane.

2. Experimental

2.1. Reagents and Equipment

Reagents: evodiamine ($\geq 98\%$, Shanghai McLean Biochemical Technology Co., LTD.); Tetrahydrofuran (THF) (Analytical pure, Tianjin East Tianzheng Fine Chemical Reagent Factory); 3-aminopropyl triethoxysilane (APTES) (99%, Shanghai McLean Biochemical Technology Co., LTD.); Ethyl orthosilicate (TEOS) ($> 99\%$, Shanghai McLean Biochemical Technology Co., LTD.); Ammonia (25%, Tianjin Yongda Chemical Reagent Co., LTD.); Methanol (analytical pure, Tianjin Yongda Chemical Reagent Co., LTD.); Acetic acid (glacial acetic acid) (Analysis pure, Tianjin Yongda Chemical Reagent Co., LTD.); Dimethylacetamide (DMAc) (analytical pure, Tianjin Yongda Chemical Reagent Co., LTD.); Polysulfone (PSF) solid small particles (Tangshan Haiqingyuan Technology Co., LTD.); Polyvinylpyrrolidone (PVP) (K30, Tianjin Guangfu Fine Chemical Research Institute).

Equipment: VERTEX70 total reflection Fourier transform infrared spectrometer, manufactured by Bruker, Germany; S-4800 Field emission scanning electron microscope, manufactured by Hitachi Instruments, Japan; JA203P electronic balance manufactured by Changzhou Lucky Electronic Equipment Co., LTD. DZF-6020 electric vacuum drying oven, Tianjin Tianyu Experimental Instrument Co., LTD. HH-1 digital display constant temperature water bath, Changzhou Dunhuang Machinery Manufacturing Co., LTD. JJ-1 precision force enhancing electric stirrer is made by Jintan Baita Xinbao Instrument Factory.

2.2. Preparation of Molecularly Imprinted Membranes

2.2.1. Preparation of PSF Substrate Membrane

Weigh 30ml of dimethylacetamide (DMAc) solution (80% of the total mass) with a measuring cylinder into a beaker and weigh the DMAc solution with an electronic balance to calculate the total mass of the required raw materials. Then 5.6g of polysulfone (PSF) particles (16% of the total mass) and 1.4g of polyvinylpyrrolidone (PVP) (4% of the total mass) were weighed. The weighted DMAc solution was poured into the three-mouth flask and stirred under the water bath heating condition of 65°C . During the stirring process, the polysulfone particles and polyvinylpyrrolidone (PVP) were added to the solution of the three-mouth flask. After all the solid raw materials were dissolved in the solution, the casting solution was obtained by standing deaeration. Then the casting solution was transformed into a membrane by the phase transformation method, and the polysulfone membrane was obtained.

2.2.2. Preparation of Evodiamine Molecularly Imprinted Composite Membrane

A certain amount of evodiamine was added to 30ml methanol-tetrahydrofuran (V: V, 5:1) in the blend solution, stir until the evodiamine is completely dissolved, add 0.3ml of 3-aminopropyl triethoxysilane (APTES), and stir for 30min to make the template molecules fully react with the monomer molecules, then add 1.2ml of crosslinking agent TEOS and stir for 15min to make it evenly dispersed in the solution. You get a prepolymer solution. The polysulfone membrane was immersed in the above solution and stirred for 15min, and about 0.3ml ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$) was added to stir to trigger the molecular-imprinted polymerization of sol-gel. After stirring at room temperature for 6h, the membrane was removed and rinsed with methanol several times. The unattached imprinted polymer was removed and dried. Then the template molecules were eluted with methanol-acetic acid (9:1, volume ratio) mixture, and the polysulfone - evodiamine molecularly imprinted composite membrane (MICM) was obtained.

after drying in air. The blank imprinted composite membrane (NICM) was prepared by the same method (excluding evodiamine template molecules) and compared with the molecular imprinted composite membrane.

3. Results and Discussion

3.1. Preparation of Evodiamine Molecularly Imprinted Composite Membrane by Sol-gel Method

The formation mechanism of evodiamine molecularly imprinted composite membrane prepared by sol-gel method is shown in Figure 1. The template molecules evodiamine with APTES and TEOS evenly dispersed methanol - tetrahydrofuran mixture gets a molecularly imprinted polymer fluid, then add the ammonia sol-gel molecularly imprinted effect, in the ability to identify the nonspecific adsorption of the polysulfone membrane surface further polymerization reaction was a thin layer of sol-gel molecularly imprinted polymer membranes. After the completion of sol-gel imprinted polymerization, the membrane was removed and washed with methanol solution several times to remove the non-attached sol-gel imprinted polymer on the membrane.

After the eluent removed the template molecule evodiamine, the functional size of the template molecule evodiamine was retained in the molecularly imprinted composite membrane. There is a unique interaction between the membrane and the template molecule evodiamine. Through this unique interaction, when the imprinted composite membrane is applied to separate the template molecule evodiamine in the complex system, the composite membrane can specifically recognize the template molecule evodiamine, thus effectively separating the template molecule evodiamine from other substances in the complex system.

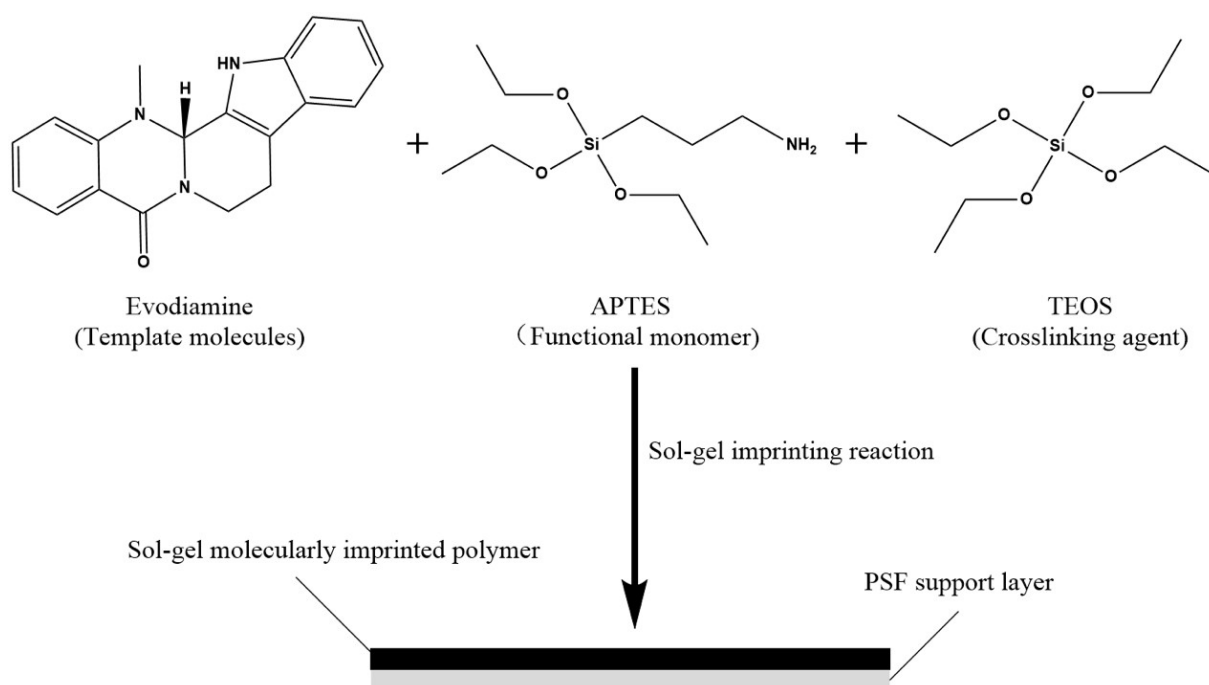
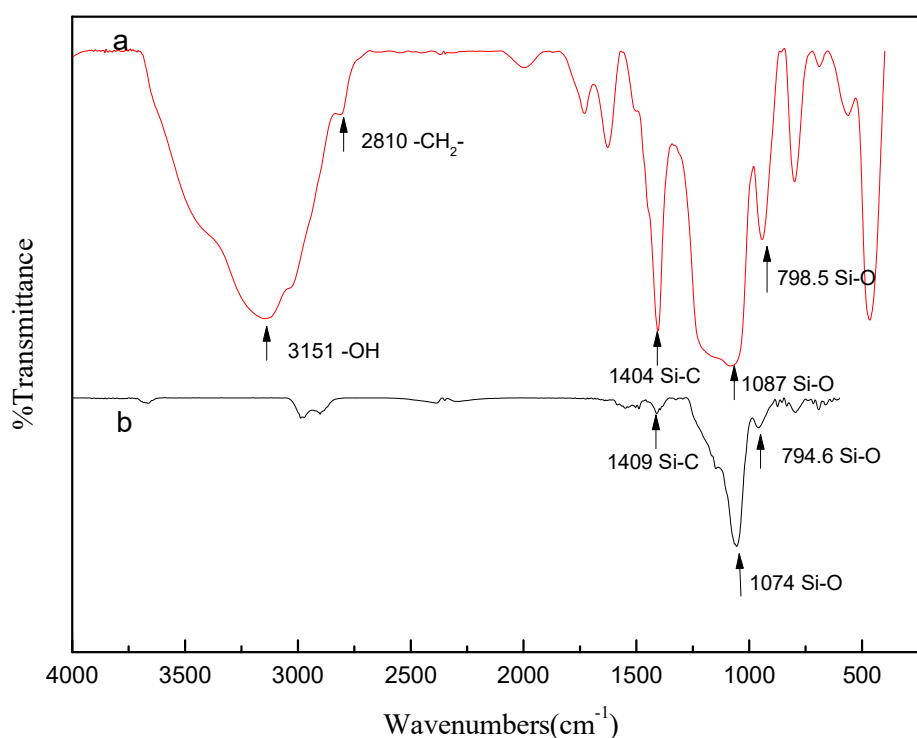


Figure 1. Film formation mechanism of evodiamine molecularly imprinted composite membrane

3.2. Infrared Characterization Analysis

To confirm that sol-gel molecularly imprinted polymers can successfully adhere to the surface of polysulfone (PSF) substrates, the infrared characteristic curves of a-- Sol-gel molecularly imprinted polymer powders and b--PSF- Evodiamine molecularly imprinted composite films

were compared and analyzed. It can be found that the asymmetric and symmetrical vibration infrared characteristic absorption peaks of Si-O appear at 1087cm⁻¹ and 798.5cm⁻¹ on the imprinted polymer, and the infrared characteristic absorption peaks of Si-C appear at 1404cm⁻¹. After the imprinted polymer is attached to the film, the characteristic peaks of Si-O transfer to 1074cm⁻¹ and 794.6cm⁻¹, and the characteristic peaks of Si-C transfer to 1409cm⁻¹ [7]. In addition, it was found that the -OH infrared characteristic absorption peaks detected at 3151cm⁻¹ on sol-gel molecularly imprinted polymer powders disappeared after the formation of molecularly imprinted composite membranes. The change of IR spectra indicates that when the PSF- molecularly imprinted composite membrane was formed, the PSF base membrane and the sol-gel molecularly imprinted polymer were polymerized so that the sol-gel molecularly imprinted polymer adhered to the surface of the basement membrane.



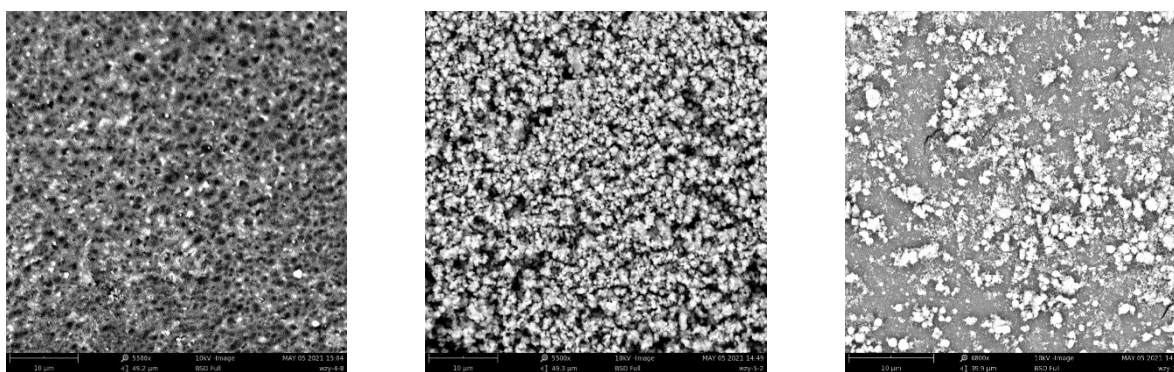
a -- Sol-gel molecularly imprinted polymer powder; b --PSF- evodiamine molecularly imprinted composite membrane

Figure 2. Infrared spectrum

3.3. Characterization of Membrane Surface Morphology and Structure

The polysulfone (PSF) base membrane is immersed in the prepolymerization solution, and then an initiator is added to initiate the sol-gel imprinting polymerization reaction. The pores and surface of the PSF base membrane will undergo polymerization to produce self-assembled polymers. After the reaction occurs and the template molecule evodiamine is eluted with the eluent, a sol-gel molecularly imprinted polymer film will be formed on the base membrane. Observing the prepared sol-gel molecularly imprinted composite film with the naked eye, the resulting film has a smoother surface than the base film, and there is no significant difference in color and morphology. However, the adhesion can be found by observing with a scanning electron microscope. The surface of the completely molecularly imprinted membrane is quite different from the surface of the PSF base membrane with no polymer attached and the blank

imprinted membrane. It can be seen from Figure 3 that the base membrane with no polymer attached (a) Although a certain amount of material has been attached to the surface, the reaction is not complete due to insufficient reaction time or slow stirring speed, resulting in a low degree of cross-linking of the polymer, so the porous structure of the PSF base film can still be clearly visible. But when the polymerization reaction is more complete, we can see that the surface of the evodiamine base molecularly imprinted composite membrane (b) can no longer find the porous structure of the PSF base membrane, but instead is a molecularly imprinted polymer membrane layer with voids. While the blank imprinted composite membrane (c) has no template molecule added, the functional monomer APTES and the cross-linking agent TEOS in the solution will directly polymerize in the pores of the base membrane and the surface of the PSF base membrane after initiation, resulting in a porous structure. It is blocked by the polymer to form a blank imprinted film layer, and at the same time, there will be some blank imprinted polymers with uneven dispersion on the surface. This shows that the sol-gel imprinting polymerization reaction has indeed occurred on the surface and inside of the PSF base film, and a layer of the molecularly imprinted polymer film is formed on the surface of the PSF base film.



(a) PSF based membrane surface with incomplete polymer attachment (b) Evodiamine molecularly imprinted composite membrane (MICM) surface (c) blank imprinted composite membrane (NICM) surface

Figure 3. scanning electron microscope

3.4. Membrane Flux Test

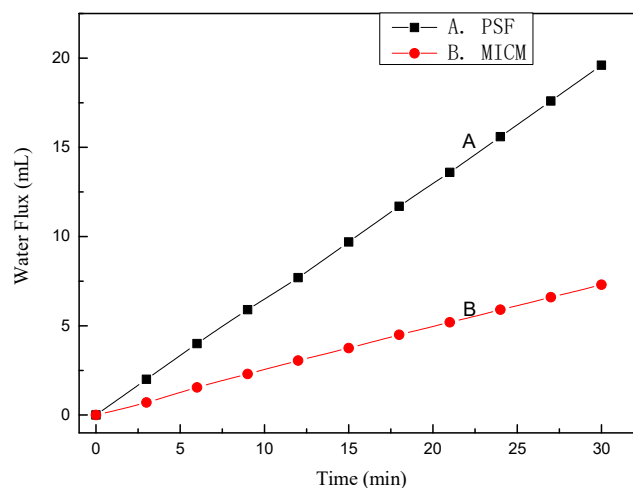


Figure 4. Comparison of polysulfone membrane and evodiamine molecularly imprinted composite membrane (MICM)

The polysulfone-based membrane prepared from the same batch and the same phase inversion and the evodiamine molecularly imprinted composite membrane (MICM) prepared by the sol-gel molecular imprinting technology were selected for membrane flux testing. The test was performed under 0.4MPa at room temperature. After the instrument was stabilized, the volume of deionized water that passed through the membrane was recorded every 3 minutes. The polysulfone base membrane and the evodiamine molecularly imprinted composite membrane (MICM) were tested respectively, and the results were as follows Shown in Figure 4.

According to the data measured in Figure 4, the membrane flux of polysulfone membrane and evodiamine molecularly imprinted composite membrane (MICM) was calculated, and the results were shown in Table 1.

Table 1. Membrane flux between PSF base membrane and MICM

Membrane	Flux /($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)
PSF	56.59
MICM	19.80

As can be seen from Figure 4 and Table 1, the membrane flux of the PSF base membrane is relatively large, while that of evodiamine molecularly imprinted composite membrane (MICM) is relatively small. Evodiamine molecularly imprinted composite membrane (MICM) compared with PSF membrane, the surface of a layer of sol-gel molecularly imprinted polymer composite membrane layer, make the film thicker. At the same time in the film hole occurred the sol-gel reaction, the polymer gap becomes smaller. Due to the mass transfer resistance of the film hole, membrane flux is smaller. Although the flux of evodiamine molecularly imprinted composite membrane is much smaller than that of PSF base membrane, its mechanical properties will be greatly improved because the molecularly imprinted composite membrane takes the base membrane as the support. At the same time, the mass transfer resistance of evodiamine molecularly imprinted composite membrane (MICM) is larger, so that the imprinted membrane can be used under more complex and severe conditions.

4. Conclusion

Using polysulfone (PSF) membrane as the supporting substrate membrane and evodiamine as the template molecule, the molecularly imprinted polymer of evodiamine was attached to the PSF substrate membrane by sol-gel method to prepare the evodiamine molecularly imprinted composite membrane. By infrared and scanning electron microscopy, it was proved that the imprinted polymer could be attached to the base membrane to obtain the imprinted composite membrane. The membrane flux was measured at 0.4MPa at room temperature, and it was found that the membrane flux of evodiamine molecularly imprinted composite membrane was $19.80 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$.

Acknowledgments

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