Charge Property Modeling of Nanofiltration Hollow Fiber Membranes

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Abstract - **The development of models that predict membrane performance has contributed a better understanding of the basic principles and mechanisms of solute rejection and deposition. It also serves as fundamental properties that allow specific characterization determination. This work fabricates hollow fiber membranes using Polyethersulfone (PES). The membranes were fabricated in-house using phase inversion technique by modification with synthesized charged-surface modifying macromolecules (cSMM). The cSMM comprise with end-group component of Hydroxybenzene sulfonate or Hydroxybenzene carboxylate. The electrical properties of the membranes were modeled by utilizing the combination of irreversible thermodynamic model, Steric-Hindrance Pore (SHP) model and Teorell-Meyer-Sievers (TMS) model. The negatively-charged of the modified hollow fiber membranes was calculated based on sodium chloride rejection experimental performance. The analysis of the modeling results revealed that the modification of nanofiltration membrane using sulfonate induce negative 1.61 electrical properties compared to carboxylate that is negative 1.49 for both type modified PES membranes.**

Keywords - mathematical modeling, negative charge, surface modification, hollow fiber membrane, ionic separations.

I. INTRODUCTION

Main membrane separation technology in water and wastewater treatment are categorized into four classes according to the separation process, namely, reverse osmosis (RO), Nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF). Membrane processes becoming more popular because the processes can disinfect water without chemical additions and avoid the formation of toxic disinfection byproducts [1]. Furthermore, membrane has received more interest in recent years due to increasingly stringent standard requirement for water supply and effluent discharge. The benefits of membrane treatment processes has been highlighted as; compact, modular construction, minimum of moving parts with low maintenance requirements, no chemical addition requirements and minimal chemical sludge disposal, absolute barriers to particles and pathogens, constant filtered water quality irrespective of feed water quality, easy system upgrading and suitable to small systems and distributed locations [2,3].

The success of any separation system involving membrane depends on the quality and suitability of the membrane incorporated in the system. Nanofiltration (NF) process is a better option than UF due to its capability to reject matters with molecular weight (MW) greater than approximately 200Da, yet it requires more energy consumption during operation [4,5]. On the other hand, the relatively coarse pore size distribution of UF made it inadequate to remove organic matter with several hundreds of MW [6]. In addition, nanofiltration separation process involves a combination influence of charge interaction and size exclusion [7].

Advancement in membrane fabrication has pushed the border of membrane limitation and improves their performance into various of application, which makes membrane formation and fabrication is an interesting subject of study. The ability of producing own made membrane allows a greater chance to produce and achieve a successful treatment system since during the production process of membrane it can be tailored to suit the requirements. However, many important factors need to be taken into account and properly controlled in order to allow production of membranes that meet the desired characteristics.

Surface membrane properties are one of the key controls used to optimize membrane performance, especially via membrane surface modification. In membrane separation processes, membrane charge correlated with electrostatic interactions between membrane and solutes [8-10]. The negative properties of membrane surface usually are contributed by the sulfonic and/or carboxylic acid groups which are deprotonated at neutral pH [11,12]. Several researches has studied the membrane surface charge dependence to feed water matrix including factor of pH [13,14], electrolyte concentrations [15] and presence of natural organic matter [16]. All was agreed that by increasing negative surface charge of membranes will increases rejection performance, especially for negatively charged compounds [17].

Surface modification of membrane by blending method has an advantage due to easy fabrication and a single step process. However, the success of surface modification by blending is highly correlated to many factors and still a challenging field of studies. The combination of different nanofiltration membrane removal mechanism namely; convection, diffusion (sieving) and charge effects, offers an advantage towards ionic solutes removal. However, in order to predict and optimize charge nanofiltration membrane performance, the charge properties of the fabricated nanofiltration membranes need to be characterized.

The limitation of specialized instrumentation on the measurement of hollow fiber membrane charge properties is overcome by the mathematical model study. The modeling incorporates retention experiments using ionic solutes. The determination of the membrane charge parameters based on the theoretical models are presented in this work. Therefore, the aim of this paper is to evaluate the influences of charged-surface modifying macromolecules modification on the polyethersulfone (PES) hollow fiber membranes for ionic separation and characterized based on the mathematical models.
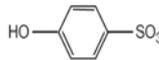
II. EXPERIMENTAL METHODS AND MATHEMATICAL MODEL

A. Hollow fiber membranes

The membranes used in this work were in-house fabricated, using N-methyl-2-pyrrolidinone (NMP, >99%) (Merck, Darmstadt, Germany) as solvent. The PES (RADEL A-300, Amoco Chemicals) hollow fiber membrane were modified with charged surface modifying macromolecules (cSMM). The cSMMs are oligomeric glycol polymers synthesized by polyurethane chemistry and tailored with end groups. Hypothetically, the charges were contributed by the end-capped group of cSMM. The end-groups used in this study were sulfonate and carboxlate ion.

The morphology observation of the hollow fiber membranes was made by Field emission scanning electron microscopy (ZEISS SUPRA 35VP). The fiber samples were prepared by immersing the fiber samples in liquid nitrogen and then fractured to obtain a clean break. Table 1 shows the fabrication process and spinning conditions, which were named as HF1 and HF2.

Table 1. Technical fabrication condition of the hollow fiber membranes

Technical fabrication process	Membranes	
	HF 1	HF 2
Dope formulation (wt%)	PES/PEGHBS (22/1)	PES/DEGHBC (22/1)
cSMM end-group formula	Hydroxybenzene sulfonate	Hydroxybenzene carboxylate
	HO—⟨⟩—SO₃	HO—⟨⟩—CO₂Na
Spinning conditions:		
Dope flow rate:	3.0 cm³/min	3.0 cm³/min
Bore fluid composition:	Distilled water	Distilled water
Dimensions of spinneret (mm):	ID/OD 0.3/0.6	ID/OD 0.3/0.6
Air gap distance	5 cm	5 cm

B. Permeation experiments

The permeation experiments were carried out in a cross-flow filtration setup as described elsewhere [18]. Each of the membranes was first permeated with distilled water to check its permeability. Then for all three membranes, permeation experiments were carried out with 0.01 M NaCl (Merck, Darmstadt, Germany). The ionic solute rejections were analyzed using digital conductivity meter (WTW handheld meter model LF330).

C. Mathematical modeling

The Extended-Nerst Planck Equation (1) forms the basis for the description of the transport of ions or solutes inside the membranes. The equation (1) which includes Donnan expression; describes the partitioning of solutes between solution and membrane [7]. The terms represent transport due to diffusion, electric field gradient and convection respectively.

$$J_{si} = -\left(D_{i,p} \frac{dC_i}{dx} \right) - \left(\frac{z_i S C_i D_{i,p}}{R \cdot T} \cdot F \cdot \frac{d\psi}{dx} \right) + \left(K_{i,c} C_i J_s \right) \quad (1)$$

where J_{si} is the flux of an ion i (mol/m^2.s), $D_{i,p}$ is the diffusivity of the ion i in the membrane (m^2/s), z_i is the valence of the ion i (dimensionless), c is the ion concentration (mol/m^3), G is the gas constant (J/K.mol), F is the Faraday constant (9.648x10^{-4} C/mol), ψ is the electrical potential (V) and $K_{i,c}$ is the convective hindrance factor of membrane (dimensionless).

The solution of the above model requires three structural and electrical parameters namely: pore radius, r_p, effective ratio of membrane thickness to porosity, Ax/Ak, and the effective charge density, X_d. These parameters can be obtained by fitting the rejection data of uncharged and charged solutes. Once these parameters are obtained, the model can be used to predict the separation performance of ions or charged solutes in the system.

Based on Irreversible thermodynamics model which is used to describe the transport phenomena in the process in NF, Spiegler and Kedem [23] further expressed the flux of solute, J_s in a differential form when high concentration difference between retentate (rejection) and permeate exist, which shown in equation (2). By integrating the equation (2) across membrane thickness, equation (3) and (4) were derived. In this study, it is assumed that the real rejection is same as the observed rejection due to the low concentration of solute used. The solute concentrations at the membrane surface, C_m and in the bulk solution, C_b are assumed to be the same. It is because the effect of concentration polarization which decreases the driving force is not obvious at a very low concentration of aqueous solute solution used [24]. With this assumption, the equation was rearranged and described rejection (R) as equation (5).

$$J_s = -P'\left(\frac{dc}{dx}\right) + (1-\sigma)J_v C \qquad (2)$$

$$R = 1 - \left(\frac{C_p}{C_m}\right) = \frac{\sigma(1-F)}{1-\sigma F} \qquad (3)$$

With $\quad F = \exp(-\left(\frac{1-\sigma}{P}\right)J_v) \qquad (4)$

$$R = \frac{\sigma\left(1 - \exp\left(-\frac{1-\sigma}{P}J_v\right)\right)}{1 - \sigma \exp\left(-\frac{1-\sigma}{P}J_v\right)} \qquad (5)$$

Where P is solute permeability, C_p is solute concentration in the permeate, C_m is solute concentration in the fluid at feed on membrane interface, σ is reflection coefficient, J_v is the flux volume and C is the mean concentration over the membrane thickness.

III. RESULT AND DISCUSSION

The results of filtration performance are shown in Figure 1. The permeate flux versus the applied pressure for all the three membranes obtain a linear profile. The slope of the lines represents the water permeability value for each membrane. As shown, the pure water fluxes of cSMM blended membranes are significantly higher than the unblended membrane at different operating pressures, i.e. the normalized pure water fluxes for HF1 and HF2 were 4.6 and 5.5 L/m^2.h.Bar, respectively. These permeability values are relatively low but still within the range normally obtained with commercial NF membranes available which range from 1.3 to 50.5 L/m^{2}h.Bar [21].
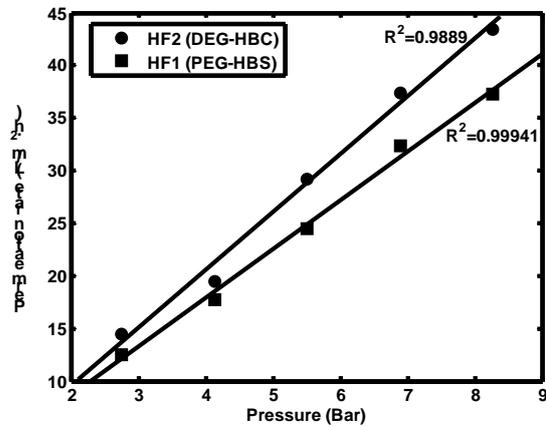

Figure 1. Water permeation performance of cSMM modified membranes at applied pressure range of 2.8-8.3 Bar
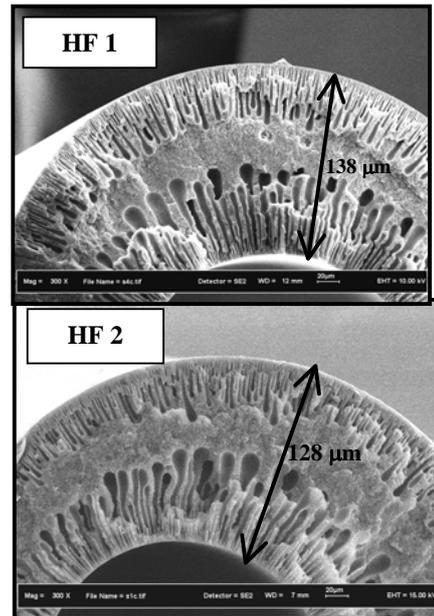

Figure 2. FESEM pictograph of hollow fiber cross-section at 300x magnification

The reason of DEGHBC (HF2) has higher pure water fluxes than PEGHBS (HF1) could be primarily attributed to the physical and morphology of fabricated membranes as observed via FESEM. From Figure 2, the FESEM pictograph estimated that the membrane thickness of HF2 is 127.7 μm whereas for HF1 is 138.3 μm. Hence HF1 have slightly thicker resistance in permeability compared to HF1, since the permeation occurs from outer to inner hollow fiber membrane.

The electrical property of self-fabricated membranes was determined using Teorell-Meyer-Sievers (TMS) model (equation (6)). TMS model is a rigorous approach that has been widely used to describe the membrane electrical properties (in the case of negatively charged membrane) by assuming a uniform radial distribution of fixed charges and mobile species [22]. With the combination with the extended Nernst-Planck model and the Donnan equilibrium theory, the parameters experimentally obtained (σ_{salt}) can be applied to determine the electrical property of membrane using NaCl electrolyte as aqueous feed solution, as follow:

$$\sigma_{salt} = 1 - \left(\frac{2}{(2\alpha-1)\xi + \sqrt{(\xi^2+4)}} \right)$$

(6)

Where

$$\alpha = \frac{D_{cation}}{D_{cation} + D_{anion}}$$

(7)

With α represent as the transport number of cations in free solution, D as the diffusion coefficient and ξ is the electrical properties of the membrane (negative unit).

σ_{salt} is determined directly from the experimental data of rejection (R) as a function of 1/Jv using one of the best-fitting methods (using MATLAB R14), which is shown in Figure 3. This is derived based on the irreversible thermodynamic model [23,24]. Based on the irreversible thermodynamic model, membrane is treated as a black box as no information about the membrane properties can be obtained from it. Hence, from the derive equation of (5), it is assume that the rejection of NaCl, (R) becomes equal to the reflection coefficient, σ (maximum solute rejection) when the volume flux, J_v is infinite as the filtration flow overtakes solution diffusion. Therefore, σ and P can be determined directly from the experimental data of R as a function of 1/Jv using one of the best-fitting methods.

In Figure 3, the rejection of 0.01M NaCl versus 1/Jv for both membranes was plotted. The electrical properties were then calculated based on the 0.01M NaCl rejection results, which is summarized in Table 2. It should be noted that the higher the electrical property (ξ), indicates the more negative charge and hence better removal of charge solutes. Shown from the results, addition of cSMM using PEGHBS

or DEGHBC has increased the electrical properties compared to pure PES (ξ=-0.5) [25]. For both cSMM types, it was found that the modification using cSMM of PEGHBS has higher charge compared to DEGHBC at this particular fabrication condition.
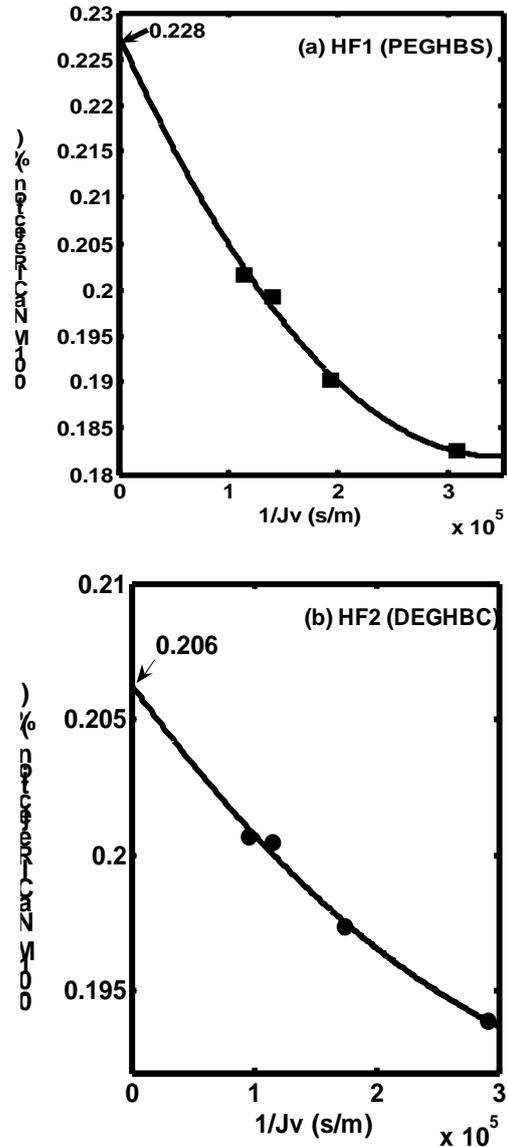

Figure 3. 0.01M NaCl Rejection performance of HF1 and HF2 towards flux

Table 2. Rejection mechanism parameter

Membrane	σ_{salt} (%)	D_{cation} (m^2/s)	D_{anion} (m^2/s)	Charge, ξ (negative)
HF1 (PEGHBS)	0.228	1.33x10^{-9}	2.03 x10^{-9}	1.61
HF2 (DEGHBC)	0.206	1.33x10^{-9}	2.03 x10^{-9}	1.49

IV. CONCLUSION

The first attempted PES hollow fiber blended with charged surface modifying macromolecules (cSMM) was successfully fabricated. This study concludes that PEGHBS and DEGHBS were successfully synthesized and having an end-capped that able to induce charge at membrane surface. From the modeling sodium chloride rejection mechanism, it was revealed that the sulfonate properties were found slightly higher charge than the carboxylate group as studied in this work.

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