Flux Profile of Graphene Oxide Based Polymer Membrane

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***Abstract*—In this work, dead-end filtration method is used to determine the water flux of commercial ultrafiltration membrane which are MK membrane, BN membrane PZ membrane, and also graphene oxide membrane. Polymer membrane had been widely used in membrane bioreactor and other industrial purposes such as wastewater treatment. One of the characterization of polymer membrane is to study the flux profile of the membrane. It is expected that different flux profile will be obtained for different types of polymer membrane. Generally, membrane with high hydrophilicity will show the ultrafast flow of water across membrane and it is due to low friction generated between water and hydrophobic region of the membrane itself. From this research, BN membrane shows highest water flux (the highest peak) at 174.95 L/m2.h.bar while the water flux for MK membrane (120.72 L/m2.h.bar), PZ membrane (14.39 L/m2.h.bar) and GO membrane (8.89 L/m2.h.bar).**

***Keywords*— graphene oxide membrane, ultrafiltration membrane, water flux profile.**

I. Introduction

The technology of membrane separation has grown rapidly over the past five decades especially for industrial purposes. Membrane technology is a rapidly growing research area with several real time applications such as desalination and water purification. Scientists and engineers have been working towards the development of this technology for a more cost-effective and a precise membrane. Membrane can be divided into two categories which is polymeric membrane and also inorganic membrane[1]. Table 1 shows the type of membrane available and their application. There are several number of membrane separation processes that are currently being used such as microfiltration (MF), reverse osmosis (RO), forward osmosis (FO), nanofiltration (NF), pervaporation (PV), ultrafiltration (UF), vapor separation (VP), membrane gas separation and also membrane distillation.(MD)[2] The advantages of using membrane separation is because the cost of operating is low[3], high selectivity and high permeation [4]as well as it is better in removal efficiency of micro pollutants.

Table 1
Type of membrane and its uses

Type of membrane	***Application/ Uses***
Polymeric membrane	Ultrafiltration, nanofiltration, reverse osmosis, and gas separation.
Hybrid Organic-inorganic membrane	Fuel cell
Inorganic membrane	Gas separation, carbon dioxide removal/capture
Inorganic membrane	Hydrogen, H2 generation
Nanowire inorganic membrane	Oil-water separation
Zeolite membrane	Reverse Osmosis
CNT membrane	Desalination, energy generation, biomolecules separation.

Ultrafiltration membrane were widely used for industrial purposes for example membrane bioreactor, condensation and purification of bio product as well as pre-treatment in desalination process with reverse osmosis membrane [5]. Ultrafiltration membrane is used to separate or removed larger molecule, colloid substances and also organic and inorganic molecules. Ultrafiltration and microfiltration is somehow related process where the ultrafiltration were used to separate or remove small colloid particle while microfiltration filter larger molecules[6]. The ultrafiltration membrane have a pore size range between 0.001 to 0.02 μm and the pressure difference is between 0.1 to 1.0 MPa [7].

Ultrafiltration membrane has its great performance in term of its flux profile. But the problem start to arrive when the ultrafiltration membrane filter large compound such as colloid molecules. The flux of the membrane drop drastically due to the blockage of the pores of membrane and thus caused fouling problem. The colloidal molecules and macromolecules deposited at the surface of the membrane. This slow down the permeation through the membrane.

There are factor that will effect performance of the ultrafiltration membrane such as the flow of fluid across the surface of membrane, the operating pressure as well as the operating temperature. According to study conducted by [8], ultrafiltration membrane is made from polymer that have chemical and thermal stability which is included Polyvinylidene fluoride (PVDF) membrane, polyethersulfone (PES) membrane, polyacrylonitrile (PAN) membrane, polyimides (PIs), polysulfone (PSF) and also polyvinyl chloride (PVC). The problem regarding the membrane is that they are hydrophobic and thus will reduce the permeate flux and lead to fouling of membrane.

Graphene oxide based polymer membrane has gain increasing interest in study in the last five years due to its high potential that can be used for separation of compound and also for filtration purposes. Graphene-derived functional membranes have recently been identified to be excellent candidate materials for filtration and separation applications because of their signature, although not well characterized, and also their porous microstructures [9]. With excellent chemical and mechanical properties, graphene-based thin films can be applied as separation membranes or protective barriers in environmental and chemical engineering applications. Graphene oxide (GO) is a cost effective precursor for large scale production of graphene-based materials.

Besides, graphene oxide is much cheaper than graphite and it is also shows excellent characteristic of membrane and also offer much higher potential which can be used in real application.[4]. Table 2 shows graphene based membrane and their application. Graphene oxide produced now is become more attractive in polymer membrane activity due to its hydrophilic characteristic that changes or improved the smoothness of the surface of polymer membrane [2]. This statement is also supported by researchers (Yoo, Shin, Lee, & Park, 2017), which is stated that graphene oxide acts as a good material for polymer membrane. According to (Yang et al., 2017), it stated that graphene oxide membrane showed a water flux of ⟦10⟧^6 g/m2/s and also salt rejection rate of almost 100%. (Yang et al., 2017) also stated that the graphene oxide membrane can provide an ultrafast water transport due to the hydrophobic non-oxidized part of graphene oxide on the membrane and the ultrafast flow of water occur due to low friction generated between water and hydrophobic region graphene oxide. Figure 1 below show the water flow through graphene membrane and graphene oxide membrane[10]

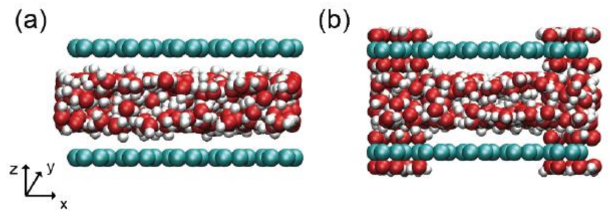

Figure 1: water flow through (a) graphene membrane (b) graphene oxide membrane

Table 2

Graphene based membrane and their applications.

Membrane type	*Application*
Graphene based membrane	Selective ion-transport
Graphene membrane	Selective gas transport
Graphene oxide membrane	Vapor transport Hydrogen separation Desalination
Graphene oxide nanoplatelet membrane	Water transport
Ozonated graphene oxide membrane	Proton exchange
Graphene oxide membrane filters	Bacterial inactivation and removal

II. METHODOLOGY

A. Chemicals and membranes.

The commercial UF membrane that had been used in the experiment are MK membrane, BN membrane and PZ membrane. Graphene oxide membrane are obtained from previous lab work done by Dr Hayati's student. Ultrapure water, ethanol and sodium hydroxide are used for membrane rinsing.

B. Experimental set-up and procedure.

The performance of GO nanoplates blended ultrafiltration membranes was characterized by measuring the pure water flux (PWF). The dead-end filtrations were carried out in a commercial stirred cell (Amicon 8050,Millipore, USA).A dead-end stirred cell system was used to study the membrane filtration performance. The system consisted of a membrane with surface area of 14.2 cm2 and a filtration cell with a total volume of 50 mL. The membrane was placed in the cell and then the cell fitted with a pressure gauge. Pressurized nitrogen gas was employed to force the liquid through the membrane and the liquid were collected in a beaker. The feed solution was stirred at a rate of 100 rpm. The suspended bar impeller inside the cell was driven by a magnetic agitator (MR Hei-standard, Heidolph, Germany). All of this experiment were performed at room temperature at about 23 ± 1◦C and average of three replicates was reported. New membrane were used for each experiment. [11]

C. Membrane preparation.

For preparation of commercial membrane, MK membrane were first cleaned with 0.1% sodium hydroxide, NaOH solution for 1 hour, and then rinsed by using ultrapure water. For BN membrane and PZ membrane, the membrane were cleaned with ethanol for 1 hour and then rinse with ultrapure water. For graphene oxide membrane, the membrane were cleaned by using ultrapure water and left overnight.

D. Calculated parameters

The flux profile of membrane were calculated by using equation below:

$$J: \frac{V}{A\ .\ \Delta t}.P$$

where V is the volume of water collected (mL), A is the membrane effective area (m2) and Δt is the permeation time (h) and P is the operating pressure (bar).

III. RESULTS AND DISCUSSION

A. The flux profile of commercial UF membrane

Generally, it can be said that different type of membrane have different flux profile. In this study, we have been determined the flux profile for three type of commercial UF membrane, which is MK membrane, PZ membrane and BN membrane, and also flux profile for GO membrane. The result obtained from the experiment conducted is tabulated in table below. The result were repeated three time to obtain the average and new membrane were used for each of the experiment.

Basically, the water flux of membrane is depends on several criteria such as its membrane pore sizing and also the structure of the membrane and the criteria may be controlled by two factors which are the hydrophilicity and also viscosity of the polymer solution [12]

Table 2 shows the result obtain for MK membrane. The average were calculated and tabulated below.

Table 2
MK membrane water flux.

Volume (mL)	*Time (min)*	*Time (min)*	*Time (min)*	*Average (min)*
0	0	0	0	0
5	1.37	1.57	2.22	2.12
10	1.19	1.51	1.53	1.41
15	1.28	1.42	2.06	1.59
20	1.26	1.46	2.01	1.58
25	1.30	1.50	2.03	2.01
30	1.38	1.52	2.08	2.06
35	1.33	1.53	1.59	1.48

Table 3 shows the result obtain for BN membrane. The average were calculated and tabulated below.

Table 3
BN membrane water flux.

Volume (mL)	*Time (min)*	*Time (min)*	*Time (min)*	*Average (min)*
0	0	0	0	0
5	1.26	1.21	1.22	1.23
10	1.26	1.16	1.17	1.20
15	1.28	1.11	1.24	1.21
20	1.23	1.13	1.14	1.17
25	1.28	1.13	1.22	1.21
30	1.28	1.16	1.22	1.22
35	1.32	1.18	1.16	1.22

Table 4 shows the result obtain for PZ membrane. The average were calculated and tabulated below.

Table 4
PZ membrane water flux.

Volume (mL)	*Time (min)*	*Time (min)*	*Time (min)*	*Average (min)*
0	0	0	0	0
5	16.46	16.20	13.49	15.38
10	12.51	14.39	11.41	13.17
15	15.02	15.24	15.39	15.22
20	14.15	14.39	15.02	14.52
25	14.56	14.42	15.08	15.09
30	15.24	14.37	14.37	15.01
35	14.38	14.27	14.46	14.37

Table 5 shows the result obtain for GO membrane. The average were calculated and tabulated below.

Table 5
GO membrane water flux.

Volume (mL)	*Time (min)*	*Time (min)*	*Time (min)*	*Average (min)*
0	0	0	0	0
2	4.12	5.02	4.48	4.54
4	2.38	3.11	3.39	3.36
6	3.24	4.48	4.24	4.49
8	2.24	5.10	3.52	4.02
10	3.28	7.19	4.05	5.24
12	3.50	8.48	4.33	5.44
14	3.55	9.34	4.52	6.20

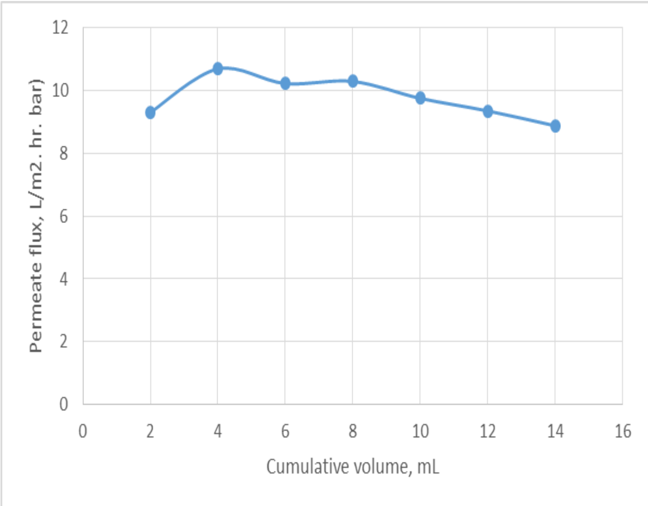

Figure 2: water flux profile for graphene oxide membrane.

Comparison of flux between those three types of commercial UF membrane and graphene oxide membrane were shown in Figure 3 below.

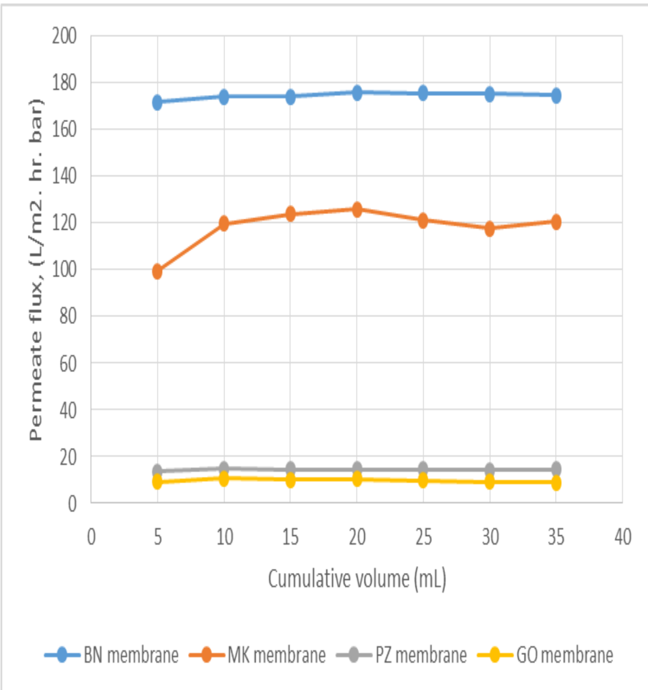

Figure 3: permeate flux against volume for different type of

membrane.

According to the comparison between those commercial ultrafiltration membranes, it shows that BN ultrafiltration membrane shows a highest water flux profile compared to MK membrane, PZ membrane and graphene oxide membrane. From this figure, it can be concluded that each membrane possessed an increase in water flux. The water flux for BN membrane (the highest peak) are 699.78 L/m2.h.bar while the water flux for MK membrane (482.88 L/m2.h.bar), GO membrane (88.85 L/m2.h.bar) and PZ membrane (57.57 L/m2.h.bar). The large surface pore size, high porosity, hydrophilic surface of the membranes were believed to weaken the resistance of water to permeate through the membranes and hence increase its water permeability. A slight decrease in pure water flux was observed for all membranes during initial filtration step, which might be due to precompaction of membrane performed under pressure before use. The pure water fluxes of BN and MK membranes are more than two times higher than that of pristine PZ membrane. This might be probably due to the high hydrophilicity and well vertically interconnected finger-like pores in BN and MK membranes.

The water flux of graphene oxide membrane were measured. From previous studies, it stated that graphene oxide membrane shows a high water flux. The water flux through graphene oxide membrane is occur due to the low friction between water and hydrophobic region of graphene oxide membrane [13]. Although graphene oxide membrane consist of larger hydrophobic region in the nanochannel, the decreased in water permeability was still observed.

However, a result of decreased in water flux is obtain during conducting the experiment. The decrease in initial water flux was observed constantly in our lab but rarely reported in previous studies [14]. A decrease in the initial pure water of rGO membranes and the water permeation of the membranes shows that it reach a steady state in less than an hour. Besides, the cause of the flux reduction was not further examined in their studies. Based on observation from previous studies, it shows that the membrane undergo compaction during filtration which then resulted in narrower wrinkles and a flux decline in the membrane substrates.[15], [16]. These are more likely due to the tightening of the nanochannels and increase in membrane surface hydrophobicity, for an example the water inlet of graphene oxide membranes. The tightening and more hydrophobicity is then prevent the water from flowing through the nanochannels. However, water permeation across narrowed nanochannels is still disputable [13]

IV. Conclusion

Based on the result obtained, it can be concluded that different type of membrane possessed different water flux profile. The water flux is mainly depends on several criteria which are membrane pore sizing and also the structure of the membrane and the criteria may be controlled by two factors which are the hydrophilicity and also viscosity of the polymer solution. BN membrane shows the highest water flux compared to other ultrafiltration membrane which are MK membrane, PZ membrane and also GO membrane. This shows that the BN membrane possessed high hydrophilicity compared to other membrane. .

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