Separation of bovine serum albumin and humic acid contaminants from aqueous stream using tailored poly (amide imide) ultrafiltration membranes

M. Sri Abirami Saraswathi[a], S. Mahalakshmi[a], S. Vetrivel[a], K. Divya[a], D. Rana[b], A. Nagendran[a,*]

[a] Polymeric Materials Research Lab, PG & Research Department of Chemistry, Alagappa Government Arts College, Karaikudi, 630 003, India
[b] Department of Chemical and Biological Engineering, University of Ottawa, 161 Louis Pasteur St., Ottawa, ON, K1N 6N5, Canada

A R T I C L E   I N F O

A B S T R A C T

An attempt of studying the effects of the Pluronic F127 (triblock-co-polymer) and pore forming PEG 600 [poly (ethylene glycol) of average molecular weight 600 Da] additives in enhancing the hydrophilicity and antifouling properties of poly (amide imide) (PAI) ultrafiltration (UF) membranes was made. PAI membranes were fabricated by the addition of optimized amount of 5 wt.% of Pluronic F127 and PEG 600 additives individually via phase inversion technique and characterized in terms of scanning electron microscopy (SEM), contact angle (CA),work of adhesion (ω_A), Fourier transform infrared spectroscopy (FT-IR), pure water flux (PWF), hydraulic resistance (R_m) and percent water content (%WC). Percent solute rejection (%SR) and permeate flux were measured using BSA (bovine serum albumin) and HA (humic acid) as modal fouling agents. Antifouling capacity of the membranes were studied by the experiments such as flux recovery ratio (FRR), reversible fouling (R_r) and irreversible fouling (R_{ir}). The results obtained from the above mentioned characterizations revealed that the PAI/ Pluronic F127 membrane exhibits better performance than that of PAI/PEG 600 membrane due to the dual performance of Pluronic F127 as pore former as well as hydrophilic surface modifier causes superior enhancement in the membrane hydrophilicity. Moreover, the strong interactions between the PAI and PEG 600, limits the performance of PAI/PEG 600 membrane. Hence, Pluronic F127 has a greater influence in effectively modifying the PAI membrane than PEG 600.

1. Introduction

The development of novel membranes with desired pore size distribution and thin barrier layer is essential to overcome the trade-off between selectivity and permeability. Hence, development of highly hydrophilic membranes, without compromising the selectivity and durability is the major deal these days. Modifying a hydrophobic polymer with macromolecular additive or pore forming agent by simple blending can be a good choice, since this way, we can impart good permeability and hydrophilicity to the membrane matrix with minimum efforts [1–4].

Herein polyamide-imide (PAI) was chosen as the hydrophobic base polymer. PAI is a copolymer of amide and imide, and possesses unique characteristic properties of both polyamide and polyimide. It has exceptional mechanical, thermal and chemical resistant properties which are the basic requirement for a good membrane. In addition to membrane base material, recently, PAI is widely employed as a modification agent in membrane technology, as it enhances the thermal and mechanical properties of resultant membranes. However, the less

hydrophilic nature of PAI polymer tends to restrict the penetration of water into the polymer solvent dope in the phase inversion process, and thereby the coagulation rate of PAI might be slowed down. This creates difficulty in the formation of pores and macrovoids in the resulting membrane. Nevertheless, the hydrophobicity of PAI membranes leads to the contagion of proteins and humic substances and therefore fouling of the membrane followed by fall in the water flux. To control the effect of fouling, hydrophilic PAI membranes were fabricated by the addition of suitable polymeric additives. Among the various additives employed Pluronic F127 and PEG 600 were received greater attention due to their simple blending with hydrophobic base polymer in the appropriate solvent [5,6].

The enhanced PEO density and superior protein adsorption resistance of amphiphilic tri-block copolymers, such as Pluronic F127 were able to produce more fouling resistance to the modified membrane matrix than linear polymers [7]. In addition, the hydrophilic PEO segment in Pluronic F127 will project towards the water interface due to the affinity between the PEO segment and water, while the hydrophobic PPO segment anchored in the membrane matrix. Further,

several researchers reported that, the Pluronic F127 also acts as a pore former and the creation of non-permeable surfaces due to its addition could cause low protein fouling [8]. Many researchers have also used Pluronic F127 as hydrophilic additive to enhance the permeation properties of base polymers [9,10]. Alternatively, pore forming PEG with a molecular weight of 600 acts has a favorable effect in improving the water permeation since it increases the overall porosity and pore size in the membrane by leaching out of the membrane in the gelation bath [11]. Pluronic F127 and PEG 600 showed good miscibility with the polymer and solvent and can form a desired thickness polymer film when added to the polymer-solvent dope. Further, the incorporation of additives causes thermodynamic instability in PAI, which further causes the separation of dope solution into two phases during de-mixing. The above phenomenon may lead to the formation of large pores once the additive rich phase in the dope was leached out due to their hydrophilic nature [12,13].

An attempt has been made to incorporate the above two macro-molecular additives Pluronic F127 and PEG 600 independently in the PAI membrane matrix and compare their effects in importing the desirable properties such as improved permeability and antifouling ability to the fabricated membranes.

2. Experimental

2.1. Materials

Polyamide-imide (PAI), Pluronic F127, bovine serum albumin (BSA), humic acid (HA), anhydrous sodium monobasic phosphate and sodium dibasic phosphate heptahydrate were procured from Sigma-Aldrich Inc., St. Louis, MO. Poly (ethylene glycol) of average molecular weight 600 Da (PEG 600) was procured from Loba Chemie Pvt. Ltd., Mumbai, India. N-methyl-2-pyrrolidone (NMP) was procured from Merck, Mumbai, India.

2.2. Membrane preparation

Neat PAI, PAI/Pluronic F127 and PAI/PEG 600 dopes with 5% of Pluronic F127 and PEG 600 respectively were fabricated through typical phase inversion technique. The detailed procedure for the polymer dope preparation and membrane fabrication was reported in our previous works [14,15]. Shortly, pre-determined amount of polymer, additive and solvent were taken in a round bottom flask and kept under mechanical stirrer for 3 h. And the polymer dope making process was kept at an environment where the relative humidity and temperature were 50 ± 1% and 24 ± 2 °C respectively. Once the homogeneous polymer dope was obtained, it was casted over a glass plate into a 0.02 mm thick film, using a Doctor's blade and immediately immersed into a gelation bath (contains 2L of DI water, 2.5% solvent and 0.2 g surfactant) for 1 h, after which prepared membranes were stored in de-ionized water for 24 h subsequently used to conduct UF experiments. Blend composition of polymer, additives and solvent for the prepared membranes and their codes were listed in Table 1.

Table 1
Blend composition of neat PAI, PAI/PEG 600 and PAI/Pluronic F127 membranes.

MembraneCode	Blend composition (Wt.%)			
	PAI	PEG 600	Pluronic F127	NMP
Neat PAI	17.5	0	0	82.5
PAI/PEG 600	17.5	5	0	77.5
PAI/Pluronic F127	17.5	0	5	77.5

2.3. Membrane characterization

2.3.1. FTIR, surface morphology and hydrophilicity

The FTIR characterizations of the membranes were done in the transmission mode using TENSOR 27, Bruker Optik GmbH, Germany with in the wavelength between 500 and 4000 cm^{-1}. The surface porosity and the cross-sectional morphologies of fabricated PAI blend membranes were probed by a scanning electron microscopy (SEM) (BRUKER, USA). The water content measurements of all the fabricated membranes were done by using weight of wet membrane (W_w) and the weight of dry membrane (W_d) in Eq. (1) [16]. The weight of wet membranes were determined by immersing the pre-determined sized membrane in de-ionized water for 24 h and weighing them immediately after the removal of surface water using blotting paper. The weights of dry membranes were obtained by drying the same membranes in an air oven at 70 °C for 24 h. The prepared membranes were cut into desired size coupons at random places and contact angle was measured by goniometer (Scherr Tumico, St. James, MN). Membrane hydraulic resistance was determined by plotting the pure water flux (J_{w_1}) of the concern membranes against their applied transmembrane pressure (ΔP) using Eq. (2). From the obtained contact angle values, the work of adhesion (ω_A) which is considered necessary to pull water from a square meter of membrane surface was calculated using Eq. (3), in which γ_w and θ represent the water surface tension (7.2 × 10^{-2} m Nm^{-1}) and contact angle respectively [17].

$$\%WC = \left(\frac{(W_w - W_d)}{W_w} \right) \times 100 \tag{1}$$

$$J_{w_1} = \frac{\Delta P}{R_m} \tag{2}$$

$$\omega_A = \gamma_w (1 + Cos\theta) \tag{3}$$

2.3.2. Permeation, rejection and fouling experiments

A dead-end UF kit provided with a stirrer inside was employed in the assessment of permeation, rejection and antifouling capacities of the fabricated pure and blend PAI membranes. The experimental setup of UF kit with feed tank and air compressor is depicted in Fig. 1. Each fabricated membrane was washed completely before fitted into the UF kit. At a pressure of 414 kPa, compaction of each membrane was done before the pure water flux (PWF) measurement. The permeate flux was measured continuously 1 h once until the attainment of steady state. After compaction, with a varying pressure from 69 to 345 kPa, PWF of each membrane was determined using Eq. (4). Fouling experiments was conducted by keeping BSA and HA as standard fouling agents for each prepared membrane. For this, the BSA and HA solutions were prepared separately using phosphate buffer solution with a pH of 7.2 and was used as feed [18]. The BSA and HA permeation experiments were done at a pressure of 345 kPa with constant magnetic stirring and the foulants permeate flux (J_{p_1} and J_{p_2}) were calculated using the Eq. (4) which is employed for the J_{w_1}calculation.With the results obtained from the fouling experiments using BSA and HA, the FRR, R_r and R_{ir} were determined by using the Eqs. (5–7), respectively [15]. And a small amount of BSA and HA permeate from the kit was collected and the percent solute rejection of membranes were determined by measuring the concentration of permeate using a UV–vis double beam spectrophotometer (Systronics, 2201, Ahmedabad, India) using Eq. (8).

$$J_{w_1} = \frac{Q}{A\Delta t} \tag{4}$$

Where, Q the permeate volume (L), A the membrane area (m^2), and Δt the permeation time (h).

$$FRR = \left[\frac{J_{w_2}}{J_{w_1}} \right] \times 100\% \tag{5}$$