

Investigation of New Polyester Nanofiltration (NF) Membrane Fouling with Humic Acid Solution

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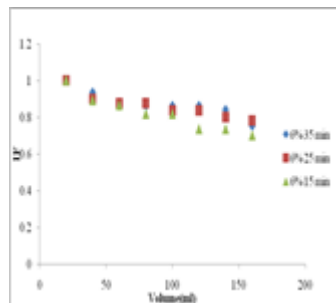
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Graphical abstract



Abstract

Ultrafiltration (UF) polyethersulfone membrane support has been modified by interfacial polymerization technique using reaction of aqueous solution and organic solution to form thin film composite (TFC) nanofiltration (NF) membrane. A new polyester layer were produced on the top surface of UF support by the reaction between triethanolamine (TEOA) (6% w/v) in the aqueous solution and solution containing trimesoyl chloride (TMC) (0.15%w/v) at different of reaction times (15, 25 and 35 min). The decrease of membrane permeability was related to the changes of the membrane morphology (i.e. membrane thickness) as the reaction times were increased. Irreversible membrane fouling has been studied by using humic acid as model of natural organic matter (NOM) solutions at two different pH values (7 and 3). At pH 7, it was observed that the NF TFC membranes exhibited practically less tendency to be irreversibly fouled by humic acid. However, the permeate flux was decreased and the irreversible fouling factor was increased with decreasing the pH to a value of 3.

Keywords: Interfacial polymerization; nanofiltration; fouling; humic acid

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1.0 INTRODUCTION

Natural organic matter that can cause fouling issues is a major problem for efficient use of nanofiltration (NF) membranes in the water treatment process.¹ Fouling problem lead a significant loss of productivity and increase operational cost. Humic acid (HA) is among many potential organic foulants, which is an important foreboding of trihalomethane, has been considered to be one of the most major foulants in the surface water.² HA exists ubiquitously in the aquatic environment and is considered as a degradation product of lignin, carbohydrates, proteins, etc.³ HA is a heterogeneous mixture having both aromatic and aliphatic components and containing three main functional groups: carboxylic acids (COOH), phenolic alcohols (OH), and methoxy carbonyls (C=O).⁴ Its electric charge, derived mainly from the ionization of these groups, results in mutual repulsion and expansion of the coil. HA macromolecules are mostly coiled densely at higher concentration, lower pH, or higher ionic strength, and behave like flexible linear colloids at lower concentration, higher pH and lower ionic strength. As a result, physical and chemical properties of HA could vary significantly at different conditions.⁵

Solution chemistry always plays a significant role in determining foulant-foulant and foulant- membrane electrostatic

double-layer interactions, and hence membrane performance.⁶⁻⁸ For HA, solution chemistry also controls the charge and configuration of its macromolecule, and hence the structure and hydraulic resistance of the foulant deposit layer.

The rate and extent of membrane fouling are influenced by operating conditions such as the applied pressure. Applied pressure determines the initial permeate flux and the resulting convective transport of foulants towards the membrane surface. Previous research done by Malgorzata Kabsch-Korbutowicz⁹, conducted an experiment using the coagulation/UF process for drinking water treatment by varying pH values and found that the maximum NOM separation was obtained at pH 6 .They concluded that increament of pH in the solution reduced membrane fouling and increase the efficiency of organic macroparticle retention.

The objective of this paper is to study the effects different pH of humic acid solution toward membrane fouling of polyester nanofiltration membrane. Membrane fouling experiments were performed with two different pH (3 and 7).

2.0 EXPERIMENTAL

2.1 Materials

The asymmetric commercial polyethersulfone membrane UF PES50 purchased from AMFOR INC (China) and the membrane details are shown in Table 1 was used as a base support for surface modification.

Table 1 Characteristic of membrane as mentioned by manufacturer

Membrane	UF PES50
Material	Polyethersulfone
Nominal MWCO	50,000 Da
Water Flux @ 25°C	260 LMH

Triethanolamine (TEOA) purchased from R & M Marketing (Essex, UK) was used as an active monomer of aqueous phase. Sodium hydroxide (NaOH) purchased from Merck (Germany) was used to mix with TEOA. Trimesoyl chloride (TMC) used as an active monomer of organic phase was obtained from Alfa Aesar (UK). n-hexane was used as the organic phase solvent, which was obtained from Merck (Germany). For membrane preservation, glycerol and sodium disulphite that purchased from R & M Marketing (Essex, UK).

Humic acid was supplied by Sigma-Aldrich Co. and was chosen as a model of organic foulants. To adjust the pH of the feed humic acid solutions to the required values, hydrochloric acid (HCl) and sodium hydroxide (NaOH) supplied by Sigma-Aldrich Co. and Acros Organics, respectively, were used.

2.2 Experimental Procedures

2.2.1 Preparation Humic Acid Solution

In order to prepare humic acid solution, 1g/L sodium hydroxide solution is prepared by dissolved 1g of sodium hydroxide (NaOH) with 1000mL of deionized water. Then, 1 gram of humic acid powder (Aldrich) is dissolved with 1000 ml of 1g/L of NaOH solution to ensure humic acid solution fully dissolved in the NaOH solution. In fact, humic acid will fully dissolved at pH higher than pH 9. Then, pH of stock solution is measured. After that, 15 mL of stock humic acid solution was diluted with deionized water up to 1000 ml. Then, the pH of humid acid solution is adjusted until pH 7 with 0.1M HCl and 0.01 M NaOH.

2.2.2 Interfacial Polymerization

Sodium Hydroxide (NaOH) solution with concentration 1% w/v prepared by dissolving 10g NaOH in 1000 ml distilled water and used as base medium for TEOA solution. Aqueous TEOA solution with concentration 6% w/v was prepared by dissolved 6 g TEOA in 100 ml NaOH aqueous solution, (NaOH 1% w/v). On the other hand, organic Trimesoyl Chloride (TMC) solution with concentration 0.15% w/v prepared in organic phase form by dissolving 0.15 g TMC in 100 ml n-hexane. Polyethersulfone (PES) supporting membrane was cut into a disc forms and immersed into an aqueous TEOA solution (6% w/v) for 30 minutes. Then, the excess TEOA solution on the membrane surface was drained at room temperature about 2 minutes. After that, the TEOA coated membrane was immersed in TMC-hexane for 15 minutes for interfacial polymerization purpose. The resulting aromatic composite polyester membrane was dried overnight at room temperature. Three membrane samples were

produced at three different reaction times (15, 25 and 35 minutes).

2.2.3 Nanofiltration Experiments

Before all NF experiments, each membrane was first immersed in distilled water and then placed in the filtration cell (Amicon stirred cell, model 8200) about one hour and pressurized at 400kPa for at least 10 minutes using distilled water. Subsequently, pure water experiments were conducted at 100-400 kPa to obtain water flux.

2.2.4 Fouling Membrane Testing

The membrane was flushed with deionized water in Amicon stirred cell about 10 minutes. Initial water flux F_i , is measured at operating pressure of 4 bar with water permeation experiment. Then, filtration was done with humic acid solution (pH 7) at 4 bar and 300 rpm stirring rate. Time is taken for every each 20 ml interval until reached 160 ml of permeate. After humic acid filtration was completed, the membrane is then flushed again with deionized water for 15 minutes at 350 rpm stirring rate in order to remove the weakly adsorbed humic acid on the membrane surface. No pressure was applied during cleaning process. After that, the membrane was tested again with deionized water at pressure 4 bar and final water flux, F_f is measured. The filtration is repeated with pH 3 humic acid solution. The fouling index in term of irreversible fouling, IF is measured by using following equation:

$$IF = (1 - F_f/F_i) \times 100\% \quad (1)$$

3.0 RESULTS AND DISCUSSION

3.1 Pure Water Permeance

As stated earlier, all membranes were modified by interfacial polymerization at different reaction time (15, 25, 35 min) at fixed monomer concentration of 6% w/v TEOA. The obtained pure water permeability, P_m of all membranes is shown in Table 2. The result shows that the permeability decreased significantly as the reaction time was increased. The range of values obtained was well within the range of values reported previously for NF membranes available commercially, which is between 1.331 and 50.50 L/m².h.bar as reported by Bowen and Mohammad¹⁰. From the water permeability data, the membrane produced in our study could be categorized as tight NF membrane. From the result obtained, it is obviously observed that the reaction time affect the water permeability very much. Ji and Mehta¹¹ reported that the growth of thin film depends very much on the reactant concentration and reaction time. In this case as the reaction was increased, the thin film composite layer was postulated to be thicker and thus resulted in lower permeabilities. In this case, longer reaction time will induce a thicker thin film layer on top of the polyethersulfone support.

Table 2 Pure water permeability of three different membranes

Membrane	Pure water permeability (L/m ² .h.bar)
6% 35 min	1.62±0.09
6% 25 min	2.40±0.60
6% 15 min	4.28 ± 1.28

Figure 1 and Figure 2 show the normalized permeate flux, J_t/J_0 , using 15 mg/L humic acid feed aqueous solution at pH values 3 and 7 respectively, when the operating pressure is 4 bar. When the pH of the humic acid solution was changed to very acidic condition (i.e. pH= 3) as illustrated in Figure 1, all the fabricated membrane show very rapid flux decline. This is attributed to the charge effect that becomes insignificant at this pH value. The humic acid loses its charge and membrane surface becomes less charged. This increases the interaction between the humic acid molecules and the membrane surface leading to a decrease of the permeate flux. It can be seen at pH 3 the lower permeate flux decline at lowest reaction time (15 min). Otherwise, the lowest reaction time (15 min) at pH 7 show the highest permeate flux decline. Previous study shows that polyester thin film composite membrane produced by Triethanolamine (TEOA) has ability to be used in desalination at different of pH environment¹².

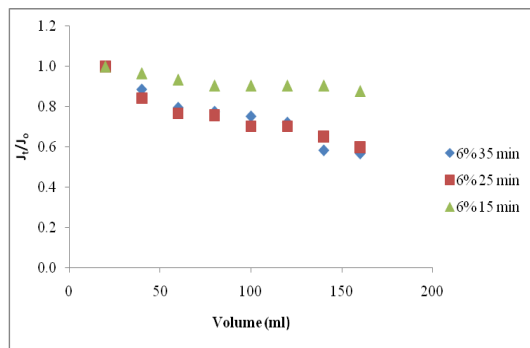


Figure 1 Normalized flux of the 15mg/L humic acid solution at pH 3

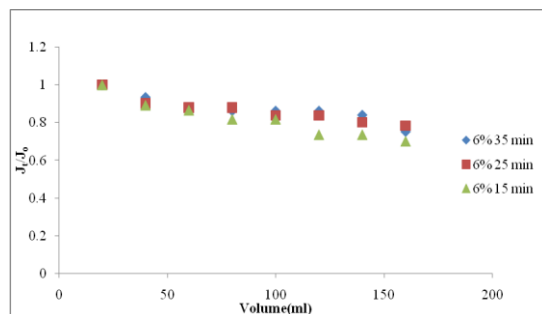


Figure 2 Normalized Flux of the 15 mg/L humic acid solution at pH 7

Based on Table 3, it shows that at pH 3 there are fouling index decreament with the reducing reaction time. However, no significant trend can be concluded at pH 7 where fouling index almost similar at all reaction times especially at 35 min and 15 min of reaction times. In general, it was observed that the fouling is more severe in acidic condition (pH 3) compared to the neutral environment. This is due to the change of pH value may affects the condition and electric charge capacity of both humic acid molecules and membrane surface indirectly creating the interaction force between both membrane surface and humic acid molecules. This interaction is related to the complex structure of humic acid molecules. Humic acid is reticulate macromolecule polymer which is linked by hydrogen bonds of functional groups. The basic unit of humic acid is aromatic nucleus which linked with more active functional groups are carboxyl and phenolic hydroxyl groups. The possibility for the hydrogen ion of Carboxyl and phenolic hydroxyl groups can be dissociated or not depends on the pH value of solution. Low pH

value can cause the formation of carboxyl and phenolic hydroxyl groups, $-COOH$ and $-OH$ respectively. High pH cause formation of $-COO^-$ and $-O^-$, respectively.¹³ The molecules take more negative charges when the dissociation degree of carboxyl group in humic acid molecules increases at high pH. The molecules existed in a more stretched state in solution are made by spatial exclusion that engendered by functional groups of humic acid. It takes more obvious negative electrical charges while the pH value is higher, because membrane surface has absorbed more OH^- . The absorption and precipitation of humic acid in the membrane weakened due to the increase of the electrostatic repulsion between membrane surface and the organic molecules, thus membrane fouling phenomena are light when pH value is high.

Table 3 Fouling Index (IF) of the three membranes at different of pH 7 and pH 3

Membrane	pH 7	pH 3
6% 35 min	21.88	47.90
6% 25 min	18.18	43.90
6% 15 min	22.20	29.00

4.0 CONCLUSION

As conclusion, humic acid filtration preferably chosen at pH 7 (6% 25 min) and pH 3 (6% 15 min). The flux decline during humic acid deposit on the membrane surface. The rate and extent of flux decline during humic acid filtration was also a strong function of pH solution. Humic acid was much more pronounced at low pH due to the reduction in electrostatic repulsion between the negatively charged humic acids and the negatively charged membrane. However, further investigation would be required to fully discussed the membrane fouling such as surface roughness, concentration polarization, osmotic pressure effect and membrane compaction. By this, important insights into the physical phenomena governing humic acid fouling during membrane nanofiltration can full demonstrated.

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