Preparation of Polyvinylidene Fluoride Membrane with Functional Anthraquinones for Nitrogen Removal

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Abstract. This study relates to a method for preparation of polyvinylidene fluoride membrane with functional anthraquinones. The method is carried out according to the following steps: step 1: preparing 2- (1- hydroxy -3- butene) -1,4,5,8- tetramethoxynaphthalene; step2: preparing polyvinylidene fluoride-aromatic ether copolymers: polyvinylidene fluoride was used as the initiator, 2-(1-hydroxy-3-butene) -1,4,5,8-tetramethoxynaphthalene was the monomer, N, N-dimethylformamide was solvent, cuprous chloride / Me6TREN was the catalytic, polyvinylidene fluoride-aromatic ether copolymer was synthesized by atomic transfer radical polymerization; step3: reducing the polyvinylidene fluoride-aromatic ether copolymer to quinone by demethoxy oxidation; step4: using the product of step3 and N, N-dimethylformamide as film-forming reagents, then scraping into a membrane. These functional membranes can effectively solve the problem of fixation of redox mediator and improve the efficiency of treatment of wastewater with high nitrogen concentration.

1. Introduction
Polyvinylidene fluoride(PVDF), because of its high mechanical strength, good chemical stability, good halogen resisting, excellent resistance to acid, alkali, oxidizing agents and anti-UV properties, has been widely used as raw materials for preparing the membrane material in the Environmental engineering. However, the disadvantages of high surface hydrophobicity and low surface energy of polyvinylidene fluoride would influence the service life of the membrane material. In order to further optimize the performance of polyvinylidene fluoride membrane, the researchers conducted a series of studies[1-4]. Such as blending and grafting, these method enable the functionalization of the polyvinylidene fluoride membrane, and the resulting membrane has good hydrophilicity and antifouling ability. Those researches have instructive significance to optimize the membrane performance and prolong the service life of the membrane, but their application principle is still based on physical separation, that is, the transfer and enrichment of pollutants, does not realize the degradation of pollutants, there is still possible harm to the environment. Therefore, it is of great significance to study and develop a membrane that can purify sewage and degrade pollutants [5-8].

The high concentration of nitrogen-containing domestic sewage, industrial wastewater and farmland surface water runoff into the lake, reservoir, river and bay waters, then cause some of the...
algae in the water to reproduce, and seriously deteriorate water quality, damage the ecological balance of water. Biological method is the most common method to solve the above-mentioned problem of water pollution, but it is limited by the electron transport rate in the process of biological denitrification, the effect of biological treatment is unstable and the treatment efficiency is low. It has been found that the redox mediator can accelerate the electron transport rate in the process of biological denitrification and improve the efficiency of biological treatment. Anthraquinone was one kind of redox mediators, there were many researches which have confirmed that anthraquinone compounds can effectively promote the degradation of nitrogenous waste water. There were many reports that anthraquinones were put into use directly, which would cause the loss of anthraquinones and bring about the secondary pollution. In order to solve the above problems, the researchers carried out a series of studies to avoid the loss of anthraquinones. Zhiyuan MA et al.[9] have found that 1,5-dichloroanthraquinone which was immobilized in calcium alginate could promote the decolorization of acid red B, but it was only bound by the physical force on the carrier, easy to fall off from the carrier. Jing LIAN et al.[10] discovered a method for the fixation of anthraquinone sulfonate by using cyclic voltammetry. The result showed that the immobilized anthraquinone sulfonate can accelerate the process of nitrite biodegradation. However, the method of cyclic voltammetry for fixing anthraquinone sulfonate was very complex as it was controlled by the preparation of polypyrrole membrane, which was affected by a variety of factors. Therefore, if the redox mediator is fixed on the membrane, it can effectively solve the problem of fixation of redox mediator and improve the efficiency of treatment of wastewater with high nitrogen concentration.

2. Experimental

2.1 Materials

PVDF powder (intrinsic viscosity = 1.11 dL/g, Mn = 431,000 g/mol, density = 1.77 g/cm³) was bought from Shanghai 3F New Materials Co., China. N, N-dimethylformamide (DMF, reagent grade) was used as the solvent from Shanghai SSS Regent Co., China. (1-hydroxy-3-buten)-1,4,5,8-tetramethoxynaphthalene, cuprous chloride, Me6TREN were from Sinopharm Chemical Regent Co., China. All materials were used without further purification.

2.2 Membrane Preparation

Step1: preparing 2-(1-hydroxy-3-buten)-1,4,5,8-tetramethoxynaphthalene;

Step2: preparing polyvinylidene fluoride-aromatic ether copolymers: polyvinylidene fluoride was used as the initiator, 2-(1-hydroxy-3-buten)-1,4,5,8-tetramethoxynaphthalene was the monomer, N, N-dimethylformamide was solvent, cuprous chloride / Me6TREN was the catalytic, polyvinylidene fluoride-aromatic ether copolymer was synthesized by atomic transfer radical polymerization;

Step3: reducing the polyvinylidene fluoride-aromatic ether copolymer to quinone by demethoxy oxidation;

Step4: using the product of step3 and N, N-dimethylformamide as film-forming reagents, then scraping into a membrane.

3. Results and Discussion

3.1 Preparing 2-(1-hydroxy-3-buten)-1,4,5,8-tetramethoxynaphthalene

3.1.1 Preparing 1,4,5,8-tetramethoxynaphthalene. Adding naphthazarin, tetramethylammonium bromide and tetrahydrofuran to a round bottom flask, stirring to dissolve, then adding sodium dithionite aqueous solution and dimethyl sulfate solution, stirring evenly; then moving the round bottom flask to ice water bath, reacting for 1 h, then slowly dropping NaOH aqueous solution into the flask. After the drop adding, removing the ice bath, continue to react at room temperature for 30 min, and stirring continuously for 18 h until the reaction was complete. Then extracting the reaction
solution with ethyl acetate, washing with saturated brine, drying by anhydrous magnesium sulfate, filtering, and recovering of ethyl acetate under reduced pressure. Finally, separating the solids by column chromatography to obtain the 1,4,5,8-tetramethoxynaphthalene; \( ^1\)H NMR (400 MHz, DMSO): \( \delta \) 6.44 (d, 4 H), 3.37 (s, 12 H, CH₃).

The mass ratio of naphthazarin, tetrahydrofuran, sodium dithionite, dimethyl sulfate and sodium hydroxide is 1.5:75:55:110:125;

3.1.2. Preparing 1,4,5,8-tetramethoxynaphthalene-2-carboxaldehyde. Adding N, N-2-methylacetamide to the 2 mouth flask, removing the flask in an ice-water bath, slowly dropping phosphorus oxychloride and 0.063 mol/L 1,4,5,8-tetramethoxynaphthalene in chloroform solution, After the drop adding, removing the ice bath, heating and refluxing reaction for 5 h; then adding ice water to stop the reaction, extracting by chloroform, saturated brine washing, anhydrous magnesium sulfate drying, then filtering, and negative pressure recovery of chloroform, separating by column chromatography; \( ^1\)H NMR (400 MHz, DMSO): \( \delta \) 6.49-6.51 (m, 3 H), 3.40 (s, 9 H, CH₃), 3.43 (s, 3 H, CH₃), 10.11 (s, 1H, CHO).

The volume ratio of N, N-2-methylacetamide, phosphorus oxychloride, 1,4,5,8-tetramethoxynaphthalene in chloroform is 2.5:3:15.

3.1.3. Preparing 2-(1-hydroxy-3-buten) -1,4,5,8-tetramethoxynaphthalene. The schematic diagram of preparing of 2-(1-hydroxy-3-buten) -1,4,5,8-tetramethoxynaphthalene is shown in Figure 1.

![Figure 1. Schematic Diagram of Preparing of 2-(1-hydroxy-3-buten) -1,4,5,8-tetramethoxynaphthalene](image)

Under the protection of argon, adding molecular sieve, anhydrous tetrahydrofuran, anhydrous chromium trichloride and manganese powder in turn in the dry 2 mouth flask, stirring until the color becomes black, then adding allyl bromide, adding 1,4,5,8-tetramethoxynaphthalene-2-carbaldehyde and trimethylchlorosilane, reacting for 3 h, adding sodium bicarbonate to stop the reaction, washing with diatomite and ether, extracting by ether, saturated brine washing, anhydrous magnesium sulfate drying, and negative pressure recovery of the concentrated residue, dissolving in tetrahydrofuran, and hydrolyzing with 10% hydrochloric acid, stirring at room temperature for 10 min, extracting with ether, washing with saturated brine, anhydrous magnesium sulfate drying and concentrating under reduced pressure, then separating by column chromatography; \( ^1\)H NMR (400 MHz, DMSO): \( \delta \) 6.47-6.51 (m, 3H), 3.37 (s, 9H, CH₃), 3.43 (s, 3H, CH₃), 8.45 (s, 1H, OH), 4.83 (t, 1H, CH), 2.39 (m, 2H, CH₂), 4.92 (d, 2H, CH₂), 5.76 (m, 1H, CH).

The mass ratio of anhydrous tetrahydrofuran, anhydrous chromium trichloride, 1,4,5,8-tetramethoxynaphthalene-2-carbaldehyde, trimethylchlorosilane, allyl bromide, manganese powder is 20:20:50:60:50:70.
3.2. Preparing polyvinylidene fluoride-aromatic ether copolymers

Adding polyvinylidene fluoride and N, N-dimethylformamide to double glass reactor, stirring evenly, then adding Me6TREN and 2-(1-hydroxy-3-buten)-1,4,5,8-tetramethoxynaphthalene, injecting argon to remove oxygen for 30 min, adding cuprous chloride, removing oxygen for 1 hour, then sealing the reactor, removing the reactor to ice-water bath, reacting 1 min under the ultraviolet irradiation in the magnetic stirring, filtering with the volume ratio of 1:1 of ethanol and water after the reaction, then extracting with chloroform several times, finally vacuum-drying to obtain the polyfluoroethylene-aromatic ether copolymer.

The mass ratio of 2-(1-hydroxy-3-buten)-1,4,5,8-tetramethoxynaphthalene, polyvinylidene fluoride, N, N-dimethylformamide, cuprous chloride / Me6TREN is 45:7:500:0.5.

The schematic diagram of preparing of polyvinylidene fluoride-aromatic ether copolymer is shown in Figure 2.

![Figure 2. Schematic Diagram of Preparing of Polyvinylidene Fluoride-aromatic Ether Copolymer](image)

3.3. Reducing the polyvinylidene fluoride-aromatic ether copolymer to quinone by demethoxy oxidation

More specifically, adding the polyvinylidene fluoride-aromatic ether copolymer of acetonitrile solution in the 2 mouth flask, adding cerium ammonium nitrate aqueous solution at room temperature with stirring, reacting for 1 hour, negative pressure recovery of acetonitrile, extracting with chloroform, washing with water, and washing with saturated brine, anhydrous magnesium sulfate drying for 1.5 hour, negative pressure recovery of chloroform, separating the solids by column chromatography to obtain the mixture of 2-(1-hydroxy-3-buten)-5,8-dimethoxy-1,4-naphthoquinone and 6-(1-hydroxy-3-buten)-5,8-dimethoxy-1,4-naphthoquinone, finally vacuum drying.

The eluent of silica column chromatography is the mixture of the petroleum ether and acetone with a volume ratio of 3:1.

3.4. Using the product of step3 and N, N-dimethylformamide as film-forming reagents, then scraping into a membrane.

The mass ratio of N, N-dimethylformamide and the product of step3 is 17:83. The sketch of double glass reactor is shown in Figure 3.
Figure 3. The Sketch of Double Glass Reactor: 1 - the place of ultraviolet light, 2 - vacuum orifice, 3 - water inlet, 4 - feed inlet, 5 - water outlet, 6 - inert port.

3.5 Nitrogen Removal Effect of the PVDF membrane modified with anthraquinones

The application of polyvinylidene fluoride membrane with functional anthraquinones in the degradation of nitrogen-containing wastewater are shown in Table 1.

Table 1. Degradation of Nitrogen with membranes

| Test items                                         | Nitrogen content | Removal rate |
|---------------------------------------------------|------------------|--------------|
| The nitrogen-containing wastewater without treatment | 200mg/L          | 0%           |
| The nitrogen-containing wastewater treated by PVDF | 56mg/L           | 72%          |
| The nitrogen-containing wastewater treated by PVDF membrane with anthraquinones | 16mg/L           | 92%          |

Figure 4. The Nitrogen Removal Effect of the Polyvinylidene Fluoride Membrane Modified with Anthraquinones

Figure 4 is the graph about the nitrogen removal effect of the polyvinylidene fluoride membrane modified with anthraquinones. The abscissa shows the times of circle application of the polyvinylidene fluoride membrane with functional anthraquinones, the ordinate shows the multiple of removal rate of nitrate. As can be seen from the graph, the ultrafiltration membrane prepared in this work has stable performance and can be recycled several times.
4. Conclusions
As pure anthraquinone compounds can not carry out the atomic radical polymerization, our work introduced the double bond of side chain into the naphthazarin by the NHK reaction, and contributed to facilitate the occurrence of the atomic transfer radical polymerization (ATRP) reaction between the polymer material and the anthraquinone. Further, the anthraquinone which fixed in the polyvinylidene fluoride membrane would not fall off.

The polyvinylidene fluoride membrane as a fixed carrier for the redox mediator can be adapted to various membrane processing apparatuses.

The membrane with functional anthraquinone can effectively promote the degradation of waste water with high concentration nitrogenous, and especially accelerate the degradation of printing and dyeing wastewater.

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