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THEORETICAL ANALYSIS ON INTERACTING EFFECT OF STERIC AND DONNAN FACTORS IN NANOFILTRATION MEMBRANE SEPARATION SYSTEM

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Abstract. The separation performance of NF membrane system is found to be significantly dependent on the steric and charge effects. Previous studies have shown that the right combination of membrane pore size (steric effect) and its effective charge density (donnan effect) will lead to an optimum separation performance. Hence, the ability to produce nanofiltration membranes with optimized properties will certainly provide significant improvement in terms of membrane performance and processing cost reduction. Therefore, the main objective of this theoretical study is to investigate the interactive effect of membrane pore size (r_p) and membrane charge density, (X_d) towards the separation performance. Two general dimensionless parameters were used namely λ ($\lambda = r_s/r_p$) and ζ($\zeta = X_d/C_b$). The electrolyte transport through nanofiltration membranes is determined using a model based on the application of the extended Nernst-Planck equation coupled with Donnan-steric pore model (DSPM). A variety of salt solution with various pore size and charge effect was tested using the above-mentioned model. It was found that for the case of membranes with high effective charge density, the Donnan factor is more prominent for loose membranes. The contribution of the factor decreased with the increase of membrane pore size. Vice versa, for the lower charge density membrane, the effect of Donnan factor towards ion rejection could be neglected, regardless of membrane pore sizes.

Keywords: Nanofiltration, DSPM, membrane charge density, pore size, theoretical

Abstrak. Prestasi pemisahan sistem membran penuras nano didapati sangat bergantung kepada kesan sterik dan cas. Kajian terdahulu telah menunjukkan bahawa kombinasi yang tepat di antara saiz liang (kesan sterik) dan ketumpatan cas berkesannya (kesan Donnan) akan memberikan prestasi pemisahan yang optimum. Justeru itu, keupayaan menghasilkan membran penuras nano bersifat optimum akan memberikan pembaikan yang signifikan dari aspek prestasi membran dan pengurangan kos pemprosesan. Oleh itu, objektif utama kajian teoritikal ini ialah untuk menyelidik kesan interaktif saiz liang (r_p) dan ketumpatan cas membran, (X_d) terhadap prestasi pemisahan. Dua parameter tanpa dimensi telah digunakan iaitu λ ($\lambda = r_s/r_p$) dan ζ($\zeta = X_d/C_b$). Pengangkutan elektrolit melalui membran penuras nano tersebut ditentukan dengan menggunakan model liang sterik-donnan (DSPM). Pelbagai larutan garam dengan pelbagai saiz liang dan kesan cas diuji dengan menggunakan model tersebut. Kajian menunjukkan bahawa untuk kes membran dengan kapasiti cas berkesan yang tinggi, faktor Donnan didapati lebih penting untuk membran yang longgar strukturnya. Sumbangan faktor Donnan ini berkurangan dengan peningkatan saiz liang membran. Sebaliknya, untuk membran

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berketumpatan cas yang rendah, kesan faktor Donnan terhadap tolakan ion boleh diabaikan, tanpa bergantung kepada saiz liang.

Kata Kekunci: Penurasan nano, DSPM, ketumpatan caj berkesan, saiz liang, teoritikal

1.0 INTRODUCTION

Nanofiltration (NF), a pressure-driven membrane process, is a relatively new class of membranes which is considered as "loose" reverse osmosis (RO) membranes since its performance is intermediate between RO and ultrafiltration (UF) membranes. Most available commercial membranes are thin-film composites made of synthetic polymers containing charged groups. These functional groups affect membrane performance. Hence, separation mechanisms of NF are not only affected by steric (sieving), but also the electrical (Donnan) effects. This combined effects allow NF membranes to be effective for a range of separations of mixtures of small organic solutes (either neutral or charged) and salts [1].

As mentioned above, the separation mechanisms in NF membranes have been attributed to steric and Donnan effects. The sieving effects have been due to the existence of pores, which its size is closely to atomic scale. The Donnan effect, meanwhile, has been due to the charged nature of the membrane, contributed by functional groups of polyelectrolyte. So far, a lot of effort has been devoted to understanding the influence of these effects on the membrane separation performance, particularly for ions rejection, but yet have not been fully understood. Previous work [2] has also shown that the commercially available NF membranes have a wide ranging characteristics of pore sizes (0.4 nm to 1.5 nm), and effective charge density (0-50 mol/m^3). In subsequent work [3], it was shown that the selection of suitable membrane characteristics for specific processes will allow for higher efficiency and improvements in the process. Hence, the dependency of both steric and Donnan effects towards rejection behavior should be further clarified in order to produce the so-called "optimized" membrane parameters, which if it were to be used, would certainly help in reducing the cost of membrane applications in the industry.

In this study, we planned to further investigate the dependency of steric and Donnan effects on the ion rejection behavior using the modeling technique based on Nernst-Planck approach, in conjunction with Donnan-steric pore model (DSPM). For the model simulation purposes, two key structural parameters were chosen i.e. pore radius (r_p) and effective charge density (X_d), which represent steric and Donnan effects respectively. It is hoped that through this study, we could highlight some significance dependency between NF membrane characteristics, and the performance of NF system.

2.0 THEORETICAL BACKGROUND

Bowen *et al.* [4] proposed DSPM, which is based on the extended Nernst-Planck equation, for the process modeling of NF membranes. In this model, the membrane

was assumed to be porous, and a parabolic profile of solute velocity is fully developed in the pores. Therefore, the fluxes, concentrations, potential, and velocity were all defined as a radially averaged quantity.

The extended Nernst-Planck equation forms the basis for the description of the transport of ions/solutes inside the membranes. The equation can be written as:

$$j_i = -D_{i,p}\frac{dc_i}{dx} - z_i c_i D_{i,p} F \frac{d\psi}{dx} + K_{i,c} c_i V \tag{1}$$

where j_i is the flux of ion-*i*. This equation contains three terms due to contributions from diffusion, electro migration, and convection respectively. The hindered nature of ions due to diffusion and convection mechanisms is accounted by the terms of $K_{i,d}$ and $K_{i,c}$ respectively. This hindrance factors which are functions of ratio of solute over pore radius ($\lambda = r_s/r_p$) are related to the hydrodynamic coefficient, K^{-1}, enhanced drag and lag coefficient, G of a spherical solute moving inside an infinite pore length of the membrane [5]. The extended Nernst-Planck equation can be solved by numerical integration for $x = 0$ to $x = \Delta x$ (with Δx the effective membrane thickness in meter), taking into account electroneutrality requirements and equilibrium conditions at both interfaces of feed-membrane, and membrane-permeate (taken as a combination of both Donnan and steric effects).

By rearranging equation (1), we will obtain the expression for electrical potential gradient and concentration gradient of ion-*i*:

$$\frac{dc_i}{dx} = \frac{J_v}{D_{i,p}}\left(K_{i,c}c_i - C_{i,p}\right) - \frac{z_i c_i}{RT} F \frac{d\psi}{dx} \tag{2}$$

$$\frac{d\psi}{dx} = \frac{\sum_{i=1}^{n} \frac{z_i J_v}{D_{i,p}}\left(K_{i,c}c_i - C_{i,p}\right)}{\frac{F}{RT}\sum_{i=1}^{n}\left(z_i^2 c_i\right)} \tag{3}$$

The equilibrium partitioning at the membrane interface will be taken to be a combination of the Donnan and steric effects.

$$\frac{\gamma_i c}{\gamma_i^o c_i^o} = \phi \exp\left(-\frac{z_i F}{RT}\Delta\psi_D\right) \tag{4}$$

where

$$\phi = (1-\lambda)^2 \tag{5}$$

The above equations are solved with the following electroneutrality conditions:

In feed,
$$\sum_{i=1}^{n} z_i C_{i,w} = 0 \tag{6}$$

In membrane,
$$\sum_{i=1}^{n} z_i c_i = -X_d \tag{7}$$

In permeate,
$$\sum_{i=1}^{n} z_i C_{i,p} = 0 \tag{8}$$

Finally, by taking into account the concentration polarization phenomena at the entrance of membrane wall, the rejection of ion-*i* can be obtained by:

$$R_{real} = 1 - \frac{C_{i,p}}{C_{i,w}} \tag{9}$$

Further details on the solution of this model can be found elsewhere [2-4].

3.0 MODEL SIMULATION METHODOLOGY

This theoretical study is conducted with the intention to analyze the interactive effect of both steric and Donnan factors towards the rejection performance. The steric effects upon rejection performance is evaluated through dimensionless parameters of lamda, which is equal to a ratio of membrane pore radius to solute stoke's radius: $\lambda = r_s/r_p$. Meanwhile, the donnan factors attributed by dimensionless parameters of zeta, which is equal to a ratio of membrane effective charge density to bulk concentration: $\zeta = X_d/Cb$. The effect of these parameters on the ion rejection performance was tested for a whole range of NF membrane spectrum. To achieve this purpose, we have divided the NF membrane system into four extreme cases:

- System A: High λ, high ζ (HL, HZ); which represents tight membrane structure with high membrane charge density
- System B: High λ, low ζ (HL, LZ); which represents tight membrane structure with low membrane charge density.
- System C: Low λ, high ζ (LL, HZ); which represents loose membrane structure with high membrane charge density.
- System D: Low λ, low ζ (LL, LZ); which represents loose membrane structure with low membrane charge density.

The NF membrane characteristics chosen were identified based on the range reported previously [2] for commercial membranes with the effective pore radius, r_p, ranging from 0.5 to 1.5 nm, and effective charge density, X_d, from 0 to 50 mol/m^3.

The simulation was carried out using the above-mentioned DSPM model, based on the parameters of membrane structure criteria as follows:

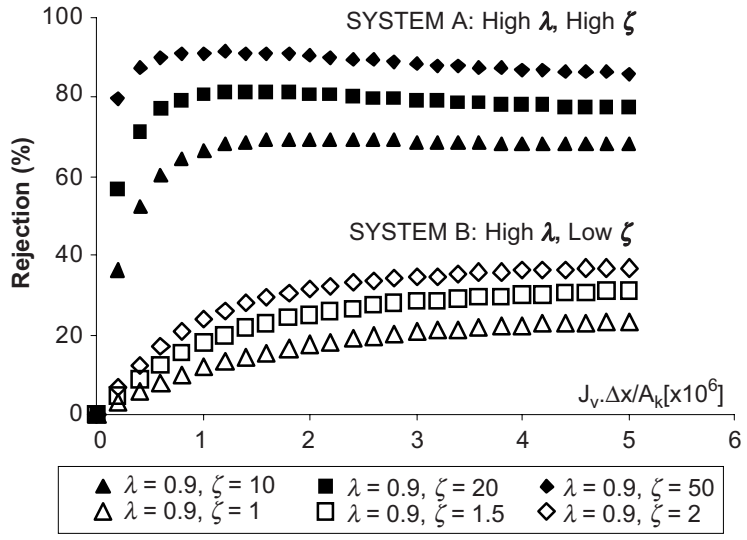
- Pore size, r_p : r_p min = 0.5 nm and r_p maximum = 1.5 nm
- Hypothetical solutes: The r_s values are determined based on the values of selected λ.
- Effective charge density, X_d between 0 to 50 mol/m^3.
- Membrane thickness per porosity, $\Delta x/A_k$ = 10 μm
- Bulk concentration, C_b – = 10 mol/m^3
- Flux range : 0 – 50 $\times$ 10^{-6} m^3/m^2.s
- Low λ values : 0.1, 0.15, 0.2
- High λ values : 0.7, 0.8, 0.9
- Low ζ values : 1, 1.5, 2
- High ζ values : 10, 20, 50

4.0 RESULT AND DISCUSSION

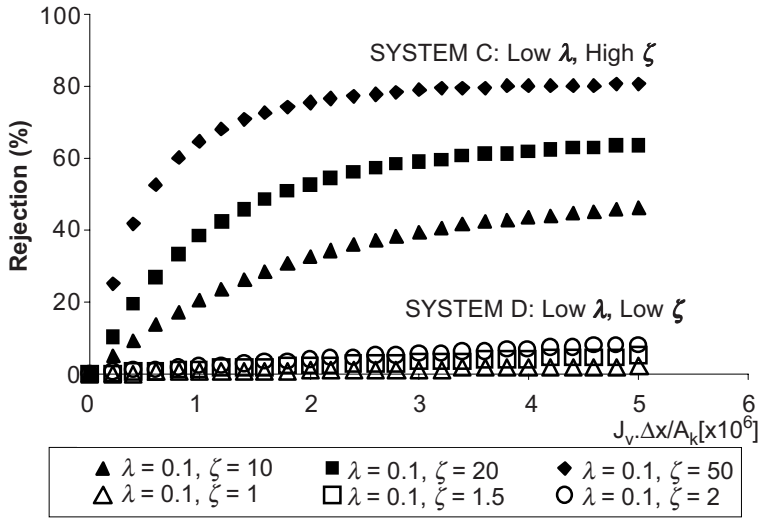
In this theoretical study, four extreme cases were considered in order to observe the interactive effect contributed by steric and Donnan effects. System A represents tight membrane structure and high membrane charge density (high λ, high ζ). System B represents tight and low charge density membrane (high λ, low ζ)). System C represents loose structure and high charge density membrane (low λ, high ζ) while system D represents the loose structure and low charge density membrane (low λ, low ζ).

Figure 1 shows a plot of % of rejection versus the normalized flux ($J_v \Delta x/A_k$) with membranes having : 1(a) fixed high λ value of 0.9, at various high ζ (ζ = 10, 20, 50 mol/m^3) and low ζ values (ζ = 1, 1.5, 2.0 mol/m^3); and 1(b) fixed low λ value of 0.1, at various high ζ (ζ = 10, 20, 50 mol/m^3) and low ζ values (ζ = 1, 1.5, 2.0 mol/m^3). This analysis will highlight the contribution of Donnan factor at various cases of λ and ζ. It was clearly shown that the ion rejection of both membrane systems (high λ and low λ), gain a significant increment with the increasing of ζ. By comparing the systems A and C, it was noticeable that the effect of Donnan factor is more prominent in system C. It can be postulated that the Donnan factor, which is contributed by effective membrane charge density plays more significant role in a looser membrane structure. The contribution of the Donnan factor is decreasing with the decrement of membrane pore size. Another comparison is made between the systems B and D. In system D (low λ low ζ), it seems that the ion rejection performance is not affected by the membrane charge density. Meanwhile, in system B (high λ and high ζ), only a slight increment in rejection is shown. From these observation, we learned that the

contribution of Donnan factors could be neglected for the cases of low charge density membrane, regardless of the membrane pore sizes.



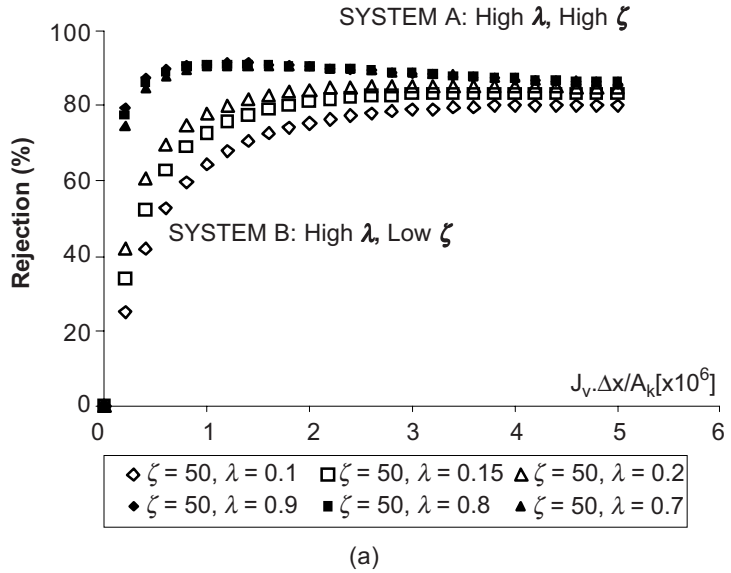
(a)



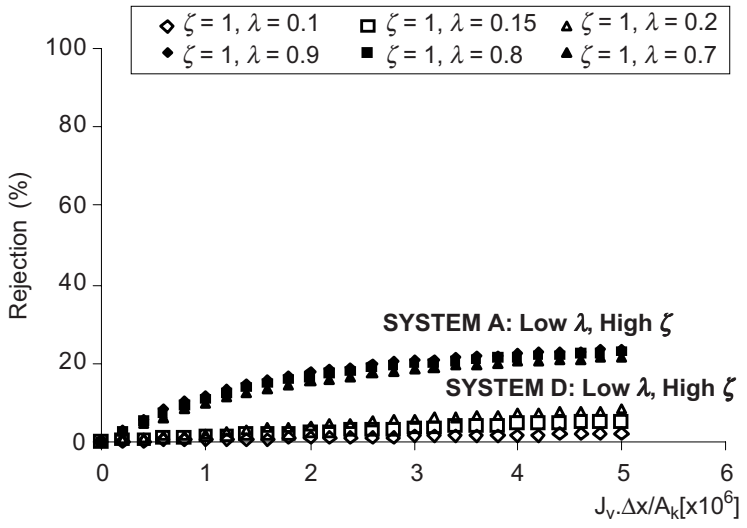
(b)

Figure 1 The graphs shows that % of rejection versus normalized flux in order to observe the effect of Donnan factor at various λ and ζ. (a) fixed high $\lambda = 0.9$, various ζ, High $\zeta(\zeta = 10, 20, 50$ mol/m^3), Low $\zeta(\zeta = 1, 1.5, 2$ mol/m^3), (b)) fixed low $\lambda = 0.1$, various ζ, High $\zeta(\zeta = 10, 20, 50$ mol/m^3), Low $\zeta(\zeta = 1, 1.5, 2$ mol/m^3)

Figure 2 shows a plot of % of rejection versus the normalized flux ($J_v.\Delta x/A_k$) with membranes having : 2(a) fixed high ζ value of 50 mol/m^3, at various high λ ($\lambda = 0.9$,



(a)



(b)

Figure 2 The graphs shows that % of rejection versus normalized flux in order to observe the effect of steric factor at various λ and ζ. (a) fixed high $\zeta = 50$ mol/m^3, various λ, High λ($\lambda = 0.7, 0.8, 0.9$), Low λ($\lambda = 0.1, 0.15, 0.2$), (b) fixed low $\zeta = 1$ mol/m^3, various λ, High λ($\lambda = 0.7, 0.8, 0.9$), Low λ($\lambda = 0.1, 0.15, 0.2$)

0.8, 0.7) and various low λ (λ = 0.1, 0.15, 0.2); and 2(b) fixed low ζ value of 1, at various high λ (λ = 0.9, 0.8, 0.7) and various low λ (λ = 0.1, 0.15, 0.2). This analysis will highlight the contribution of steric factor at various cases of λ and ζ. For all systems, it can be postulated that the steric effects did not contribute so much in ion rejection performance, regardless of the membrane charge density. This finding contradicted with the previous works [6], that highlighted both steric and Donnan factor as playing equal roles in membrane separation behavior. However, a low increment in ion rejection performance with the increasing of λ is shown by the systems C and D. These results at least clarify the contribution of steric effect, which is obviously more significant in a higher membrane charge density, regardless of the membrane pore size.

Based on these results, the optimum NF membranes should be loose with high charge density. The loose structure will help to increase the permeate fluxes at lower applied pressure while the high charge density will increase the rejection, especially of multivalent ions. The loose structure will definitely reduce the operating and capital costs as have been studied previously [7] since the requirement for high pressure pumps and higher number of modules can be reduced. Further work on NF membrane fabrication should look towards achieving NF membranes with this type of properties.

5.0 CONCLUSION

In this study, NF membranes with high effective charge density (Donnan factor) will result in higher rejection of ions. The contribution of the factor, however, decreased with the increase of membrane pore size. Vice versa, for the lower charge density membrane, the effect of Donnan factor towards ion rejection could be neglected, regardless of membrane pore sizes. Based on this results, it is recommended that NF membranes should be produced with high charge density capacity and preferably, loose or high pore radius.

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