Preparation of AQS/GO/PVDF redox mediator membrane and the decolorization of azo dyes

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Abstract. AQS/PVDF and AQS/GO/PVDF redox mediator membranes were prepared with poly (vinylidene fluoride) (PVDF) as the raw supporting material of membrane, anthraquinone-2-sulfonic acid (AQS) as the redox mediator, and graphene oxide (GO) as an additive by an immersion precipitation method. The AQS content in the redox mediator membrane was optimized with the formation performance of AQS/PVDF membrane. With the optimal casting solution for AQS/PVDF membrane, GO was introduced as an additive to form AQS/GO/PVDF membrane. The effects of the redox mediator membranes on the bacterial decolorization of dye wastewaters were investigated. The results suggest that both AQS/PVDF and AQS/GO/PVDF membranes can promote the bacterial decolorization of dyes and the introduction of GO improves the decolorization rate more significantly because it can accelerate the electron transfer. Therefore, the conductivity of GO and the electron shuttle of AQS show a synergetic effect on accelerating the bacterial decolorization of dyes.

1. Introduction

With the industrial development and economic growth, ginormous amounts of wastewaters have been produced from industrial production. Dye wastewater is one of most complex and refractory wastewaters. In particular, the high chromaticity, difficult treatment, toxicity, and stable and complex structures of the synthetic dyes in wastewater [1-3] aggravate the shortage of freshwater resources in China. At present, dye wastewaters are mainly treated by biological treatment methods due to lower costs, less sludge production and more environmental friendliness, as compared with the chemical and physical methods, yet most of these biological methods show slow dye consumptions and low efficiencies [4-5].

Studies have shown that quinones can promote the electron transfers between electron donors and electron acceptors, increase the reduction/oxidation efficiencies of pollutants by one to several orders of magnitude, and accelerate the redox reaction of pollutants. However, the secondary pollution caused by the loss of mediators greatly limits its application [6]. Some conductive materials, such as activated carbon, biochar, nano-iron oxide, and graphene, especially graphene oxide (GO), can promote the direct interspecific electron transfer. In particular, they can enhance the extracellular electron transfer ability of anaerobic microorganisms, and thereby improve their anaerobic activity and reaction rate [7-8]. In this study, anthraquinone-2-sulfonic acid (AQS) and GO were immobilized on a membrane carrier as the redox mediator and additive, respectively, to form a redox mediator
membrane. The synergetic effect of the conductivity of GO and the anthraquinone electron shuttle on electron transfer utilized to promote the bacterial decolorization of dyes.

2. **Methodology**

2.1. **Materials**

Polyvinylidene fluoride (PVDF) was purchased from Shanghai Sanaifu New Materials Co., Ltd (Shanghai, China) and used as the main raw material for membrane preparation. N,N-dimethylacetamide (DMAc) and glutaraldehyde were obtained from Sinopharm Holding Co., Ltd (Beijing, China) as the solvent and crosslinking agent, respectively. Anthraquinone-2-sulfonic acid (AQS) was purchased from Aladin Holdings Group Limited (Shanghai, China) and used as the redox mediator. Graphene oxide (GO) was supplied by Suzhou Carbon Technology Co., Ltd. (Suzhou, China). All materials were used without further purification.

2.2. **Membrane preparation**

PVDF powder, AQS, GO and glutaraldehyde were added into a conical flask containing DMAc solution at a certain ratio (Table 1) and stirred at 70 ℃ for 4 h with a magnetic heating stirrer. The mixture was defoamed in a 70 ℃ oven for 24 h until no obvious powder was observed and the liquid can evenly flow. The casting solution was then cooled to room temperature and cast on a clean and dry glass plate with a 5 mm surface using a clean scraper. The glass plate was then immersed in pure water for at least 24 h to form an AQS/GO/PVDF membrane for further analyses

| No. | DMAc(%) | PVDF(%) | AQS(%) | GO(g) | Glutaraldehyde(ml) |
|-----|---------|---------|--------|-------|-------------------|
| M1  | 84.5    | 15      | 0.5    | 0     | 2.5               |
| M2  | 84      | 15      | 1      | 0     | 2.5               |
| M3  | 83      | 15      | 2      | 0     | 2.5               |
| M4  | 82      | 15      | 3      | 0     | 2.5               |
| M5  | 81      | 15      | 4      | 0     | 2.5               |
| M6  | 84.5    | 15      | 0.5    | 0.05  | 2.5               |
| M7  | 84.5    | 15      | 0.5    | 0.1   | 2.5               |
| M8  | 84.5    | 15      | 0.5    | 0.2   | 2.5               |
| M9  | 84.5    | 15      | 0.5    | 0.3   | 2.5               |
| M10 | 84.5    | 15      | 0.5    | 0.4   | 2.5               |
| M11 | 84.5    | 15      | 0.5    | 0.5   | 2.5               |

2.3. **Membrane characterization**

2.3.1. **Structural characterization.** The prepared membranes were characterized by scanning electron microscopy (SEM, TM3030 PLUS, HITACHI) for the surface and cross section morphologies. Before the SEM imaging, the sample membranes were dried, and the cross sections were obtained by breaking the membranes with liquid nitrogen. The species were then fixed on an aluminum table with a conductive double-sided adhesive and sputter-coated with a layer of gold to provide a conductive surface.

2.3.2. **Dye static adsorption.** The AQS/PVDF and AQS/GO/PVDF membranes with the same sizes were respectively immersed in 0.1 g/L azo dye solutions for the static adsorption measurements. The dye solutions were first measured for UV absorption, shaken in a shaker at the rotating speed of 130 R/min at 33 ℃. The absorptions of the solutions were further measured at the intervals of 1 h, 2 h, 3 h, 6 h, 10 h, 24 h, 30 h and 48 h respectively. The dye concentration in solution was determined from the standard curve.
2.3.3. Dye decolorization. The sterilized dye solution (100 mg/L) was inoculated with a mixed bacterial solution in the logarithmic growth phase and transferred into an anaerobic bottle. A piece of sterilized and dye saturated mediator membrane was added into the anaerobic bottle, sealed and shaken in a constant temperature oscillator of 33 °C at 150 R/min for anaerobic culture. The dye solution was sampled at the pre-set intervals. The sampled aliquots were centrifuged at 10000 r/min for 5 min, and the supernatant was measured for the absorption at the maximum absorption wavelength of the dye. The dye concentration was obtained from the standard curve and the dye decolorization rate was calculated with Eq. (1).

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  r = \left( \frac{A_0 - A_t}{A_0} \right) \times 100\% \tag{1}
\]

3. Results and discussion

3.1. Performance of AQS/PVDF membrane

Sodium anthraquinone-2-sulfonate was selected as the mediator additive material. The effects of its amount on the membrane formation and performance were investigated (Table 1).

3.1.1. Structures of AQS/PVDF membranes with different AQS contents. Fig. 1 shows the SEM images of the AQS/PVDF membranes prepared with different amounts of AQS. As can be seen, with the increase of AQS amount the morphology of the redox mediator membrane evolves from a relatively flat and smooth surface to a surface with spread cracks. It can be explained that the blend of AQS changes the porous properties of the membrane surface. AQS cannot fully integrated with PVDF at high contents. Spherical crystals are observed on the surface of membrane M2 prepared with 1% AQS, possibly because the addition of AQS redox mediator increases the viscosity of the casting solution, and thus slows down the membrane formation. The long growth time of PVDF crystals leads to the formation of spherulites. The membrane shows poor mechanical properties and is easily broken. Therefore, membrane M1 prepared with 0.5% AQS is superior to other membranes in terms of surface morphology and mechanical properties. In the following experiments, the AQS/GO/PVDF membranes were prepared with 0.5% AQS.

![Figure 1. SEM images of membranes M1-M5 prepared with amounts of AQS.](image)

3.2. Performance of AQS/GO/PVDF membranes

A series of AQS/GO/PVDF membranes were prepared with different amounts of GO and 0.5% AQS (Table 1 M6-11). It was found that GO could not be completely dissolved in the casting solution at the doses of 0.4 g and 0.5 g, suggesting that the doses are over the compatible range with casting solution containing 0.5% AQS. Therefore, membranes M10 and M11 are not further discussed.

Structures of AQS/GO/PVDF membranes with different compositions. The surface and section morphologies of membranes M6-M9 were imaged by SEM. As can be seen from Figure 2, the
surfaces of M6 and M7 AQS/GO/PVDF mediator membranes (upper row of Figure 2) are relatively flat and smooth with many uniformly distributed tiny pores, suggesting the membrane formation performance is good. This judgment is further supported by the SEM images of their cross sections (bottom row of Fig. 2). In contrast, large holes with different sizes and unevenly distributed spherical crystals are observed on the surfaces and cross-sections of membranes M8 and M9. Membrane M7 also contains holes as shown in its cross section SEM image, but the hole sizes are more uniform and most of them are evenly distributed finger holes and sponge holes. After the comprehensive consideration, M7 membrane is selected for the dye decolorization experiment.

3.3. Dye static adsorption
The dye adsorption performances of AQS/PVDF and AQS/GO/PVDF membranes were evaluated using Acid Red B and Reactive Red X-2B as the model dyes. It is found that the adsorption rates of the azo dyes on AQS/GO/PVDF membrane are higher than those on AQS/PVDF membrane. The adsorption rates of Acid Red B and Reactive Red X-3B on M7 membrane are measured to be 6.7% and 6.3%, respectively, while those on M1 membrane are 4.9% and 5.1%, respectively. In addition, as can be seen from Fig. 3, the Reactive Red X-3B and Acid Red B adsorption capacities of membrane M1 and M7 are relatively low, and the membranes tend to be saturated in 30 h. To avoid experimental errors, the subsequent dye decolorization experiments were carried out using the dye saturated membranes.

**Figure 2.** SEM images of the surfaces (upper row) and cross sections of membranes M6-M9.

**Figure 3.** Decolorization curves of Acid Red B (left) and Reactive Red X-3B (right) in the presence of the redox mediator membranes M1 and M7 prepared with 84.5% DMAc+0.5% AQS+15 %PVDF and 84.5% DMAc+0.5% AQS+15% PVDF+0.1g GO, respectively.
3.4. Dye decolorization

The effects of membranes M1 and M7 on the dye decolorization by bacteria were then investigated. The dye saturated membranes were respectively added to the Acid Red B and Reactive Red X-3B wastewaters inoculated with mixed bacteria and oscillated at 33 °C. The dye concentration change was monitored.

As can be seen from Fig. 4 (left), the Acid Red B wastewaters inoculated with the mixed bacteria of three groups are completely decolorized to be transparent in 40 h. Yet, the introduction of redox mediator membrane M7 shortens the complete decolorization to 30 h under the same condition, and redox mediator membrane M1 is able to shorten the time to 36 h. In addition, the dye decolorization rate between 5 h and 20 h in the presence of redox mediator membrane M7 is much higher than those of other two groups.

Similar effects of the redox mediator membranes are observed in the wastewater containing Reactive Red X-3B. The bacteria alone are able to decolorize the Reactive Red X-3B wastewater in 72 h (Fig. 4, right). The presences of M7 and M1 redox mediator membranes reduce the complete decolorization time to 60 h and 65 h, respectively.

These results suggest that both redox mediator membranes M1 and M7 can promote dye decolorization by bacteria, and the introduction of GO can further enhance the promoting effect of the redox mediator membrane on the bacterial dye decolorization.

4. Conclusion

AQS/PVDF and AQS/GO/PVDF redox mediator membranes were prepared by an immersion precipitation phase inversion method using AQS as the redox mediator and graphene oxide as an additive. The membrane formation performances of the casting solutions containing different amounts of AQS and GO were investigated and the effects of the mediator membranes on the bacterial decolorization of azo dye wastewater were studied. The following conclusions can be drawn.

(1) The optimal AQS/GO/PVDF membrane can be prepared with 0.5% AQS+15% PVDF+84.5% DMAc+0.1 g GO, with which Acid Red B and Reactive Red X-3B wastewaters can be completely decolorized by bacteria in 30 h and 60 h, respectively.

(2) The comparison of several gradient experiment results suggests that the blending modification of PVDF with AQS is effective, but insufficient as only a small amount of AQS can be blended into the casting solution.

(3) The AQS mediator in PVDF membrane can accelerate the bacterial decolorization of azo dyes, while introduction of GO further promote the decolorization due to their synergistic effect on accelerating electron transfer.

(4) The selection of bacteria is also very crucial to the decolorization efficiency.
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