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Surface Modification of Polyacrylonitrile Membrane Through Photochemical Graft Polymerization of Acrylic Acid

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Abstract: Polyacrylonitrile (PAN) membrane has been prepared by phase inversion method and subsequently modified by surface grafting polymerization of acrylic acid (AA). The influence of the surface modification on membrane properties has been investigated through the surface characteristics and separation performance. The experimental results indicated that the grafting polymerization of AA leads to the reduced membrane skin pore size and the lower surface roughness. The separation performance of the modified PAN membrane is highly impoved due to the enhanced flux and the higher protein (BSA) retention; the antifouling property of membranes is also improved compared with that of the unmodified one.

Keywords: Polyacrylonitrile membrane, surface modification, photochemical graft polymerization, acrylic acid.

1. Introduction

Membrane filtration technology has been widely used for multiple purposes such as hemo-ultrafiltration, separation of enzyms and proteins, concentration of milk and fruit, clarification of beer and beverage, production of drinking water, pure water and ultrapure water, desalination and etc. [1]. Polyacrylonitrile (PAN) membranes have advantages because of their good chemical and thermal resistances. PAN membranes could be used for ultrafiltration processes to separate organic substances having a small molecular weight. However, PAN material is rather hydrophobic, thus resulting the fouling phenomenon during filtration, especially for organic feed solutions [2, 3]. Recently, the improvement of separation and antifouling properties of PAN membranes is carried out by grafting of hydrophilic polymeric layer onto membrane surface [4, 5]. The UV-photo-induced graft polymerization has been known as a convenient technique for the surface modification of polymeric membranes [6, 7]. In this work, PAN membrane was prepared by phase inversion method and subsequently modified by surface grafting polymerization of

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acrylic acid (AA), using UV-photo-induced graft polymerization technique. The influence of surface modification conditions on membrane characteristics has been investigated through membrane retention and flux, as well as the antifouling to bovine serum albumine (BSA). The experimental results indicated that both of the filtration and antifouling properties of PAN membranes have been significantly improved after the surface modification.

2. Experimental

The PAN membranes were prepared by phase inversion method. The casting solution containing PAN concentrations of 18 wt-% in N, N'-dimethylformamide (DMF) was spreaded on the glass plate with the thickness of 300 µm. The casting film was then immersed into coagulation medium at low temperature to obtain a thin solid PAN membrane. The formed membranes were rinsed carefully by pure water and dried before the surface modification.

Membrane surfaces were modified by the photochemical graft polymerization technique. Benzophenone (BP) was used as photoinitiator. The BP-coated membranes were immersed into an acrylic acid (AA) solution under UV irradiation (300nm, 60W). After surface grafting, the modified membranes were rinsed carefully and dried before testing the membrane characteristics. The membrane surface morphology was observed through a scanning electron microscope (SEM, Hitachi SU8000) and an atomic force microscopy (AFM, Multimode Scanning Probe Microscope). The membrane separation performance was determined through the retention (R) and flux (J) for the filtration of protein (BSA).

3. Results and Discussion

3.1. SEM images

Figure 1 shows the SEM images of the prepared PAN membrane. It can be observed that the membrane has an asymmetric structure with a dense skin layer located on a porous support layer. The filtration performance of the membrane is determined by the skin active layer, while the support layer protects the skin from the damage which may be caused by the pressure driving force.

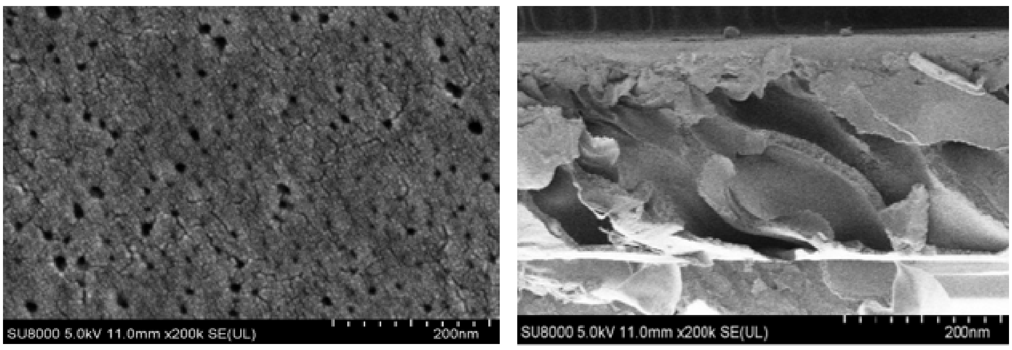

Fig.1. SEM images of PAN membrane surface (left) and cross-section (right).

3.2. AFM images

The surface AFM images of unmodified and modified PAN membranes are given in Fig.2. As shown in this figure, characthized by dark areas represent the membrane surface pores [8, 9], the surface of the modified PAN membrane is more compact than the base. This implies the membrane skin pore size is reduced after grafting polymerization of AA onto membrane surface. Furthermore, due to the formation of the AA-grafted, membrane surface is smoother, as shown in the Table 1, the surface roughness of the modified membranes is reduced. The changes of the membrane surface morphology could lead to the alters membrane filtration characteristics, including of separation performance and antifouling property.

3.3. Graft degree

The graft degree on the modified membrane surfaces was calculated through the graft density, GD ($\mu g/cm^2$) = $[(m_1 - m_o)/A]$, where m_0 and m_1 are the weights of the dried membrane before and after surface grafting, respectively; A is a grafted membrane surface area. As shown in Fig.3, the graft density increases for the prolonger grafting time and for the higher AA concentration in the graft solution.

Table 1: Membrane surface roughness

Membranes	Ra (nm)	Rms (nm)
Unmodified PAN	24.8	29.6
Modified PAN (5g/L AA-1min)	17.8	22.8

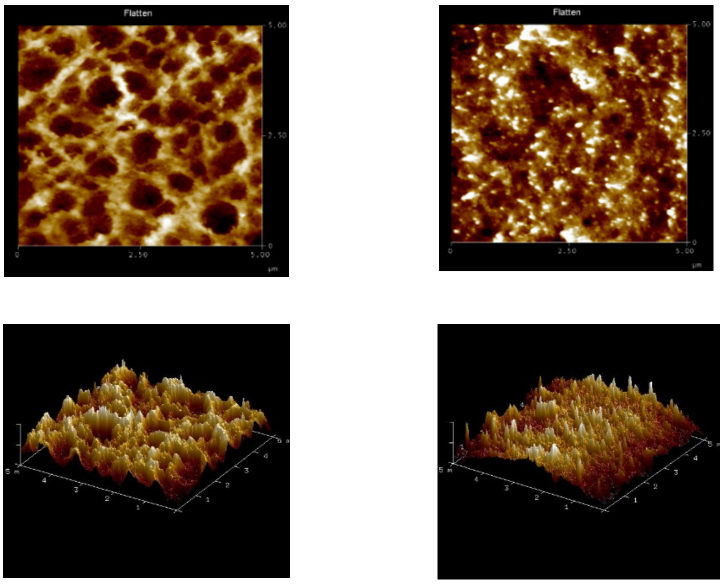

Fig.2. AFM images of unmodified (left) and modified (right) membranes.

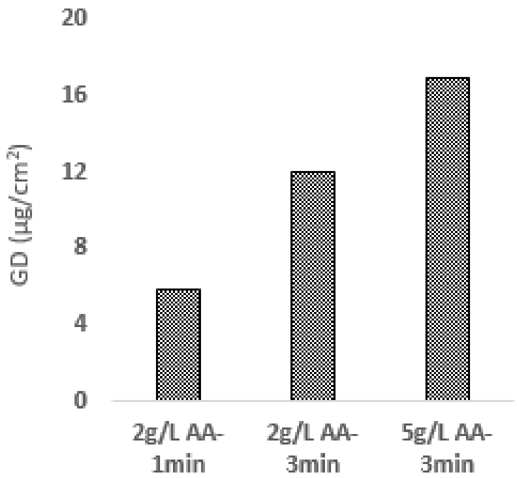

Fig. 3 Graft degree on the membrane surface.

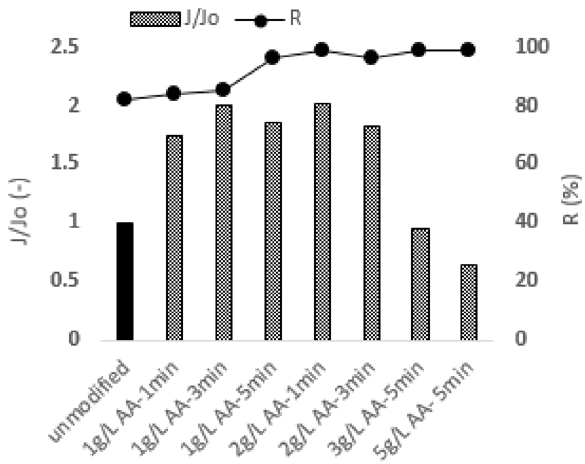

Fig. 4. Retention and flux of the membranes.

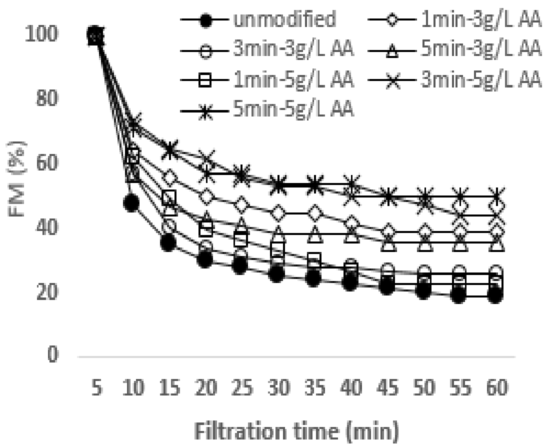

Fig.5. Maintained flux ratios of the membranes.

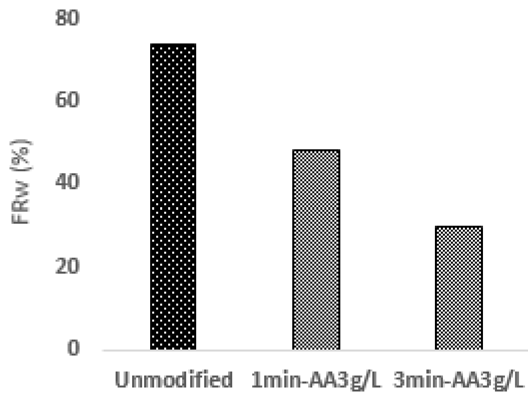

Fig.6. Irreversible fouling factors.

3.4. Membrane filtration property

3.4.1. Retention and flux

The membrane retention is determined by R (%) = {[(C_0 - C)/C_0].100}, where C_0 and C are the concentrations of BSA in the feed and filtrate, respectively. The flux is calculated by J (L/m^2h) = [V/(A.t)], where V is a filtrate volume collected after the time of t, through membrane area of A at determined pressure. The normalized permeate flux ratio (J/J_o), where J and J_o are fluxes of the modified and unmodified membranes, respectively, was used to determine the flux improvement of the modified membranes as compared with that of the unmodified one.

Figure 4 showed the changes in the separation performance of the PAN membranes before and after surface modification. The results demonstrate the increase of BSA retention, from 84 % for unmodified membrane to approximate 99 % for the modified ones; meanwhile, the fluxes of the modified membranes are also higher (from 1.5 to 2.2 times increase) for the AA concentrations of 1 and 2 g/L with the graft polymerization time varied from 1 to 3 min. However, for the further increasing of AA concentration to 3 and 5 g/L, the flux of the modified membranes is reduced, while the BSA rejection is still maintained well (R ~ 99%). The increase of the membrane retention is due to the decrease of the membrane skin pore size after surface grafting, while the enhancement of flux is resulted by the improved membrane surface hydrophilicity, because of the hydrophilic AA-grafted layer on the modified membrane surface. However, for the excess of AA polymeric grafted density formed at high AA concentration, the higher hydraulic resistance of polymeric grafted layer could reduce flux of the modified membranes.

3.4.2. Antifouling property

The antifouling property of the membranes was determined through the maintained flux ratio (FM, %) and an irreversible fouling factor (FR_W, %), which was calculated by $FR_w = \{[(J_{w1} - J_{w2})/J_{w1}].100\}$, where J_{w1} and J_{w2} are the pure water fluxes of the membrane before and after use for the filtration of protein solutions, respectively. The higher maintained flux ratios and the lower irreversible fouling factors, the better antifouling property could be obtained. Fig.5 illustrates the higher maintained flux ratios of the modified membranes as compared with that of the unmodified one. For example, after 60 min of filtration of 1000 ppm BSA feed solution, the flux maintained ratios of the unmodified and modified membranes (3 min- 5 g/L AA) are 19 and 60 %, respectively. In addition, as shown in Fig.6, the irreversible fouling factors of the modified membranes are much lower than the unmodified one. The improvement of the membrane antifouling property is mainly due to the formation of the hydrophilic AA-grafted layer on the surface, thus reducing the protein adsorption on membrane surface during filtration. In addition, the smoother surface of the modified membrane also contributes to the enhancement of the membrane fouling resistance.

4. Conclusions

Polyacrylonitrile (PAN) membrane surface was succesfully modified by the photochemical graft polymerization of acrylic acid (AA). The experimental results indicated that the modified membrane surface morphology has been changed with the lower surface roughness and the reduced skin pore size due to the polymeric AA-grated layer formed on the membrane surface. Under the relevant graft polymerization conditions, the separation performance of the PAN membranes is clearly improved with the increase both of the membrane flux and protein retention; the antifouling property of the modified membranes is also improved because of the higher maintained flux ratio and the lower irreversible fouling factor as compared with that of the unmodified membrane.

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Nghiên cứu biến tính bề mặt màng lọc polyacrylonitrile bằng trùng hợp ghép quang hóa axit acrylic

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Tóm tắt: Màng lọc polyacrylonitrile (PAN) được chế tạo bằng phương pháp đảo pha. Bề mặt màng được biến tính bằng phương pháp trùng hợp ghép quang hóa với axit acrylic (AA) dưới bức xạ tử ngoại. Ảnh hưởng của quá trình trùng hợp ghép được đánh giá qua đặc tính bề mặt và tính năng tách lọc của màng, với đối tượng tách là protein (BSA) trong dung dịch nước. Kết quả thực nghiêm cho thấy việc biến tính bề mặt bằng trùng hợp ghép quang hóa AA làm thay đổi cấu trúc hình thái bề mặt màng, màng trở nên trơn nhẵn hơn với kích thước lỗ bề mặt giảm. Tính năng tách lọc protein của màng được cải thiện sau khi trùng hợp ghép AA với sự tăng đồng thời năng suất lọc và độ lưu giữ, khả năng chống tắc của màng trở nên tốt hơn so với màng ban đầu.

Từ khóa: Màng lọc polyacrylonitrile, biến tính bề mặt, trùng hợp ghép quang hóa, axit acrylic.