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Insights into the effect of preparation variables on morphology and performance of polyacrylonitrile membranes using Plackett–Burman design experiments

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ABSTRACT

In this study, polyacrylonitrile (PAN) flat-sheet membranes were prepared using phase inversion method for the wastewater treatment by membrane bioreactor (MBR). Twelve processing factors in the membrane preparation were investigated by Plackett–Burman design (PBD) in order to prepare high-performance membranes. Test results showed that none of the twelve processing factors had a significant effect on membrane pore size. The casting thickness, non-woven fabric type and casting speed were found to have substantial negative effects on the pure water flux values, and were identified as the significant factors determining the membrane pure water flux. It was also found that the non-woven fabric type, casting speed and casting thickness had significant positive effects on the fouling rate. Moreover, the model using membrane fouling rate as a response value was more credible and in good linear correlation within the tested range.

1. Introduction

In recent years, membrane technology has emerged as a viable and cost-effective alternative for water and wastewater treatment. The membrane-assisted biological treatment, e.g., membrane bioreactor (MBR), has been widely employed for municipal and industrial wastewater treatment. In MBRs, microfiltration (MF) or ultrafiltration (UF) membrane is used as a solid–liquid separation device, which offers remarkable advantages over conventional activated sludge (CAS), including a higher biomass concentration, reduced footprint, and highly-improved effluent quality, etc. [1–3].

The most important part of MBRs is the membrane itself and polymeric membranes are the widely used ones in MBR processes. Polyacrylonitrile (PAN) membrane is one of popular membrane materials due to its good solvent resistance, strong chemical stability, and high mechanical strength [4]. It also has been reported that PAN membrane is relatively hydrophilic and has lower fouling rate in aqueous filtration compared with polysulfone (PSF) and polyethersulfone (PES) [5].

There are several ways to prepare porous polymeric membranes, such as solution casting, sintering, stretching, track etching and phase inversion. The phase inversion process induced by immersion precipitation is a well-known technique to prepare asymmetric polymeric membranes and the complex phase separation conditions have been recognized as major factors determining the ultimate membrane structure [6,7]. Research efforts have been dedicated to determine optimal preparation conditions for achieving better membrane morphology and performance [8–10]. Saljoughi and Mohammadi [11] identified three controllable factors for the asymmetric cellulose acetate (CA) membranes and determined the main effects of each factor using Taguchi design of experiments. Idris et al. [12] also used the Taguchi design to optimize the membrane preparation and clarified the most important factors determining the performance of the CA membranes. The orthogonal array method was adopted by Chau et al. [13] to study the phase inversion factors influencing membrane and it was found that the PVP content and the temperature of the coagulation bath were the factors governing the molecular weight cut-off of polysulfone membranes. In addition, Bulut et al. [14] and Cawse [15] also used evolutionary optimization via genetic algorithms to develop high-throughput and combinatorial membranes. Although the methods mentioned above are very helpful to screen the important factors influencing membrane preparation and to optimize membrane properties, it is insufficient to establish a general rule for manufacturing a certain kind of membrane. This is partially because there are enormous factors affecting membrane preparation. Another reason is due to the fact that some factors are interacted. It is difficult to obtain the comprehensive effects of some factors through a number of experiments. Plackett–Burman design (PBD) method which can examine up to $N-1$ factors ($f \leqslant N-1$) in N experiments, are commonly used in the optimization experiments of fermentation. It has been proven to be an efficient way of evaluating a large number of variables and identifying the significant ones [16,17].

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Therefore, in this study, PBD method was taken into use to study the processing factors influencing flat-sheet membrane and to identify the significant ones in the fabrication of PAN membrane for wastewater treatment by phase inversion process. The effects of twelve controllable processing factors on the membrane morphology and performance were studied. The twelve factors included the polymer dissolving temperature, polymer dissolving time, non-woven fabric type, casting speed, casting thickness, evaporation time, coagulation bath temperature, coagulation bath time, post-treatment reagent concentration, post-treatment agent time, heat-treatment temperature, and heat-treatment time. Membrane pore size, pure water flux and membrane fouling rate were chosen as the response values of the PBD experiments. The results obtained in this study are expected to provide a sound understanding of PAN membrane preparation using the phase inversion method.

2. Materials and methods

2.1. Materials

PAN polymer with molecular weight (MW) 70,000 Da was used as the membrane-forming polymer which was supplied by the Sinopec Shanghai Petrochemical Co. Ltd. (China). *N,N*-dimethylformamide (DMF) of reagent grade was used as solvent without further purification. The non-woven fabrics used as supporting materials, TA3618 and PH554, were supplied by the Tianlue Advanced Textile Co. Ltd. (China) and Teijin Co. Ltd. (Japan), respectively. The fabric TA3618 with 170 μm thickness which was synthesized by thermal method was made of polyester filament. The fabric PH554 with 140 μm thickness which was synthesized by wet method was made of polyester filament. Distilled water was used as the external coagulant. Glycerin was used as the post-treatment reagent.

2.2. Membrane preparation

PAN flat membranes were prepared by phase inversion via immersion precipitation. PAN was dissolved in DMF to form 20 wt.% of casting solution and was then stored at a certain temperature for a set of predetermined time. The polymer solution was sprinkled and cast into a film with 100 or 400 μm on the non-woven fabric at a certain speed using a motorised film applicator (Elcometer 4340, Elcometer Instruments Ltd., England). The cast film was exposed to air at 30% relative humidity for a series of preset evaporation time, and then, immersed into a coagulant bath of distilled water to form the porous membrane. In order to protect the structure of the nascent membrane, the prepared porous membranes were post-treated by immersing into water/glycerin of a group of ratios. At the final stage, membranes were heat-treated at various preset temperature for different prefixed time.

2.3. Membrane characterization

2.3.1. Field emission scanning electron microscopy (FESEM) analysis

FESEM (S-4800, Hitachi, Japan) was used to investigate the surface morphologies of membranes. The membranes were freeze-dried in vacuum and gold sputtered for producing electric conductivity. The micrographs were observed and the average pore sizes were obtained from the images using Image-Pro Plus 6.0 software [18].

2.3.2. Pure water flux measurement

The membrane pure water flux was measured by a dead-end filtration apparatus. The area of tested membrane was 12.56 cm^2. Each sample was soaked in distilled water for 24 h before testing and pre-compacted for 30 min at 0.08 MPa. Then, the trans-membrane pressure was lowered and the pure water flux (J) was obtained at 0.03 MPa by measuring filtrate volume within a certain period of time. To minimize the experimental error, each membrane was measured at three random locations and the average value was reported. The pure water flux was calculated according to the following equation:

$$J = V/(S \cdot t) \tag{1}$$

where J is the pure water flux (L/(m^2 h)), V volume of permeated water (L), S effective area of tested samples (S = 0.001256 m^2), and t record time (h).

2.3.3. Membrane fouling rate determination

In order to test the performance of membrane samples for wastewater treatment, a short-term filtration experiment in a mini-MBR (an MBR cell) was carried out to determine the fouling rate of each membrane. The prepared flat-sheet membranes were firstly processed into modules with a filtration area of 0.01 m^2. Then the modules were put into a mini-MBR with an effective volume of 2.5 L in which the activated sludge was taken from a long-term stable pilot-scale bioreactor. Filtration performance of the mini-membrane module was conducted with the constant flux of 40 L/(m^2 h), and the change of trans-membrane pressure (*TMP*) was monitored within 30 min. The aeration rate was controlled as 15 m^3/(m^2 h). The membrane fouling rate was evaluated by membrane filtration resistance, which was calculated by the following equation according to the literature [19,20]:

$$R = (TMP_{30} - TMP_0)/\mu \cdot J \cdot \Delta t \tag{2}$$

where TMP_{30} and TMP_0 are the *TMP* values of membrane samples at starting time and after a 30-min filtration (Pa), respectively, J is the membrane permeate flux (m^3/(m^2 s)), μ is the viscosity of filtrate (Pa s), and Δt is filtration time (h). In order to ensure the credibility of the results, each membrane was examined for three times and after each test the membranes were immerged in 0.5% (w/v) NaClO solution to recover the permeability.

2.4. Experimental design

The purpose of PBD was to evaluate the effect of the processing factors and identify the key ones influencing the membrane characteristics. Before designing the experiment, suitable values for the twelve controllable factors were selected according to previous studies [8–13] and our preliminary tests. PBD was developed using the Minitab software (Version 15.1.30, Minitab Inc., USA). Each factor was investigated at two widely spaced levels: −1 for low level and +1 for high level [21]. The 12 variables were evaluated by 20 runs of experiments. Table 1 shows the factors under investigation as well as the levels of each factor used in the experimental design, whereas Table 2 lists the design matrix. Each row of Table 2 represents a run, which is a specific set of factor levels to be applied. Each run was conducted twice, and 40 membrane samples were thus obtained. The response values used in this study included the membrane pore size, pure water flux and fouling rate. A commonly used statistical method, analysis of variance (ANOVA), was also used to analyze the results of experiments. The fitted first-order model could be analyzed as follows:

$$Y = \beta_0 + \Sigma \beta_{\mathrm{i}} X_{\mathrm{i}} \tag{3}$$

where Y is the predicted response, β_0 and β_{i} are constant coefficients, and X_{i} is the coded independent factors.