SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF REDUCED
GRAPHENE OXIDE MEMBRANE FOR HUMIC ACID REJECTION

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Philosophy

Faculty of Science
Universiti Teknologi Malaysia

MARCH 2018

To my beloved family

ACKNOWLEDGEMENT

First and foremost, I am grateful to Allah swt for giving me chance to complete my research.

My deepest gratitude goes to my supervisor, Prof. Dr. Madzlan Aziz who expertly guiding me throughout this research. His unwavering support and mentorship have been major driving force for me to finish this research.

Also, I would like to thank my friends for always helping and giving ideas in my research. My appreciation also extends to all staffs from Universiti Teknologi Malaysia (UTM).

Not forgetting, my beloved family. Thank you for the non-stop moral support that have been given. Without all the supports, this research might not be finished.

ABSTRACT

Polyethersulfone (PES) has received tremendous attention in water treatment because it has excellent membrane-forming capability. However, PES is naturally hydrophobic which tends to increase the potential of fouling. Therefore, in this study, a modification was carried out by adding reduced graphene oxide (rGO) into the polymer matrix to improve the hydrophilicity of the membrane, thus reducing the fouling problem. The effect of reduction time on the properties of rGO was investigated. Graphene oxide (GO) was prepared via modified Hummer's method and it was reduced using 0.5 M sodium borohydride ($NaBH_4$). The effects of different reduction times (8, 16, 24 and 32 hours) were studied. The prepared rGO was then added into PES to produce membrane for ultrafiltration process. Polyvinylpyrrolidone (PVP) was added into the polymer matrix to study the effect of the material on the pores formation. The membrane was prepared using phase inversion method. X-ray diffraction (XRD), attenuated total reflectance Fourier-transform infrared spectroscopy (ATR FTIR), field emission scanning electron microscope (FESEM) and energy dispersive X-ray spectroscopy (EDX) were used to characterize the material. It was found that the interlayer spacing of GO was reduced from 7.87 to 3.68 Å after reduction process due to the removal of some of the functional groups from the material. The FTIR peak at 1718 cm^{-1}, attributed to the carbonyl (C=O) group, was absent after GO was reduced. The morphology of GO showed that the surface was smooth and had wrinkles while rGO was rough and agglomerated. EDX results suggested that the percentage of oxygen was lower due to effective reduction process. All the membranes were characterized using scanning electron microscopy (SEM), water contact angle, water flux and humic acid (HA) rejection. Based on the SEM of membrane cross section, it was found that the addition of PVP greatly improved the formation of pores. When rGO was added, the finger-like porous sub-layer increased. Besides that, the hydrophilicity showed a significant improvement after rGO was introduced into the polymer matrix. PES/rGO 24 hour showed the greatest contact angle (32.99°). Meanwhile, PES/GO showed the highest water flux (174.29 L/m^2h). Nevertheless, in terms of HA rejection, PES/rGO 24 hour showed the best performance where the rejection reached up to 46.88% as compared to that of PES/GO which was only 24.68%.

ABSTRAK

Polietersulfon (PES) telah mendapat banyak perhatian dalam rawatan air kerana ia boleh membentuk membran yang sangat baik. Walau bagaimanapun, PES asli adalah hidrofobik yang cenderung meningkatkan potensi pembusukan. Oleh itu, dalam kajian ini, pengubahsuaian telah dijalankan dengan menambah grafin oksida terturun (rGO) ke dalam matriks polimer untuk memperbaiki sifat hidrofilik membran, dengan itu mengurangkan masalah pembusukan. Kesan masa penurunan terhadap sifat rGO telah dikaji. Grafin oksida (GO) telah dihasilkan melalui kaedah Hummer terubahsuai dan ia diturunkan menggunakan natrium borohidrida ($NaBH_4$) 0.5 M. Kesan masa penurunan yang berlainan (8, 16, 24 dan 32 jam) telah dikaji. Bahan rGO yang terhasil kemudian ditambah kepada PES untuk menghasilkan membran bagi proses ultra-penapisan. Polivinilpyrrolidon (PVP) telah ditambah ke dalam matriks polimer untuk mengkaji kesan bahan tersebut terhadap pembentukan liang. Membran telah disediakan dengan kaedah penyongsangan fasa. Pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier pantulan total dilemahkan (ATR FTIR), mikroskopi elektron pengimbas pemancaran medan (FESEM) dan spektroskopi serakan tenaga sinar-X (EDX) telah digunakan untuk mencirikan bahan. Didapati jarak antara lapisan GO berkurang dari 7.87 Å ke 3.68 Å selepas proses penurunan kerana sebilangan kumpulan berfungsi telah terkeluar dari bahan. Puncak FTIR pada 1718 cm^{-1} yang menunjukkan kumpulan karbonil (C=O) tidak hadir selepas GO terturun. Morfologi GO menunjukkan bahan tersebut mempunyai permukaan yang licin dan berkedut manakala rGO lebih kasar dan bergumpal. Hasil keputusan EDX mancadangkan bahawa peratusan oksigen telah berkurang oleh kerana proses penurunan yang berkesan. Semua membran dicirikan dengan menggunakan mikroskopi elektron pengimbas (SEM), sudut sentuh air, fluks air dan penolakan asid humik (HA). Berdasarkan SEM keratan rentas membran, didapati penambahan PVP telah meningkatkan pembentukan liang dengan baik. Apabila rGO ditambah, lapisan berliang seperti jejari telah meningkat. Selain itu, hidrofilik menunjukkan peningkatan yang ketara selepas rGO ditambah ke dalam matriks polimer. PES/rGO 24 jam menunjukkan sudut sentuh air yang terbesar (32.99^o). Sementara itu, PES/GO menunjukkan fluks air yang tertinggi (174.29 L/m^2h). Namun, dari segi penolakan HA, PES/rGO 24 jam menunjukkan prestasi terbaik di mana penolakan mencapai sehingga 46.88% berbanding PES/GO dengan hanya 24.68%.

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LIST OF ABBREVIATIONS

EDX   -   Energy dispersive X-ray spectroscopy

FESEM   -   Field Emission Scanning Electron Microscopy

FTIR   -   Fourier transform infrared

GO   -   Graphene oxide

SEM   -   Scanning Electron Microscopy

HA   -   Humic acid

NOM   -   Natural organic matter

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Natural organic matter can cause an unpleasant odor and taste in water (Shankar *et al.*, 2017). The major species of NOM that has caught various attention from researchers are humic substances (HS). HS can be further categorised into three categories which are humin, humic acid (HA) and fulvic acid (FA) (Lowe and Hossain, 2008; Hamid *et al.*, 2011). Researchers always used HA in the studies of membrane performance in water treatment because it is the major species in NOM (Hamid *et al.*, 2011). HA is the main result of the degradation of plants and animals. This substance will then enter the water surface through rainwater run-off. HA is a very complicated mixture which it cannot be illustrated by any single formula. However, HA is believed to have a high level of carboxyl $(-COOH)$ and phenolic hydroxyl $(-OH)$ groups which attached to aromatic rings (Szymanski *et al.,* 2016). HA does not contribute to severe problem until it reacts with chlorine during chlorination process in conventional water treatment process which forms carcinogenic by-products such as trihalomethane (THM) and haloacetic acid (HAA) (Lowe and Hossain, 2008). Exposure to the aforementioned by-products can lead to serious diseases like cancer, miscarriages and nervous system complications (Hamid *et al.*, 2011). Hence, membrane treatment is an alternative water treatment process to remove the pollutants (Sathish *et al.,* 2015).

Thus, it is vital to make a suitable selection of polymer. Polyethersulfone (PES) has great membrane-forming and excellent physicochemical properties which lead it to be used widely as a membrane in water treatment (Forati *et al.,* 2014).

Unfortunately, PES suffer from fouling that will affect the performance of the membrane (Zinadini *et al.,* 2014). Therefore, it is suggested that PES can undergo a few modification to overcome the fouling problem such as blending with amphiphilic polymer (Forati *et al.*, 2014), blending with hydrophilic polymers (Peyravi *et al.,* 2012), grafting with hydrophilic monomer or blending with inorganic nanoparticles (Zinadini *et al.*, 2014).

Graphene oxide (GO) is a hydrophilic material as it has hydrophilic groups attached to it. Furthermore, GO also able to improve the roughness as well as mechanical strength of the host polymer (Zinadini *et al.*, 2014). Meanwhile, reduced graphene oxide has hydrophobic characteristics. Therefore, PES is suggested to undergo modification with GO and rGO to improve the hydrophilicity of the membrane.

1.2   Problem Statement

Currently, there are a lot of conventional methods to eliminate HA from water which includes coagulation, adsorption, Fenton oxidation, TiO_2 photocatalysis, biological treatment, membrane filtration, UV-photolysis and ozonation (Zhang *et al.*, 2017). Nevertheless, some of this process suffers from several disadvantages. For example, in coagulation process, some metal ions from the metallic compounds used might enter the treated water and lead to health risk (Zhang *et al.*, 2017). Nowadays, membrane technology has been accepted globally as an alternative for potable water production and wastewater reuse (Guiying *et al.*, 2016). The interest in the use of membranes for microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) has increased in the water treatment process due to the need for potable drinking water supply (Lowe and Hossain, 2008). In this process, pressure is used as the driving force to separate contaminants from water supplies (Lowe and Hossain, 2008). Unfortunately, fouling has been a significant problem for membrane filtration technologies (Guiying *et al.*, 2016). Thus, a right choice of polymer host is essential.

PES has great thermal and hydrolytic stabilities with superior mechanical and film-forming properties (Cao *et al.*, 2009). Therefore, it has been used widely as a membrane for water treatment (Sadeghi *et al.*, 2013; Susanto and Ulbricht, 2009). However, the low hydrophilicity characteristics of PES will lead the membrane to fouling problem and deteriorates the final performance (Rahimpour *et al.*, 2008). Fouling will have a strong adhesion on the surface as well as in the pores of hydrophobic membrane. Thus, foulants will give rise to fouling in membrane which then deteriorates the selectivity and flux (Kumar *et al.*, 2016). Besides foulants, surface characteristics (roughness and hydrophilicity), feed solution chemistry and process conditions also lead to fouling. Therefore, to avoid membrane fouling many approaches are proposed such as a proper selection of polymer host, modification of operating parameters and process fluid pretreatment (Vatanpour *et al.*, 2014). Study shows that the major factor of membrane fouling is affected by the surface characteristics. To reduce fouling, the hydrophilicity of the membrane need some enhancements because most foulants are hydrophobic in nature (Rana and Matsuura, 2010).

Graphene promises that it can improve the physicochemical properties of polymers by forming interfacial bonding between graphene layers and the polymer matrix. This bonding will determine the final properties of graphene/polymer composites (Kuilla *et al.*, 2010). Unfortunately, pristine graphene is not suitable in forming homogeneous composite because it agglomerates during the process (Shah *et al.*, 2015). Therefore, it is expected that the modified graphene can be dispersed easily to form nanocomposites (Shah *et al.*, 2015). For instance, GO has hydrophilic characteristics which causing them to readily swell and disperse in water. However, there are few factors which affect the dispersion of graphene which includes composite preparation technique, type of modification and the presence of polar groups in polymer and filler (Shah *et al.*, 2015).

Since PES is hydrophobic, GO is recommended to undergo chemical reduction to decrease the oxygen functional groups. The reduction process will cause the surface of rGO become hydrophobic (Liu *et al.*, 2011). Therefore, this property is compatible with the polymer. However, it is believed that the residual oxygen functional groups

on rGO will give hydrophilic property in the polymer matrix which is important for the membrane performance and forming a hydrogen bond with PES (Prince *et al.*, 2016). Many approaches have been taken out to produce a good quality of rGO. This includes the different methods and reducing agents used. However, even enormous efforts have been taken the final product is still in doubt. This is because, residual functional groups and defects greatly change the structure of the carbon plane (Pei & Cheng, 2012). In order to produce rGO, top-down approach via chemical reduction will be chosen (Chua & Pumera, 2014). Therefore, in this study $NaBH_4$ will be chosen as reductant because it is a strong reducing agent (Pei and Cheng, 2012) and environmental friendly (Yang *et al.*, 2015) to reduce GO. $NaBH_4$ is known to be as a good reductant to reduce aldehydes and ketones to alcohol on the surface of GO (Yang *et al.*, 2015). Therefore, the oxygen-containing groups will be less and the insulating properties of GO can be decreased. Hence, the rGO is able to form interfacial bonding with polymers easier. Then, it will be blended with PES polymer to form polymer composites membrane. PES is chosen in this study because it has been used in water treatment extensively (Rana *et al.*, 2005; Qu *et al.*, 2010; Ahmad *et al.*, 2013; Jin *et al.*, 2013; Zhang *et al.*, 2013, 2014; Zhao *et al.*, 2013; Forati *et al.*, 2014; Vatanpour *et al.*, 2014).

1.3   Objectives of Study

The aim of this work is to study the relationship between the reduction time of rGO on the hydrophilicity of the membrane composites and the formation of pores for HA rejection. The objectives of this study are:

1. To study the effect of reduction time on the properties of rGO.
2. To produce rGO/polymer composites for ultrafiltration process and to evaluate the performance of the membrane for HA rejection.
3. To study the effect of PVP on the formation of pores in the membrane.

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