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Preparation and properties of Fe^{3+}/PVDF-PMMA catalytic membrane

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ABSTRACT

A new kind of Fe^{3+}/polyvinylidene fluoride membrane (PVDF)-poly methyl methacrylate (PMMA) asymmetric catalytic membrane was prepared by the blending method. The hydrophilicity and antifouling properties of Fe^{3+}/PVDF catalytic membrane was increased significantly after blended with PMMA. The influence of some factors such as polymer blending ratio, polymer concentration, additives, temperature of coagulation bath on the pure water flux, and BSA retention were discussed. The catalytic activity of Fe^{3+}/PVDF-PMMA catalytic membrane was evaluated by the degradation of refractory dye Orange IV in the presence of H_2O_2. The results showed that the addition of appropriate PMMA in the preparation of Fe^{3+}/PVDF membrane has greatly decreased the contact angle of the membrane. Fe^{3+}/PVDF-PMMA membrane had better anti-fouling than Fe^{3+}/PVDF membrane. The Fe^{3+}/PVDF-PMMA catalytic membrane's retention rate decreased and pure water flux increased with the increase of PMMA. When the mass ratio of (PVDF)/(PMMA) was 7:3 and the additive was poly (ethylene glycol) (PEG600), the properties of this membrane were better. This kind of Fe^{3+}/PVDF-PMMA catalytic membrane has not only good filtration efficiency but also good catalytic activity to effectively decompose Orange IV.

Keywords: Modified PVDF membrane; Catalytic oxidation; PMMA; Membrane fouling

1. Introduction

The polyvinylidene fluoride (PVDF) membranes for its extraordinary chemical stability, radiation resistance, nontoxic and heat resistance have been widely used in many fields [1]. Due to this feature, the PVDF could be a promising candidate for catalyst support for Fenton-like reaction. Our group [2] investigated PVDF loading with 8.3 wt.% Fe^{3+} iron as a Fenton-like catalyst to deal with Orange IV in the presence of H_2O_2 and found that the degradation rate could reach 90%. However, the hydrophobicity and low pure water flux of Fe^{3+}/PVDF catalyst membrane remains a problem and limits its application. It is well known that PMMA possesses good hydrophilicity and other advantages [3]. Some papers have indicated that PMMA is a polymer miscible with PVDF [4–6], and a high degree of intermolecular interaction presents between PVDF and PMMA chains [7]. But the effect of blending with PMMA on the properties of Fe^{3+}/PVDF catalyst membrane has not been reported yet.

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In this study, membranes were prepared by hydrophilicity materials PMMA blending with PVDF and Fe^{3+} ions, which is a new type of hydrophilicity catalyst membranes. The effects of membranes' pure water flux, bovine serum albumin (BSA) retention and porosity factors such as PVDF/PMMA-blending ratio, percentage of polymer content, coagulation bath temperature and additives were researched. The hydrophilicity and antifouling properties of Fe/PVDF-PMMA catalytic membranes were studied. The catalytic activity of Fe/PVDF-PMMA for the degradation rate of Orange IV in the presence of H_2O_2 was investigated.

2. Materials and methods

2.1. Experimental materials

PVDF powder (Chenguang Chemical Engineering Institute), PMMA (The Heilongjiang LongXin Chemical Co., LTD), DMAc, $Fe(NO_3)_3{\cdot}9H_2O$, LiCl, PVP K30, PEG-600, 30% H_2O_2, $C_4K_2O_9Ti{\cdot}2H_2O$, $Na_2C_2O_4$,·CH_3-COOH, Orange IV, BSA, and other chemicals were of analytical grade and used without further purification. The pH of the solution was adjusted by a diluted aqueous solution of NaOH or $HClO_4$.

2.2. Preparation of catalyst membrane

The casting membrane solution is composed of PVDF, PMMA, DMAc, 5 wt.% additives and 8.3 wt.% Fe^{3+} ion. It was stirred for 6 h and then deaerated for 15 h to film.

2.3. Analytical and calculation methods

The pure water flux and rejection ratio was measured on Shanghai Mosu ultrafiltration cup system. The tensile strength of membrane was measured with a universal mechanical testing machine (3369, Instron, USA) with the speed of 10 mm/min. The pH value was monitored by a pHs-3C pH meter. Contact angle θ was measured in a SL 200 A/B dynamic/static contact anglometer. The concentration of Orange IV was analyzed with Unico Double Beam UV-4802 UV/Vis spectrophotometer at 440 nm. Hydrogen peroxide (H_2O_2) was analyzed by titanium oxalate spectrophotometry [8]. Each experiment was repeated for two times and an average value was calculated.

The pressure difference across the membrane is 0.1 MPa. The flux (J) was calculated by Eq. (1):

$$J = \frac{V}{S \times t} \tag{1}$$

where V is the total permeation (m^3), S is the total permeation area (m^2), and t is the total permeation time (s).

The rejection ratio (R) of the membranes was measured with 0.1 g/L BSA solution under the press of 0.1 MPa. The rejection ratio was calculated by Eq. (2):

$$R(\%) = \left(1 - \frac{C_P}{C_j}\right) \times 100\% \tag{2}$$

where C_p is the permeate concentration and C_j is the feed concentration.

The porosity (ε_k) of the sample was calculated according to Eq. (3):

$$\varepsilon_k(\%) = \frac{W_1 - W_2}{V \times \rho} \times 100\% \tag{3}$$

where W_1 is the weight of the wet membrane, W_2 is the is the weight of the dry membrane, V is the apparent volume of the membrane, and ρ is the density of water.

The increase coefficient of resistance (m) was calculated by Eq. (4):

$$m = \frac{(J_0 - J_1)}{J_1} \tag{4}$$

where J_0 is the initial water flux and J_1 is the water flux of the membrane which was fouling by 2 g/L BSA solution for 2 h. The larger the value of m is, the worse anti-fouling membrane is.

3. Results and discussion

3.1. Effect of PVDF/PMMA blending ratio (quality ratio)

PMMA and PVDF were miscible polymers and form a homogeneous blend [9]. As shown in Fig. 1, the experimental conditions were as follows: polymer content 15 wt.%, PEG-600 5 wt.%, coagulation bath (water) temperature 40°C, Fe^{3+} 8.3wt.%, DMAc as solvent and the blending ratio of PVDF/PMMA were, respectively, 10:0, 9:1, 8:2, 7:3, 6:4, and 5:5. The effect of PVDF/PMMA-blending ratio (quality ratio) on membrane's pure water flux, BSA retention and porosity were investigated. Obviously, with PMMA content increasing, the pure water flux increased while the rejection ratio decreased, but the porosity had no great change. That means PMMA in the casting solution did not have the higher porosity, the

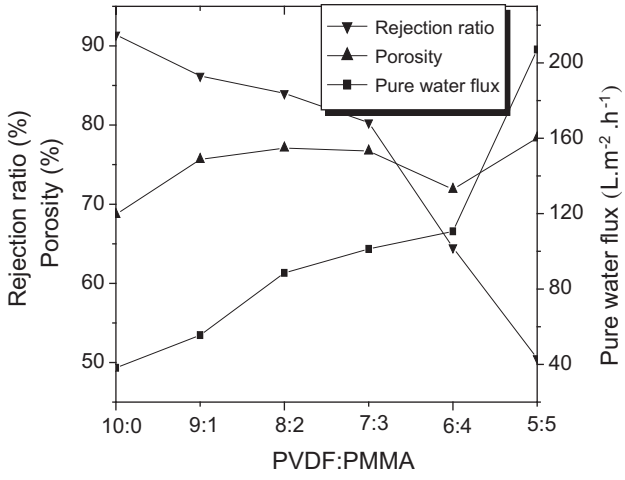

Fig. 1. Effect of PVDF/PMMA blending ratio on membrane's pure water flux, BSA retention and porosity.

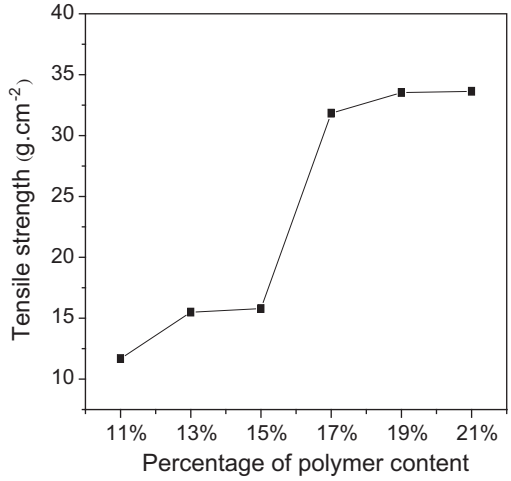

Fig. 3. Effect of percentage of polymer content on membrane's tensile strength.

number of larger pores was higher [10]. This accounted for the low solute retention. The hydrophilic polymer PMMA may favor a faster transport of water into the casting membrane solution with formation of larger cavities. The formation of very large cavities in the membrane was undesirable since it could lead to compressed and may collapse under pressure. The structure and performance of membranes were preferable when PVDF/PMMA was 7/3.

3.2. Effect of percentage of polymer content

The experimental conditions of Figs. 2 and 3 were as follows: PVDF/PMMA 7/3 wt/wt, PEG-600 5 wt.%, coagulation bath (water) temperature 40°C, Fe^{3+} 8.3 wt.%, DMAc as solvent and the percentage of polymer content from 11 to 21 wt.%. As can be seen in Figs. 2 and 3, the pure water flux and porosity of the blend membranes decreased with increasing percentage of polymer content, but the rejection ratio and tensile strength increased. When the polymer concentration increased, the polymer molecular number of per unit volume increased, easily to form a compact structure, and lead to the phenomenon as we seen in Figs. 2 and 3. Tensile strength of blended membrane was proper when the polymer concentration from 17 to 21%. However, the pure water flux and porosity decreased very much but rejection ratio less from 17 to 21%, so the proper weight percentage of polymer content should be 17%.

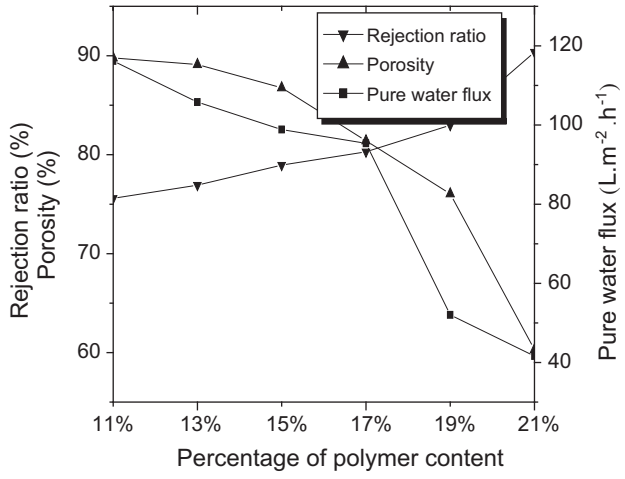

Fig. 2. Effect of percentage of polymer content on membrane's pure water flux, BSA retention and porosity.

3.3. Effect of coagulation bath temperature

In Fig. 4, the experimental conditions were as follows: polymer content 17 wt.%, PVDF/PMMA 7/3 wt/wt, PEG-600 5 wt.%, Fe^{3+} 8.3 wt.%, DMAc as solvent, water as coagulation bath and the coagulation bath temperature were respectively 0, 20, 40, 80°C. It was found that as the coagulation bath temperature changed from 0 to 80°C the pure water flux and porosity increased while rejection ratio decreased. At high temperature, the speed of solvent and nonsolvent mutually diffuse through the membrane/coagulation bath was relatively quick, and membrane separation speed was relatively fast, easily forming larger and more pores [11], which were helpful for the pure water flux and porosity. But when coagulation bath temperature was relatively high, it caused large cavities and the rejection ratio of membrane would substantial decline. The optimum coagulation bath temperature was 40°C.

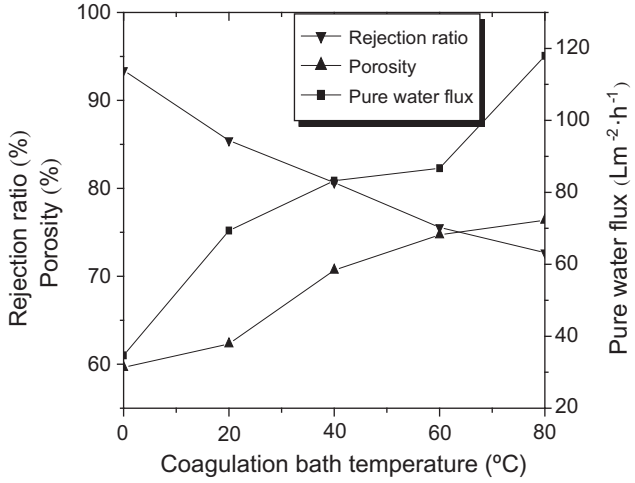

Fig. 4. Effect of coagulation bath temperature on membrane's pure water flux, BSA retention and porosity.

3.4. Effect of additives

Additive as an important component of casting solution, it strongly influenced the structure of casting solution and evaporation speed of solvent, which affected the structure and performance of the membrane Table 1. shows membranes were prepared as follows: polymer content 17 wt.%, PVDF/PMMA 7/3 wt/wt, coagulation bath (water) temperature 40°C,Fe^{3+} 8.3 wt.%, DMAc as solvent, the additives (5 wt.%) of Fe^{3+}/PVDF-PMMA were respectively LiCl, PVP K30, and PEG-600. As can be seen in Table 1, adding PVP K30 as additive, which is a low-molecular-weight additive, the membrane has big water flux and low retention rate. Adding LiCl as additive, which is a high-molecular-weight additive, the membrane has low water flux and high retention rate. Another type of polymeric additive, poly (ethylene glycol) (PEG-600), has a relatively high water flux, rejection rate and porosity, the comprehensive performance of the film is outstanding.

3.5. The antifouling properties, hydrophilicity, and catalytic activity of membranes

The antifouling properties of blend membranes were characterized by the increase coefficient of resistance. The larger the value of m is, the worse anti-fouling membrane is. PMMA possesses a strong hydrophobic property that can be taken to improve the hydrophilicity of Fe/PVDF membrane through blending. As shown in Table 2, The preparation conditions of PVDF membrane were as follows: PVDF 17 wt.%, PEG-600 5 wt.%, coagulation bath (water) temperature 40°C, DMAc as solvent. The membrane preparation conditions of Fe/PVDF are same as PVDF expect for adding Fe^{3+} 8.3 wt.%, and the different of Fe/PVDF-PMMA and Fe/PVDF membrane are the percentage of PVDF/PMMA (7/3 wt/wt) is 17 wt.%. From Table 2, Fe/PVDF-PMMA catalytic membrane's pure water flux was far greater than PVDF and Fe/PVDF membrane whatever before or after fouling. The Increase coefficient resistance and contact angle of Fe/PVDF blend membrane was lower than that of PVDF membrane, but the Fe/PVDF-PMMA membrane was the lowest one. The result shown PMMA can improve the antifouling property, hydrophilicity and pure water flux of Fe/PVDF membrane.

Table 1
The pure water flux, rejection ratio and porosity of membranes with different additives

Additives	LiCl	PVP K30	PEG-600
Pure water flux ($L\,m^{-2}\,h^{-1}$)	55.49	114.45	100.58
Rejection ratio (%)	87.54	64.53	83.66
Porosity (%)	68.35	74.72	76.72

Table 2
The increase coefficient of resistance, degradation rate of Orange IV and contact angle of membranes

Sample	PVDF	Fe/PVDF	Fe/PVDF-PMMA
Pure water flux before fouling ($L\,m^{-2}\,h^{-1}$)	31.21	43.35	100.58
Pure water flux after fouling ($L\,m^{-2}\,h^{-1}$)	8.67	20.54	58.02
Increase coefficient of resistance	0.72	0.53	0.42
Contact angle (°)	112.83	97.06	70.03
Degradation rate of Orange IV after 5 h (%)	8.70	90.81	90.80

The catalytic activity of membranes was studied based on the degradation rate of Orange IV in the presence of H_2O_2. The conditions of degradation Orange IV were as follows: Orange IV (0.4 mmol L^{-1}) 50 mL, pH = 4.1, H_2O_2 15 mmol L^{-1}, membrane area 18.75 cm^2, degradation temperature 20°C. The degradation rate of Orange IV has a very small change in the processing of PVDF membrane. Orange IV is the anionic dyes, PVDF membrane can adsorb them, but the adsorption rate is less than 10%. This indicates that PVDF membrane has no catalytic activity to degrade Orange IV. The catalytic activity of the Fe/PVDF membrane and Fe/PVDF-PMMA membrane for the degradation rate of Orange IV in the presence of H_2O_2 can reach 90.8%. So PMMA has no obvious influence on Fe/PVDF catalytic activity.

Fe/PVDF-PMMA membrane has a great catalytic activity on degradation of Orange IV.

4. Conclusions

By blending process, it was possible to produce Fe/PVDF-PMMA catalytic membranes with a hydrophilicity nature. The results of this study indicated that the Fe/PVDF-PMMA catalytic membranes which had ideal high quality of pure water flux and rejection rate can be made when the blending ratio of PVDF/PMMA was 7/3, percentage of polymer content was 17%, additives were PEG-600, coagulation bath temperature was 40°C. The hydrophilicity of Fe/PVDF catalytic membranes could be improved evidently by blending PMMA, which could be illuminated by the decrease of contact angle. Moreover, PMMA could improve the anti-fouling property and the pure water flux of Fe/PVDF catalytic membranes. The catalytic activity of Fe/PVDF-PMMA membrane degradation rate of Orange IV could reach 90.8%.

Acknowledgments

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