Preparation of Quinone Mediator / Polyvinylidene Fluoride Functionalized Membrane

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Abstract. In this study, the redox mediator accelerated the degradation of dyes and improved the efficiency of dye wastewater treatment by immobilizing quinone mediators on the membrane. Specifically, polyvinylidene fluoride, quinone, and lithium chloride were used as the membrane substrate, redox mediator modifier, and porogen, respectively. By changing the type of quinone, the concentration of quinone, and the concentration of crossing-linker, the effect of quinone mediator-functionalized polyvinylidene fluoride membrane on the decolorization of dye wastewater was investigated. This study has shown that the cross-linking agent could effectively improve the compatibility of the quinone mediator casting solution system, and the increase in the addition amount of quinone mediator increased the decolorization rate of the membrane. The increase of the quinone content could also improve the decolorization effect of the dye. The decolorization rate of the original membrane without adding quinone was only 36%, whereas the decolorization rate of the blend membrane reached 75%, which shows the PVDF film with immobilized quinone mediator exhibited a significant dye degradation effect.

1. Introduction

Dye wastewater has various distinct characteristics, such as high chemical oxygen demand, high organic content, high chroma, complex composition, and high toxicity. Dye wastewater treatment includes physical, chemical, and biological methods, of which biological methods are commonly used at present, especially anaerobic biological treatment methods.

Studies have demonstrated that quinone mediator substances could accelerate dye degradation and improve treatment efficiency without changing the biomass when biologically treating dye wastewater[1-4]. However, if the mediator reagent was directly added to the dye wastewater, it tended to cause secondary pollution and water poisoning, which restricts the application of mediator materials. In this study, quinone immobilized on the carrier was investigated to prevent the loss of mediators. In particular, the separation membrane is a good choice of carrier. Due to a large specific surface area and stable performance, the separation membrane has been widely used in the field of sewage treatment[5,6]. Simultaneously, it can combine the advantages of membrane bioreactors to accelerate the degradation of dye wastewater.
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-dimethylacetamide (DMAc, reagent grade) was used as the solvent from Shanghai SSS Regent Co., China. 1,8-dichloroanthraquinone, Riboflavin, Anthraquinone, Glutaraldehyde, LiCl were from Sinopharm Chemical Regent Co., China. All materials were used without further purification.

2.2. Membrane preparation
A certain mass of PVDF, LiCl, quinone mediator, and glutaraldehyde was added to the solvent DMAc. After stirring with a magnetic stirrer at 80°C for at least 4h to homogeneous, the casting solution was placed into an electrothermal constant temperature blast drying oven (80°C). The casting solution was ready for use after standing and degassing at a constant temperature (24h-72h). After poured on the glass plate, the casting solution on the glass plate was scraped into a thick uniform membrane with a 0.5mm scraper. The scraped casting solution was gently placed into water. After put in water for 3 hours, it was taken out and soaked in pure water.

2.3. Characterization of the membrane

2.3.1 Fourier infrared spectroscopy. A Vertex 70 Fourier Transform Infrared Spectrometer manufactured in German was used to record the infrared spectrum from 4000 cm⁻¹ to 400 cm⁻¹. The membranes before and after modification were analyzed with a resolution of 4 cm⁻¹.

2.3.2. Dye decolorization experiment. The standard curves of Rhodopseudomonas palustris and Congo red dye were plotted. Rhodopseudomonas palustris were cultivated in LB medium. The bacterial liquid that grew to the end of the logarithmic phase were collected and centrifuged (8000 r/min, 10 min). After removed the supernatant, the bacterial cells were transferred to the sealed serum bottle (135mL) containing inorganic salt anaerobic culture medium. The amount of inoculation was controlled so that the initial OD660 value was about 0.5. A certain concentration of carbon source, dye, and quinone mediator functionalized membrane was added into the culture medium sequentially. With the adjusted pH value and 37°C shaker (150r/min), the bacterial cells were cultivated under anaerobic conditions. At the initial timing, the concentration of the added dye was measured with an ultraviolet spectrophotometer. After one day of anaerobic incubation, the concentration of the dye was measured again to calculate the decolorization rate.

3. Results and discussion

3.1 The influence of the mediator type on the membrane-forming performance
Three redox mediators, Riboflavin, Anthraquinone, and 1,8-dichloroanthraquinone were selected as mediator modification materials and added to the casting solution (No1,2,3,4) separately. The composition of the casting solution is shown in Table 1. The casting solution and membrane formation were investigated with different redox mediators. The casting solution prepared by adding riboflavin exhibited a high viscosity. The blended membrane produced by scraping faded very seriously, indicating that Riboflavin cannot be firmly immobilized on the membrane. The membrane casting solution prepared by adding Anthraquinone crystallized readily during the dissolution process, which cannot form a homogeneous phase via dissolution. In addition, the mechanical strength of the formed membrane was very low and easy to break. 1,8-dichloroanthraquinone blended well with PVDF, forming a homogeneous casting solution system and a prepared membrane with a smooth and flat surface. Therefore, 1,8-dichloroanthraquinone was selected as the experimental object for follow-up experiments.
3.2 The influence of the amount of mediator on the membrane performance.

According to preliminary experimental results, 1,8-dichloroanthraquinone was selected as the mediator additive material, and the influence of the additional amount on the membrane performance was examined. Experimental results show that when the concentration of 1,8-dichloroanthraquinone was higher than 2.5%, the casting solution could not be completely dissolved, which is not conducive to the immobilization of quinone mediators. Therefore, the maximum concentration of 1,8-dichloroanthraquinone was set at 2.5%. The content of other compositions remained constant in the casting solution, and the concentration of 1,8-dichloroanthraquinone varied from 0.5%-2.5% (No.5,6,7,8,9). The composition of the casting solution is shown in Table 2.

### Table 1. Composition of Casting Solution

| No. | DMAC (%) | PVDF (%) | LiCl (%) | Quinone (%) |
|-----|----------|----------|----------|-------------|
| 1   | 83       | 15       | 2        | 0           |
| 2   | 82       | 15       | 2        | 1% 1,8-dichloroanthraquinone |
| 3   | 82       | 15       | 2        | 1% Riboflavin |
| 4   | 82       | 15       | 2        | 1% Anthraquinone |

### Table 2. Composition of Casting Solution

| No. | DMAC (%) | PVDF (%) | LiCl (%) | 1,8-dichloroanthraquinone (%) | Glutaraldehyde (ml/100g) |
|-----|----------|----------|----------|-----------------------------|--------------------------|
| 5   | 82.5     | 15       | 2        | 0.5                         | 3ml                      |
| 6   | 82       | 15       | 2        | 1                           | 3ml                      |
| 7   | 81.5     | 15       | 2        | 1.5                         | 3ml                      |
| 8   | 81       | 15       | 2        | 2                           | 3ml                      |
| 9   | 80.5     | 15       | 2        | 2.5                         | 3ml                      |

3.2.1 Membrane structure. The microscopic morphology of the prepared membrane was observed by SEM, as shown in Figure 1. It can be seen from the Figure that the surface of the blended membrane was rougher than that of the original membrane, forming a needle-like crystalline state (No. 2 membrane). This phenomenon could be attributed to the addition of 1,8-dichloroanthraquinone that increased the viscosity of the casting solution system, which further slowed down the phase formation rate, prolonged the growth time of PVDF nuclei, forming a crystalline morphology. As a result, the mechanical strength of the membrane was low and easy to break. The addition of glutaraldehyde can improve the compatibility of the casting solution system, thus increasing the homogeneity of the casting solution and reducing the viscosity. Although the membrane formed by the No.6 membrane had a small amount of needle-like crystals, compared with the No.2 membrane, the crystals on the membrane were significantly reduced. Moreover, the prepared membrane exhibited a more homogeneous surface, improved mechanical strength, and enhanced resistance to breaking.
3.2.2 Fourier Infrared Spectroscopy. Dry No.1 membrane and No.9 membrane were mixed with KBr separately at a ratio of 1:150 and pressed into tablets. The samples were analyzed with a Fourier transform infrared spectrometer. The results are shown in Figure 2. No.9 Membrane exhibited two more absorption peaks at 1609 cm\(^{-1}\) and 1720 cm\(^{-1}\) compared with No.1 Membrane, which are the strong quinone-based vibration peaks. This result indicated that 1,8-dichloroanthraquinone was successfully immobilized on the PVDF membrane.

![Figure 1](image1.png)  
**Figure 1.** Electron Microscope figures of Membranes(Top surface) NO.1 Membrane(original film); 2. NO.2 Membrane(1% 1,8-dichloroanthraquinone); 3. NO.6 Membrane(1% 1,8-dichloroanthraquinone +3ml glutaraldehyde)

![Figure 2](image2.png)  
**Figure 2.** Infrared spectra of NO.1 and NO.9 Membranes
3.2.3 Decolorization of dyes. The prepared redox mediator membrane was added to the dye wastewater. After 24 hours of degradation, the absorbance was measured, and the decolorization rate was calculated. The experimental results are shown in Figure 3. It can be seen from Figure 3 that as the concentration of 1,8-dichloroanthraquinone increased, the decolorization rate showed a rising trend. However, the increase was insignificant, and the decolorization rate remained in the range of 65% to 75%. For the original membrane NO.1 Membrane without adding quinone, the 24h decolorization rate was only 36.85%. It can be concluded that the addition of quinone mediators could significantly accelerate the degradation of dyes, and the reduced content could achieve significant decolorization effects.

![Decolorization Ratio of Membranes](image)

Figure 3. Decolourization Ratio of Membranes (No.1,5,6,7,8,9 and No.10,11,12,13,14)

3.3. The influence of the additional amount of glutaraldehyde on the membrane performance

According to preliminary experiments, glutaraldehyde was selected as the cross-linking agent, and the influence of the additional amount on the membrane-forming performance was examined. Experimental results showed that when the amount of cross-linking agent added was greater than 3ml, the casting solution could not be completely dissolved. Therefore, the maximum additional amount of cross-linking agent was set to 3ml. The content of other compositions in the casting solution remained constant, and the concentration of glutaraldehyde varied from 1-3ml (No.10,11,12,13,14). The composition of the casting solution is shown in Table 3.

| No. | DMAC (%) | PVDF (%) | LiCl (%) | 1,8-dichloroanthraquinone (%) | Glutaraldehyde (ml/100g) |
|-----|----------|----------|----------|-------------------------------|--------------------------|
| 10  | 80.5     | 15       | 2        | 2.5                           | 1ml                      |
| 11  | 80.5     | 15       | 2        | 2.5                           | 1.5ml                    |
| 12  | 80.5     | 15       | 2        | 2.5                           | 2ml                      |
| 13  | 80.5     | 15       | 2        | 2.5                           | 2.5ml                    |
| 14  | 80.5     | 15       | 2        | 2.5                           | 3ml                      |

3.3.1 Decolorization of dyes. The prepared redox mediator membrane was added to the dye wastewater. After 24 hours of degradation, the absorbance was measured, and the decolorization rate
was calculated. The experimental results are shown in Figure 3. It can be seen from Figure 3 that with the increase in the amount of glutaraldehyde (1-2.5ml), the decolorization rate increased steadily. This phenomenon may be due to the fact that although the content of quinone remains constant, increasing the concentration of the cross-linking agent can increase the solid loading amount of quinone and enhance the immobilization, which results in a higher decolorization rate. When the addition amount of glutaraldehyde was 3ml, the decolorization rate decreased (NO.14 Membrane), indicating that the addition amount of glutaraldehyde reached saturation. This result indicated that the 2.5ml of glutaraldehyde was the most optimal addition amount, which exhibited a decolorization rate of 75%.

4. Conclusion
In this paper, quinone was used as a mediator additive and blended with PVDF to prepare a mediator membrane. The influence of the quinone type, the content of quinone, and the content of cross-linking agent on the decolorization of dye wastewater was investigated. The following conclusions were drawn from this study.

(1) According to Fourier infrared analysis and electron microscope observation, it can be concluded that the quinone mediator material was successfully immobilized in the PVDF membrane.

(2) Among the three redox mediators, Riboflavin, Anthraquinone, and 1,8-dichloroanthraquinone, 1,8-dichloroanthraquinone was the best membrane-based immobilization material.

(3) The concentration of 1,8-dichloroanthraquinone affected the decolorization rate of the dye. The higher the concentration of 1,8-dichloroanthraquinone, the higher the decolorization rate. However, the decolorization rate generally remained in the range of 65% to 75%.

(4) The amount of cross-linking agent significantly affected the compatibility between 1,8-dichloroanthraquinone and PVDF membrane. The surface of the blend membrane with 3ml of cross-linking agent added was smoother and flatter than that of the blend membrane without a cross-linking agent. With increasing amount of glutaraldehyde (1-2.5ml), the decolorization rate exhibited a continuously increasing trend.

(5) The dye decolorization rate of the original membrane without adding quinone was only 36%, while the decolorization rate of the blend membrane reached 75%. It can be concluded that the PVDF membrane immobilized with quinone mediator significantly affected dye degradation.

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