Glutaraldehyde functionalized modified chitosan and grafted on PVDF membrane to achieve oil-water separation

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Abstract. In recent years, there have been frequent offshore oil spills, and the discharge of industrial oily wastewater has not been properly solved, seriously affecting biological and water quality, and people's requirements for water quality are getting higher and higher, so it has become increasingly urgent to find green and efficient technologies and methods for separating oil-water mixtures. In this work, glutaraldehyde, a widely used crosslinker, is used to graft natural polysaccharide chitosan onto PVDF membrane, which greatly enhances the hydrophilicity of PVDF membrane, and the superhydrophilic superoleophobic CG-PVDF membrane prepared can be used to treat oily wastewater. The materials for preparing membranes are inexpensive, easy to obtain, and environmentally friendly, recyclable, and will not cause secondary pollution. Therefore, this green and simple membrane separation method for the treatment of oily wastewater is of great significance in sustainable development.

1.Introduction

Nowadays, the rational treatment of oily wastewater is becoming increasingly important. The traditional methods of treating oily wastewater are incineration, neutralization and fencing, but these methods are easy to cause secondary pollution to the environment, and the separation time is long and the separation efficiency is low[1]. Therefore, it is urgent to find a green, pollution-free, time-saving and efficient way to treat oily wastewater. At present, researchers have developed a variety of lipophilic and hydrophobic separation materials, but after multiple separations of this material, the oil molecules are easy to block the pores, resulting in low subsequent separation efficiency[2]. Therefore, it is necessary to develop a hydrophilic oleophobic material that is resistant to oil contamination.

Polyvinylidene fluoride is an excellent semi-crystalline polymer, which has become a common material for the manufacture of oil-water separation membranes due to its significant chemical stability, thermal stability, mechanical properties and oxidation resistance, and has broad application prospects in sewage treatment. The advantages of PVDF material make it an excellent polymer membrane material, but PVDF membrane also has defects, the main defect is that its surface energy is low, showing hydrophobicity, difficult to be wetted by water, in the process of treating oily wastewater, the water flux is extremely small. And when the polyvinylidene fluoride membrane treats the sewage water, due to the presence of many adsorptive substances in the sewage, it will adhere to the surface of the PVDF membrane and the membrane pores, causing blockage of the pores and polluting the membrane, reducing the separation efficiency and flux, which limits the wide application of PVDF membrane in the field of oil-water separation. However, the separation performance and antifouling performance of PVDF membrane can be improved by hydrophilic modification. Modification methods mainly include blending modification, hydrophilic modification and membrane surface modification, membrane surface modification is a fast and convenient method, chemical modification is more studied, mainly surface coating modification and surface grafting modification.

Chitosan is a natural polysaccharide that is widely used by researchers because of its degradability and biocompatibility, low cost and easy access[3]. Chitosan is a potential adsorbent with poor stability in water with low pH and is easily soluble, thus losing adsorption properties. Secondly, chitosan is a linear structure with low porosity and limited adsorption area, but its functionalization modification can solve these problems. According to different reaction conditions, it can be divided into two types: chemical crosslinking and physical crosslinking. Chemical crosslinking mainly forms intermolecular covalent bonds, physical crosslinking is mainly interion interaction, chemical crosslinking has higher stability and crosslinking efficiency, and is a commonly used method in chitosan modification. Glutaraldehyde is an extremely widely used crosslinking agent, through the crosslinking of glutaraldehyde can make linear chitosan molecules form a network structure through chemical bonds, which can improve the mechanical properties of chitosan[4]. In addition, polyvinylidene fluoride (PVDF) is widely used as a membrane material because of its good chemical resistance, high mechanical properties, good thermal

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stability and film formation, and low cost. However, when PVDF membranes come into contact with water molecules, it is difficult to form O-H...F hydrogen bond, so the surface is hydrophobic, causing pollutants to be adsorbed on the membrane surface and pore wall, greatly shortening the service life of the membrane[5]. In order to solve the problem of membrane susceptibility to contamination, the researchers chose to increase the hydrophilicity of the membrane.

In this study, the crosslinking agent glutaraldehyde was used to graft chitosan on the PVDF membrane, and the use of chitosan could greatly enhance the hydrophilicity of the PVDF film, but chitosan was unstable and easy to dissolve in water with low pH, so glutaraldehyde functionalization was used to modify chitosan to make it more stable grafting on PVDF membrane, and a green and durable CG-PVDF membrane was prepared to treat oily wastewater. The membrane is environmentally friendly and of great significance in the field of sustainable development

2.Experimental section

2.1. Preparation of CG-PVDF membrane

The PVDF membrane was pretreated, the PVDF membrane was soaked in ethanol and put into an ultrasonic cleaning machine for 1 minute, then soaked in deionized water. First, the pretreated PVDF film was soaked in a Five percent concentration of chitosan solution dissolved with acetic acid for 1h, so that the chitosan was fully and uniformly attached to the PVDF film, then the PVDF film was soaked in glutaraldehyde solution with a concentration of two percent, so that chitosan was firmly grafted on the PVDF film.

2.2. Characterization

Contact angle measurements are performed at ambient temperature using the JY-82 Contact Angle Meter (Chengde Prosper Co., Ltd., China).

2.3. Separation of oily wastewater

150ml deionized water was put in a beaker containing 0.3g diesel and 0.03g cetyltrimethylammonium bromide, and put it on a blender for 2 hours of stirring at 2000 rpm to obtain a stable emulsified oil. Put the prepared oil-water separation membrane into the filtration instrument, and put 15ml of emulsified oil into the filtration instrument, and started the vacuum pump to apply negative pressure to the filtration instrument. A glass tube was placed at the lower end to receive the filtered liquid. The separation efficiency is based on the formula $R=(1-c_1/c_0)\times 100\%$, where: c_0 is the oil concentration in the oil-water mixture before separation; c_1 is the concentration of oil in the filtrate after separation

3.Result and discussions

3.1. Wettability of sample

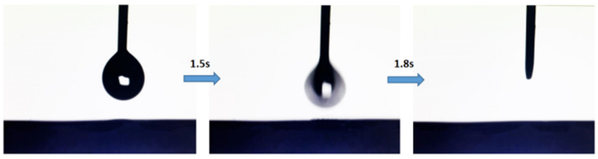

Figure 1. CG-PVDF water contact angle.

The preparation of high-performance and low-cost oil-water separation materials has gradually become a hot topic in this field, and oil-water separation materials have attracted widespread attention because of their high separation efficiency, low cost and good reusability, mainly including hydrophilic oleophobic type and lipophilic hydrophobic type. At present, lipophilic hydrophobic oil-water separation materials are the most widely studied and applied, but the material shows the following shortcomings. First of all, in the process of oil-water separation, the material is easily contaminated or even blocked by oil, so it needs to be cleaned in time to ensure a good separation rate; Secondly, because the density of most oil is smaller than that of water, gravity cannot be used to separate oil and water, and external forces are required to assist separation, and the process is complicated; Finally, the separation interface of the material is easy to form a water layer, which also hinders the collection of oil.

In summary, the research and development of a hydrophilic oleophobic material can effectively overcome the above problems, which will be of great significance to water pollution control. When the material is hydrophilic, water droplets can penetrate the surface of the material under the action of gravity. As shown in Figure 1, water droplets rapidly immerse themselves in the membrane, indicating that the membrane is superhydrophilic. When the material is oleophobic, the oil droplets will drop on the surface of the material under the action of gravity, but will not be absorbed by the material, and a certain oleophobic angle will be formed on the surface of the material, as shown in Figure 2. Since oil and water are two incompatible substances, the selective passage of materials enables the separation of oil-water mixtures quickly and efficiently. The surface wettability of the membrane was characterized by JY-82 contact angle meter (Chengde Dingsheng Co., Ltd.).

Figure 2. CG-PVDF Oleophobic angle

3.2. Tensile performance test

Tensile strength is one of the important indicators for testing the physical and mechanical properties of materials. Because the tensile strength of the material is much smaller than the compressive and shear resistance, it is often ignored by researchers during the experiment. Long-term use of materials is prone to oxidation, tensile cracks and other problems, so it is especially necessary to test the tensile strength. The tensile properties of PVDF film and CG-PVDF film were tested, and it can be seen from Figure 3 that with the addition of chitosan and glutaraldehyde, the membrane material hardens and the tensile strength doubles, consistent with the expected results. CG-PVDF film has high flexibility, and the film will not be folded, bent and rolled to destroy, which is due to the modification effect of chitosan pair effectively improves the mechanical properties of CG-PVDF film.

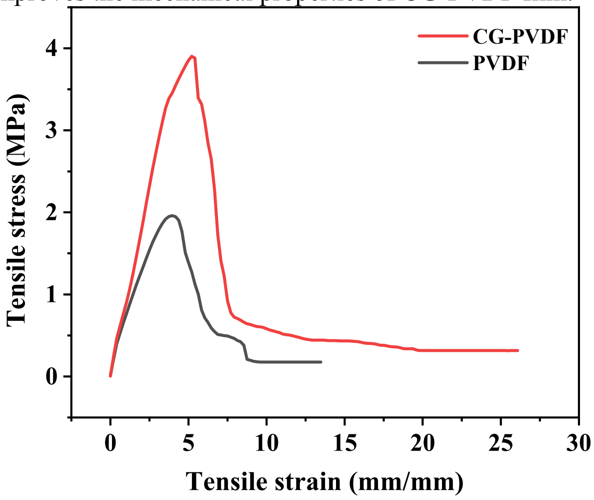

Figure 3. Tensile performance test of CG-PVDF film

3.3. Self-cleaning property of sample

Membrane separation technology has been widely used in the field of water treatment because of its low energy consumption, no phase change and strong adaptability, but the problems of membrane membrane pollution such as fouling and organic pollution are still the bottlenecks that limit its application. Therefore, self-cleaning is particularly important in the field of oil-water separation. Therefore, we verified the oil resistance and self-cleaning of the membrane under water by means of a needle injection test. The experimental method is as follows: put 200ml of deionized water in a beaker, hold the CG-PVDF membrane with tweezers and put it into a beaker containing water, dye tetrachloroethylene red with Sudan III, and then inhale 2ml of stained oil with a needle, and spray red oil droplets to the surface of the CG-PVDF membrane, as shown in Figure 4, the membrane surface is not contaminated, and the red oil droplets slide rapidly from the membrane surface, indicating that the CG-PVDF membrane shows oil resistance under water, that is, it is superoleophobic underwater. It also shows that CG-PVDF film has good self-cleaning performance. This study provides new ideas and basic exploration for the design of high-throughput and sustainable separation membranes.

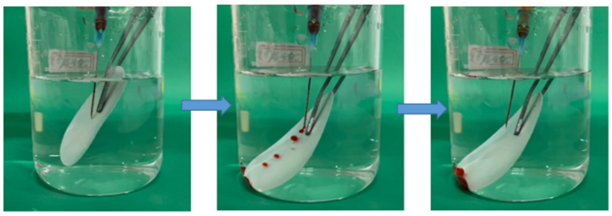

Figure 4. The self-cleaning property of SA-PVDF

3.4. Oil/water separation

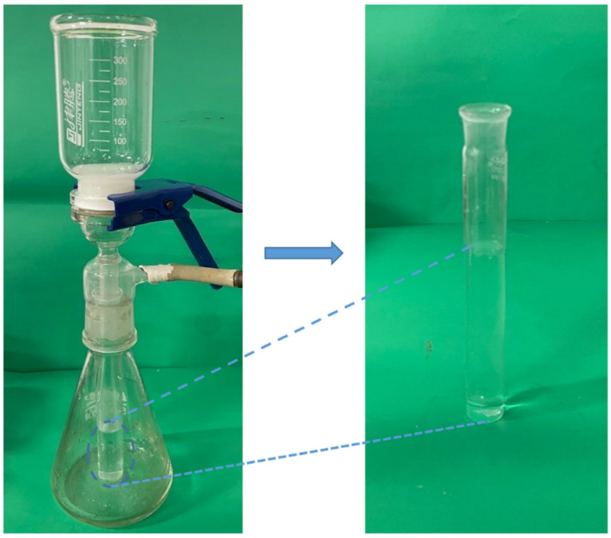

Figure 5. CG-PVDF is used to separate emulsified oil

In order to test the oil-water separation ability of CG-PVDF membrane, we tested the membrane by vacuum pressure to separate emulsified oil, and tested the separation efficiency and flux of PVDF membrane and CG-PVDF membrane. The construction of superhydrophilic/superoleophobic surfaces in air requires interfaces with higher surface free energy than water and lower than oil. Since oil generally exhibits lower surface free energy than water, hydrophilic surfaces are generally lipophilic, and fewer surfaces exhibit both wettability in air. The preparation of superhydrophilic/superoleophobic surfaces can be realized by using stimulus-responsive rearrangement of the material surface. With chitosan as the modified material, under the condition of pentylene glycol, chitosan is grafted on the PVDF film, and the PVDF film is grafted and modified, due to the addition of chitosan, the roughness of the surface of the PVDF film is enhanced, so the hydrophilic performance is enhanced, and this has no obvious effect on the pore size and distribution of the membrane. And after modification, the membrane interception of oil in the emulsified oil and the flux of water are significantly increased. When the oil content is high, the flux and separation efficiency will be significantly reduced, but after rinsing with distilled water, the CG-PVDF membrane can return to the original separation state and restore high separation efficiency and high water flux, which indicates that the CG-PVDF membrane has good reusability.

The oil-water separation performance of CG-PVDF membrane was tested by suctioning emulsified oil, the upper end of the membrane was poured with emulsified oil, and a measuring tube was placed at the lower end of the membrane to receive the separated liquid, as shown in Figure 5, the separated liquid after filtration had almost no impurities, indicating the good separation performance of CG-PVDF membrane. Comparing PVDF membrane with CG-PVDF membrane in a conventional filter, as shown in Figure 6, it is found that PVDF membrane is difficult to remove oil in oil-in-water emulsion, and the separation efficiency is only 80%, and the flux is only 250, while the separation efficiency of CG-PVDF membrane can reach 99%, and the flux can reach 450, indicating that CG-PVDF membrane has a good separation effect. Therefore, CG-PVDF film has great practical application potential.

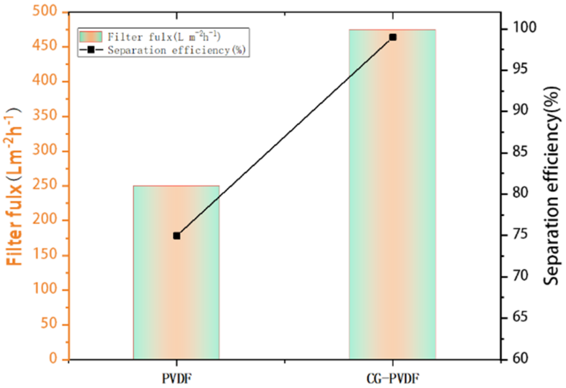

Figure 6. Separation efficiency and throughput of PVDF membranes and CG-PVDF membranes.

4.Conclusion

In this study, natural polysaccharide chitosan, which is degradable and biocompatible, and low-cost and easy-to-obtain, and the cross-linking agent glutaraldehyde was used to graft chitosan, which improved the defects of chitosan that is easily soluble in water with low pH and loses adsorption performance. The use of chitosan can greatly enhance the hydrophilicity of PVDF membrane, but chitosan is unstable and easy to dissolve in water with low pH, so glutaraldehyde functionalization is used to modify chitosan, so that it is more stable grafted on PVDF membrane, and a green and durable CG-PVDF membrane is prepared to treat oily wastewater. The membrane is environmentally friendly, easy to make, and has a large range of use, which is of great significance in the field of oil-water separation.

A superhydrophilic/underwater oleophobic oil-water separation membrane was prepared with PVDF film with good mechanical properties and flexibility as the substrate and grafted chitosan coating on its surface, which was used for the separation of oil-water mixture and emulsified oil. After chitosan grafting, the mechanical properties are doubled, the roughness of the material increases, the greater the surface roughness of the material, the greater the hydrophilicity of the material, so the hydrophilicity of the PVDF membrane is greatly enhanced, and the use of glutaraldehyde is conducive to the grafting of chitosan on the PVDF membrane, which realizes the superhydrophilic modification of the oil-water separation membrane, and prepares a superhydrophilic super-oleophobic CG-PVDF film, which can be better applied to the field of oil-water separation. In addition, the prepared CG-PVDF membrane has a simple preparation process, low cost, good hydrophilicity, high separation efficiency and excellent antifouling performance, and has a good application prospect in the field of oily wastewater treatment.

Acknowledgements

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