Preparation of Activated Carbon-PVDF Blend Membrane and Its Effect on the Decolorization of Azo Dyes

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Abstract. In this article, various ratios of activated carbon and amounts of the cross-linking agent were used to prepare mediator functionalized PVDF membrane with N, N-dimethylacetamide (DMAc) as the solvent and polyvinylidene fluoride (PVDF) as the polymer. The membrane structure was characterized by an electron microscope. Moreover, the influence of the prepared membrane on the decolorization rate of the dye was investigated to optimize the addition amounts of activated carbon and the cross-linking agent. As the addition amount of cross-linking agent in the blend membrane increased, the decolorization effect continuously improved. However, the decolorization rate tended to be stable when the cross-linking agent reached a specific value. The addition of activated carbon significantly accelerated the rate of degradation and decolorization of the microbial system.

1. Introduction
Azo dyes account for 70% of the chemically synthesized dyes, which have various advantages, such as high fixation rate, optimal dyeing fastness, and bright colors. Therefore, azo dyes have been widely used in many industrial applications such as textile printing and dyeing, pharmaceuticals, food, and cosmetics. The total annual output of dyes around the world is about one million tons, and about 10%-15% of azo dyes flow directly into water bodies without treatment during the production process. The azo dye wastewater has a complex composition, poor biodegradability, high chroma, and a high level of “trigeneric (carcinogenic, teratogenic, mutagenic)” substances, which are extremely harmful to the environment and recognized as one of the difficult to treat wastewater. Previous studies have shown that the introduction of redox mediators in the biological anaerobic degradation process can reduce the difficulty of transfer between electron donors and acceptors, thereby enhancing the electron transfer rate[1-3]. As a result, the rate of oxidizing (reducing) pollutants is increased by one or even several orders of magnitude, which indirectly promotes the degradation of dyes [4-7].

Activated carbon is a natural redox mediator, which has various advantages, such as moderate pore size, large specific surface area, uniform distribution, and less impurities. In this work, a certain proportion of activated carbon and glutaraldehyde were added to the casting solution of the PVDF membrane. The activated carbon is immobilized in the PVDF membrane to afford a PVDF blend membrane with a mediator function. Furthermore, the influence of activated carbon on the decolorization of dyes was investigated.
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. Activated Carbon, Glutaraldehyde, LiCl were from Sinopharm Chemical Regent Co., China. All materials were used without further purification.

2.2 Membrane preparation

| No. | DMAC (%) | PVDF (%) | LiCl (%) | Activated Carbon (%) | Glutaraldehyde (ml) |
|-----|----------|----------|----------|----------------------|---------------------|
| a   | 83       | 15       | 2        | 0                    | 0                   |
| b   | 81.8     | 15       | 2        | 1.2                  | 0                   |
| c   | 82.6     | 15       | 2        | 0.2                  | 5                   |
| d   | 82.4     | 15       | 2        | 0.6                  | 5                   |
| e   | 82.2     | 15       | 2        | 0.8                  | 5                   |
| f   | 82       | 15       | 2        | 1                    | 5                   |
| g   | 81.8     | 15       | 2        | 1.2                  | 5                   |
| h   | 81.8     | 15       | 2        | 1.2                  | 4                   |
| i   | 81.8     | 15       | 2        | 1.2                  | 3                   |
| j   | 81.8     | 15       | 2        | 1.2                  | 2                   |
| k   | 81.8     | 15       | 2        | 1.2                  | 1                   |

A certain ratio of N, N-dimethylacetamide (DMAc), polyvinylidene fluoride (PVDF), lithium chloride, glutaraldehyde (cross-linking agent), and activated carbon powder were formulated into a casting solution (see Table 1 for the specific formula). After the solution was ultrasonically dispersed for 10 min under the effect of a 20~106 kHz mechanical wave, the conical flask containing casting solution was placed into a vacuum constant temperature oven (80°C) for standing and degassing (at least 24 hours). The conical flask was taken out and cooled to 40-60°C naturally. The casting liquid was poured on a clean and dry glass plate and was scraped off the glass plate with a spatula (500um). The detached casting solution was immediately placed in a coagulation bath (composed of deionized water) to solidify into a membrane. The coagulation bath was replaced after 3 hours.

2.3 Characterization of the membrane

2.3.1 The structure of the membrane. A field-emitting scanning electron microscope (SEM, EVO 18, ZEISS) was used to observe the micromorphology of the membrane and perform energy spectrum analysis.

2.3.2 Decolorization experiment of azo dyes. A certain area of the mediator functional membrane was added to a 250ml medium containing 200mg/L Congo red (containing microorganisms). In the meantime, a set of blank control experiments were performed. The same area of the original membrane was added to another 250ml medium containing the same concentration of dye (containing
microorganisms) at the temperature of 30°C and pH of 7. After a certain period of time, the concentration of the dye in the medium was measured, and the decolorization rate was calculated.

3. Results and discussion

3.1 The influence of the amount of cross-linking agent on the membrane performance

According to the preliminary experiment results, when the addition amount of activated carbon was greater than 1.2g, it could not be dispersed uniformly. Therefore, the added amount of activated carbon remained constant at 1.2g, and the added amount of glutaraldehyde varied in the range of 0-5ml (No.b, g, h, i, j, k). The composition of the casting solution is shown in Table 1.

3.1.1 The structure of the membrane. The microscopic morphology of the prepared membrane was observed by SEM, as shown in Figure 1. It can be seen that the pore size of the membrane surface from the casting solution with only activated carbon was larger with uneven distribution (No.b). After adding glutaraldehyde, the casting solution was significantly more uniform, and the pore size of the formed membrane surface was smaller with a more uniform structure (No.g). After ultrasonic dispersion of the casting solution (No.g) with the same composition, it can be seen that ultrasonic dispersion facilitated the uniform distribution of pore size and enhanced the mechanical strength of the prepared membrane with the same casting solution composition.

![Figure 1. Electron Microscope figures of Membranes.](image-url)
3.1.2 Energy Dispersive X-Ray Spectroscopy Analysis (EDX). From the energy spectrum analysis results in Table 2, it can be seen that the membrane with activated carbon (NO.g Membrane), the mass% of C increased from 40.46% of the original membrane to 52.85%, which is significantly more than the C content of original membrane. Because the depth of the EDX scan is deep, it indicates that the activated carbon was thoroughly mixed and immobilized in the PVDF membrane rather than attached to the surface of the membrane.

Table 2. The EDX analysis of Membranes

| Membrane                                      | Element | Mass % | At %  |
|-----------------------------------------------|---------|--------|-------|
| NO.a Membrane (original film)                 | C K     | 40.46  | 51.81 |
| NO.g Membrane (1.2% activated carbon +5ml glutaraldehyde) | C K     | 52.85  | 62.68 |
|                                               | F K     | 47.15  | 37.32 |

3.1.3 Decolorization of dyes. The membrane was cut into a size of 2cm×3cm and placed in the microbial dye system. The absorbance was measured after 24 hours to calculate the decolorization rate of different membranes. The experimental results are shown in Figure 2 below. It can be seen from Figure 2 that with the constant added amount of activated carbon at 1.2%, as the content of cross-linking agent (glutaraldehyde) increased from 1ml to 5ml (No.k, j, i, h, g), the overall decolorization rate showed an increasing trend. When the addition amount of glutaraldehyde increased to 4ml, the decolorization rate tended to be stable. This result could be due to the increase in the content of the cross-linking agent, which continuously increases the solid loading rate of activated carbon and the decolorization rate. After the addition amount increased to 4ml, the decolorization ability of the system tended to be saturated and no longer increased.

Figure 2. Decolourization Ratio of Membranes (No.g, h, i, j, k)

3.2 The effect of activated carbon addition amount on membrane-forming performance

With the addition amount of glutaraldehyde remained constant at 5ml, the addition amount of activated carbon varied from 0.2-1.2g (No.c, d, e, f, g), and the composition of the casting solution is
shown in Table 1. The 24h decolorization rates of No.c, d, e, f, g membranes were measured, respectively, and their decolorization rates were generally above 50%. In addition, with the increase of activated carbon content, there was a slight upward trend, but the change was insignificant. To further investigate the decolorization rate in the decolorization process, the water samples with 2, 4, 6, 20, and 24h decolorization time were tested to calculate their decolorization rates during the decolorization process. The data is shown in Figure 3.

![Figure 3. Decolourization Ratio of Membranes (No.a, c,g and with none membrane)](image)

It can be seen from the Figure that although the final decolorization rate of 24h was hardly different than decolorization with a short time, the decolorization efficiency was obviously different. With the increase of activated carbon content, the decolorization efficiency of No.g membrane with 1.2g activated carbon added was significantly higher than that of membranes without or less activated carbon. At a decolorization time of 6h, the original membrane No.a without activated carbon did not exhibit a decolorization effect. In contrast, the decolorization rate of No.g membrane with 1.2g activated carbon reached 25%. This result demonstrated that the blended membrane with activated carbon could promote and accelerate dyes’ degradation in the microbial system.

4. Conclusion
In this paper, blended with PVDF, activated carbon was used as a mediator additive to prepare mediator membranes. In addition, the decolorization effect of activated carbon on dye wastewater was investigated. The results indicated that the cross-linking agent should be added at the same time when the activated carbon was added. Otherwise, the apparent performance and mechanical strength of the membrane would be relatively low. At the same time, adding activated carbon and cross-linking agent reduced the pore size of the membrane. Moreover, the surface of the resulting membrane was smoother, and the membrane pores were more evenly distributed.

Increasing amount of cross-linking agent glutaraldehyde increased the decolorization rate of the system. However, it generally reached saturation at 4ml, and the increase of cross-linking agent no longer affected the decolorization effect. The addition of activated carbon significantly accelerated the decolorization efficiency, and the decolorization effect was observed at 2h, reaching 25% at 6h and 62% at 24h. Activated carbon has an adsorption effect and catalytic decolorization effect in an anaerobic biological system. However, owing to the low content of added activated carbon, the activated carbon in the blend membrane mainly catalyzes decolorization.
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