Experimental research on the Performance of Hydrogen Peroxide-Exfoliated Titanium Diboride Supported Co^{2+} Composite Film

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Abstract: A certain amount of TiB_2 was added to deionized water and uniformly dispersed. Then, H_2O_2 was added and the mixture was continuously stirred at low temperature. After the reaction was completed, the solution was centrifuged and the precipitate was discarded. The supernatant was taken to obtain the boron-loaded titanium oxide (TiO_x@B) after the stripping process. A separate Co^{2+}/Ni^{2+} solution and solutions with different proportions of Co^{2+} were mixed with the TiO_x@B solution to load Co^{2+}. The TiO_x@B after loading was mixed with sodium alginate to prepare the casting solution. The solution was cross-linked with calcium ions to prepare the Co^{2+}/TiO_x@B-CaAlg composite membrane. The mechanical properties of the composite membrane and its catalytic degradation performance for orange-yellow G pollutants were studied.

Keywords: TiB_2; H_2O_2; Co^{2+}; Sodium alginate; Cross-linking

1. Introduction

With the increasingly serious problem of microplastic pollution, wastewater treatment plants have attracted much attention as a key node for intercepting microplastics into the natural environment [1]. This type of wastewater is complex in composition, highly toxic, difficult to degrade and hard to decolorize. How to properly treat this wastewater has become a research hotspot in the field of water treatment technology nowadays. For instance, Orange Yellow G is an anionic dye belonging to the azo group, presenting a p-aminobenzene azo compound. Among the traditional technologies used for wastewater treatment, adsorption is the most commonly adopted method to reduce the harm caused by harmful compounds, due to its short operation time, simplicity, high efficiency and wide availability of adsorbents.

In this experiment, hydrogen peroxide was used for chemical exfoliation, taking advantage of its dual functions of oxidation and gas release to achieve the effective exfoliation of titanium diboride and thereby fabricate Co^{2+}/TiO_x@B-CaAlg membranes. As a green oxidant, hydrogen peroxide is easy to operate and environmentally friendly, replacing traditional strong acid and strong base exfoliation agents and reducing environmental pollution and equipment corrosion. By adjusting the concentration of H_2O_2, reaction temperature and time, precise control can be achieved to optimize the material performance. During the hydrogen peroxide exfoliation process, hydroxyl and other functional groups are introduced on the surface of TiB_2, providing effective binding sites for the subsequent loading of metal ions.

2. Co2+/TiOx@B-CaAlg Preparation of Membranes

First, TiB_2 was treated with 30% H_2O_2. A combination of spectroscopic and microscopic investigations reveals that these Box species develop at lattice-disordered boron sites along the edges of BN particles[2]. One gram of TiB_2 was uniformly dispersed in 10 ml of deionized water. After stirring for two minutes, 10 ml of 30% H_2O_2 was added and stirred at high temperature for one hour to form a mixture. The temperature of the mixed solution rose and it turned dark green. The solution after reaction was centrifuged at 8000 r for 25 minutes. The precipitate was discarded and the supernatant was taken as the TiO_x@B solution and stored at 2-4℃.

Then, 1 g of $CoCl_2$ was dissolved in 100 mL of deionized water to prepare a 1% $CoCl_2$ solution for later use. Then, an equal volume of TiO_x@B solution, 1% $CoCl_2$ solution, and deionized water were mixed in a beaker. Subsequently, 2 wt.% of alginate sodium was slowly added and stirred magnetically for 5 hours. After settling and defoaming, a glass rod with 0.5 mm thick copper wire was used to scrape the film, and 2.5 wt.% $CaCl_2$ was used to cross-link the film. The film was named Co^{2+}/TiO_x@B-CaAlg film. Schematic diagram as shown in Figure 1.

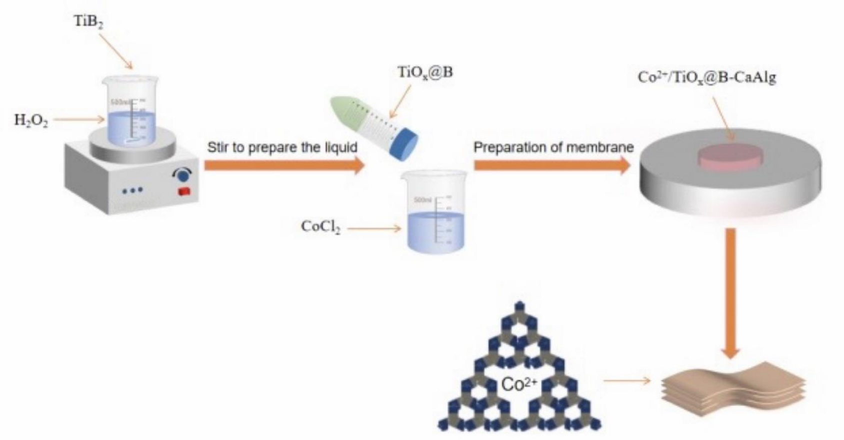

Figure 1: Schematic diagram of the preparation of Co2+/TiOx@B-CaAlg membrane.

3. Specimens Results

We investigated the performance of the Co^{2+}/TiOx@B-CaAlg membrane in catalytic degradation of pollutants using a laboratory self-assembled counter-flow filtration device. This device consists of a water pump, pipelines, pressure valves, pressure gauges, a membrane tank and a raw liquid tank.

Firstly, the cross-linked membrane is rinsed with deionized water to remove the metal ions on the membrane surface [3]. Then, the membrane is placed in a membrane chamber (with an effective filtration area of 19.63 cm^2), and a specific concentration of OG solution is added to the original liquid chamber. The pre-pressure is applied at 0.1 MPa for 30 minutes [4]. Subsequently, a specific concentration of PMS is added for the catalytic degradation experiment [5]. At regular time intervals, samples are taken from the original liquid chamber, and the absorbance is measured using a UV spectrophotometer and the experimental results are recorded. The removal rate R of the dye is calculated according to Equation (1), and the removal process of the pollutant follows the pseudo-first-order kinetic model. The reaction rate constant k can be calculated using Formula (2).

$$R = \frac{C_0 - C}{C_0} \times 100\% \tag{1}$$

$$\ln\left(\frac{C}{C_0}\right) = -kt \tag{2}$$

3.1 The Influence of Different Systems on the Catalytic Degradation Effect.

In the stock solution tank, add 200 mL of OG with a concentration of 30 ppm. Try adding only PMS; add PMS and use the Co^{2+}/TiO_x@B-CaAlg membrane, but do not use the experimental setup; use the Co^{2+}/TiO_x@B-CaAlg membrane and the experimental setup, but do not add PMS; add PMS and use the Co^{2+}/TiO_x@B-CaAlg membrane and the experimental setup simultaneously. Here, PMS is all 0.3 mmol/L.

The degradation effect varies with the system. As shown in Figure 2, when PMS is added and the Co^{2+}/TiOx@B-CaAlg membrane is used along with the experimental setup, the degradation effect is the best. The degradation rate of 30ppm OG is as high as 97.80%. However, when only PMS is used without the membrane or the experimental setup, there is almost no degradation. The degradation rate is ranked from high to low. The second and third places are respectively the group using PMS and the group using Co^{2+}/TiO_x@B-CaAlg membrane and the experimental setup. This also indicates that the catalyst PMS has an irreplaceable catalytic effect.

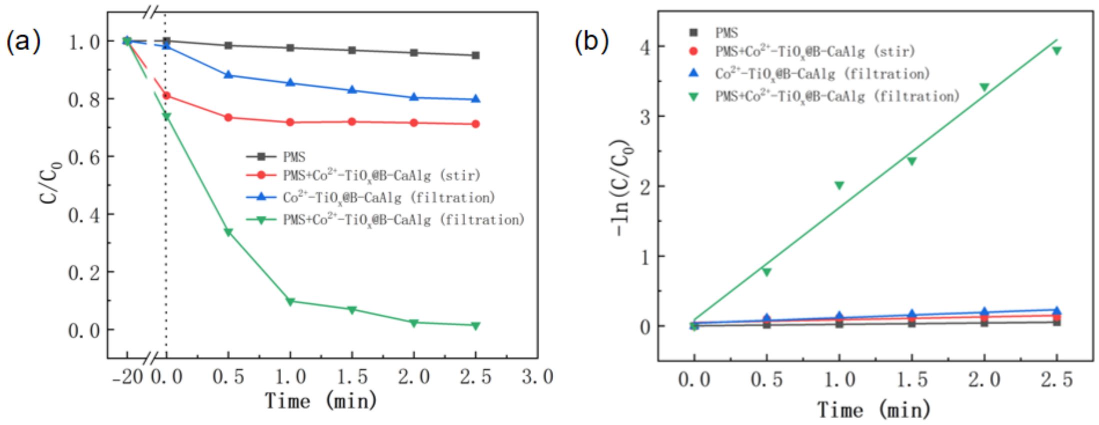

Figure 2: (a) The influence of different systems on the catalytic degradation effect and; (b) The pseudo-first-order kinetic curve.

3.2 The Influence of Different Crosslinking Times on the Catalytic Degradation Effect

To investigate the influence of different cross-linking times on the catalytic degradation effect, membranes with cross-linking times of 10 min, 30 min, 60 min, 120 min, and 300 min in $CaCl_2$ were used. The OG concentration in the original liquid tank was 30 ppm, with a volume of 200 ml. After pre-pressurization at 0.1 MPa for 30 minutes, 0.3 mmol/L PMS was added to start the catalytic experiment.

As shown in Figure 3-11, in the Co^{2+}/TiOx@B-CaAlg membrane, the loading of Co^{2+} is unstable and prone to loss. Even during the crosslinking process, a portion of Co^{2+} is easily lost through ion exchange and other pathways, and the longer the crosslinking time, the greater the loss. Considering all these factors, a crosslinking time of 10 minutes was selected for the subsequent experiments.

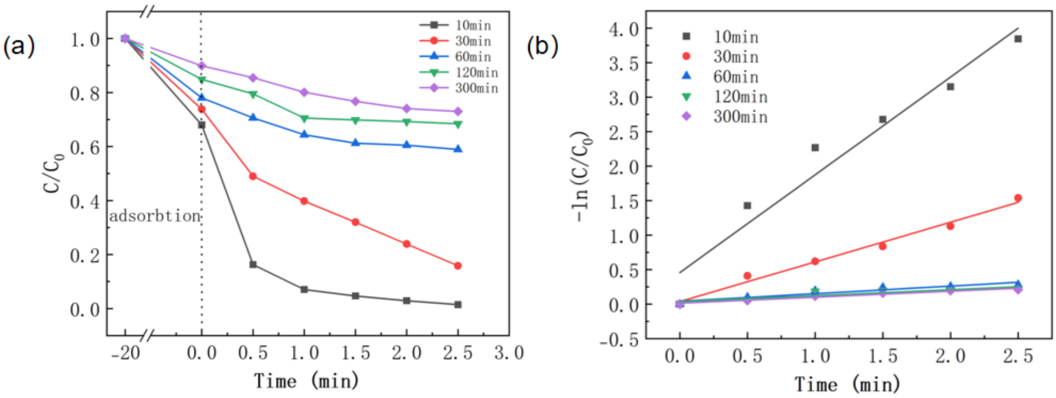

Figure 3: (a) The influence of different crosslinking times on the catalytic degradation effect and; (b) pseudo-first-order kinetic curve.

3.3 Mechanics Performance Testing

The mechanical properties of the Co^{2+}/TiOx@B-CaAlg membrane were tested using a single fiber strength tester. The membranes, which were cut into equal strips, were measured for thickness using a micrometer. The test was conducted five times and the average value was selected. Then, tensile tests were performed on each type of membrane using the strength tester, and their average values were calculated. The measurement parameters were room temperature. The initial gap of the fixture was 10 mm. The stretching rate was 10 mm/min; the fracture threshold was 80%; the linear density was 1 dtex. The stress-strain curve was plotted using formula (3).

$$\lambda = \frac{L - L_0}{L_0} \tag{3}$$

In the formula, L_0 represents the original length of the sample (in mm), and L represents the length after stretching (in mm).

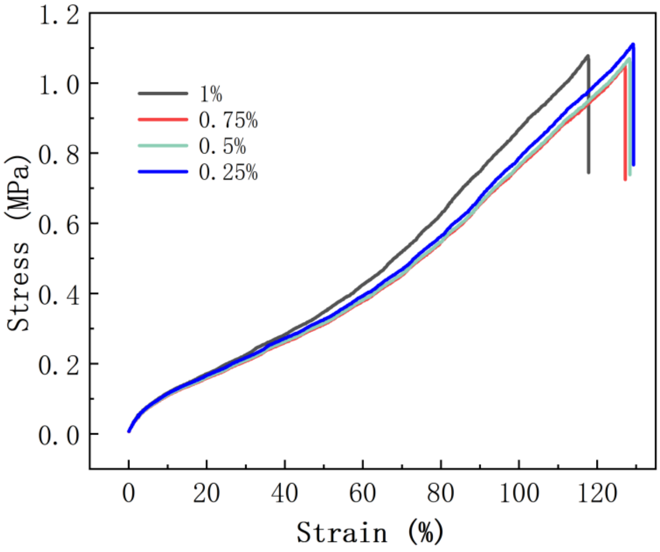

Figure 4: Stress-strain curve of the Co^{2+}/TiOx@B-CaAlg membrane.

4. Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

(1) The degradation effects vary depending on the system. The experiments were conducted

under different conditions. Through the experiments, it can be known that adding PMS and using the Co^{2+}/TiOx@B-CaAlg membrane along with the experimental set up resulted in the best degradation effect.

(2) The time of cross-linking Co^{2+}/TiOx@B-CaAlg membranes with $CaCl_2$ also has an impact on the catalytic degradation effect. Through experiments, it can be known that within a certain range, the shorter the cross-linking time, the less Co^{2+} is lost and the better the degradation effect is.

(3) Figure 4 shows the stress-strain curves of the Co^{2+}/TiOx@B-CaAlg membranes with different concentrations of Co^{2+}. From the three curves of 0.75%, 0.50%, and 0.25%, it can be seen that within a certain range, as the concentration of Co^{2+} decreases, the fracture strength of the membrane gradually increases.

5. Expectation

Through single-atom catalysis, the Co^{2+}/TiOx@B-CaAlg membrane was prepared, which has a very good catalytic effect on the degradation of organic pollutants and has made certain progress. However, there are still many shortcomings. Future research can be carried out from the following aspects:

(1) The membrane preparation method used in this paper is relatively simple. Future research will focus on multiple membrane preparation methods.

(2) Future research can explore methods to better fix single atoms on the membrane.

(3) The types of organic wastewater studied in this paper are relatively limited. In reality, the components of organic pollution wastewater are usually complex and variable, which may affect the usage effect. Future experiments can try using wastewater from actual production and life for testing.

Acknowledgments

This work was financially supported by the Tianjin University of Technology, China.

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