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FABRICATION AND CHARACTERISATION OF POLYMER/GRAPHENE OXIDE/TITANIUM DIOXIDE COMPOSITES NANOFILTRATION MEMBRANE FOR METHYLENE BLUE REMOVAL

ROSMANISAH MOHAMAT

UNIVERSITI PENDIDIKAN SULTAN IDRIS

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THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

FACULTY OF SCIENCE AND MATHEMATICS
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ABSTRACT

This study aimed to fabricate and characterise graphene oxide (GO) and reduced GO (rGO)-based composite nanofiltration (NF) membrane for water treatment application. Electrochemical exfoliation method assisted by customised triple-tail 1-butyl-3-imidazolium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl) 1,4-dioxobutane 2-sulphate (BMIM-TC14) and sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulphonate (TC14) surfactants were used to synthesise GO with N, N-dimethylacetamide (DMAC) used as solvent. Chemical reduction process utilising hydrazine hydrate was then performed to produce rGO from GO. Next, GO- and rGO-based composite NF membrane were then fabricated via non-solvent induced phase separation method utilising DMAC-GO and -rGO, titanium dioxide (TiO_2), multi-walled carbon nanotubes (MWCNTs), polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP) and poly (methyl methacrylate) (PMMA) as additives, while polyvinylidene fluoride (PVDF) and polyethersulfone (PES) were used as main polymer material. The fabricated NF membranes were then used as membrane separation for methylene blue (MB) dye removal investigated using dead-end cell filtration system. The findings showed that PVDF/GO_{TC14}/TiO_2 composite NF membrane presented excellent MB dye rejection efficiency (92.63 %) and antifouling properties (> 100 %) compared to other samples. This was due to the excellent compatibility between the incorporated hydrophilic additives and PVDF polymer assisted by triple-tail TC14 surfactant. In conclusion, the fabricated PVDF/GO_{TC14}/TiO_2 showed a potential to be applied as NF membrane material for dye rejection. Implication of this study is a novel, simpler, low-cost and greener method for NF membrane fabrication.

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FABRIKASI DAN PENCIRIAN MEMBRAN PENAPISAN-NANO KOMPOSIT POLIMER/GRAFIN OKSIDA/TITANIUM DIOKSIDA UNTUK PENYINGKIRAN METILENA BIRU

ABSTRAK

Kajian ini bertujuan untuk memfabrikasi dan mencirikan membran penapisan-nano (PN) komposit berasaskan grafin oksida (GO) dan penurunan GO (pGO) untuk aplikasi rawatan air. Pengelupasan elektrokimia yang dibantu oleh surfaktan buatan rantaian bercabang tiga 1-butil-3-imidazolium 1,4-bis(neopentiloksi)-3-(neopentiloksikarboni)-1,4-dioksobutana-2-sulfat (BMIM-TC14) dan sodium 1,4-bis (neopentiloksi)-3-(neopentiloksikarbonil)-1,4-dioksobutana-2-sulfonat (TC14) digunakan untuk mensintesiskan GO dengan N, N-dimetilasetamida (DMAS) sebagai pelarut. Proses penurunan kimia menggunakan hidrazin hidrat kemudiannya dilakukan untuk menghasilkan pGO daripada GO. Seterusnya, membran PN komposit berasaskan GO dan pGO difabrikasi melalui kaedah pemisahan fasa induksi tanpa pelarut dengan menggunakan DMAS-GO dan -pGO, titanium dioksida (TiO_2), nanotiub karbon berbilang dinding (NTK), polivinil alkohol (PVA), polivinilpirolidone (PVP) dan poli (metal metakrilat) (PMMA) sebagai bahan tambahan, manakala polivinilidin florida (PVDF) dan polietersulfone (PES) sebagai bahan polimer utama. Sampel membran PN kemudian digunakan sebagai pemisahan membran untuk penyingkiran warna metilena biru (MB) yang diukur menggunakan sistem penapisan hujung mati. Dapatan kajian menunjukkan membran PN komposit PVDF/GO_{TC14}/TiO_2 mempunyai kecekapan penyingkiran warna (92.63 %) dan antikotor (> 100 %) yang paling tinggi berbanding sampel yang lain. Ini disebabkan oleh kesesuaian di antara gabungan bahan tambahan hidrofilik dan PVDF yang dibantu oleh surfaktan buatan rantaian bercabang tiga TC14. Kesimpulannya, PVDF/GO_{TC14}/TiO_2 yang telah difabrikasi menunjukkan potensi untuk digunakan sebagai bahan membran PN bagi penyingkiran warna. Implikasi kajian ini adalah sebuah pendekatan baharu, lebih mudah, kos rendah dan kaedah yang lebih hijau untuk fabrikasi membran PN.

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LIST OF ABBREVIATIONS

A	Area
AA	Acid Activated
AFM	Atomic Force Measurements
AGMD	Air Gap Membrane Distillation
Al_2O_3	Aluminium Oxide
AOT4	Sodium Bis(3,5,5-Trimethyl-1-Hexyl) Sulphosuccinate
ATR	Attenuated Total Reflection
ATRP	Atom Transfer Radical Polymerisation
Au	Aurum
BMIM-TC14	1-Butyl-3-Imidazolium 1,4-Bis(Neopentyloxy)-3 (Neopentyloxycarbonyl) 1,4-Dioxobutane-2-Sulphate
BSA	Bovine Serum Albumin
C	Carbon
C_o	Initial Dye Concentration
C_p	Permeate Dye Concentration
CNTs	Carbon Nanotubes
CR	Congo Red
CVD	Chemical Vapor Deposition
CZTS	Copper Zinc Tin Sulfide
DI	Deionized
DMAC	N, N-Dimethylacetamide
DMAEMA	P(MMA-co-2-ethyl Methacrylate)

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DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
DSSCs	Dye-Sensitized Solar Cells
EDX	Energy Dispersive X-Ray
F	Fluorine
Fe_3O_4	Iron Oxide
FESEM	Field Emission Scanning Electron Microscopy
FRR	Flux Recovery Ratio
FTIR	Fourier Transform Infrared
GO	Graphene Oxide
GONRs	Graphene Oxide Nanoribbones
H	Hours
HA	Humic Acid
HBE	Hyperbranched Epoxy
HF-MoS_2	Flower-like Molybdenum Disulfide
HI	Hydrogen Iodide
HNO_3	Nitric Acid
HPEI	Hyperbranched Polyethyleneimine
H_2SO_4	Sulphuric Acid
I_D/I_G	Ratio of D- and G-band Intensity
J	Permeated Flux
$KClO_3$	Potassium Chlorate
LBL	Layer-by-layer
m	Mass
MABS	4-methacrylamidobenzenesulfonic acid

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MB	Methylene Blue
MD	Membrane Distillation
MF	Microfiltration
MMT	Montromorillonite
MO	Methylene Orange
MPD	M-phenylenediamine
MW	Molecular Weight
MWCNTs	Multi-walled Carbon Nanotubes
MWCO	Molecular Weight Cut-Off
NF	Nanofiltration
NIPS	Nonsolvent Induced Phase Separation Process
NMP	N-methyl-pyrrolidinone
NOM	Natural Organic Matter
O	Oxygen
OA	Oleic Acid
OCNTs	Oxidised Carbon Nanotubes
OMWCNTs	Oxidised Multi-walled Carbon Nanotubes
PA	Polyamide
PAA	Poly(Acrylic Acid)
PACMO	Polyacryloylmorpholine
PAM	Polyacrylamide
PAN	Polyacrylonitrile
PDA	Poly-dopamine
PDMA	Poly (Dimethylaminoethyl Methacrylate)
PDMS	Poly(Dimethylsiloxane)

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PDMAA	Poly (N, N-dimethyl Acrylamide)
PEG	Polyethylene Glycol
PEI	Polyethylenimine
PES	Polyethersulfone
PHBA	Para Hydroxybenzoate Alumoxane
pK_a	Acid Dissociation Constant
PMEMA	Poly(2-N-morpholino)ethyl Methacrylate
PMMA	Poly(Methyl Methacrylate)
PNIPAM	Poly (N-Isopropyl Acrylamide)
POEM	Poly (Ethylene Glycol) Methyl Ether
P(PEGMA-MMA)	Poly(Poly(Ethylene Glycol) Methyl Ether Methacrylate-methyl Methacrylate
PrGO	Partial Reduced Graphene Oxide
PSA	Polysulfide-Amide
P(TFE-VP)	Poly(tetrafluoroethylene-co-vinylpyrrolidone
PVDF	Polyvinylidene Fluoride
PVA	Polyvinyl Alcohol
PVP	Polyvnylpyrrolidone
ppm	Parts Per Million
R	Dye Rejection Efficiency
R_a	Roughness Average
R_q	Root Mean Square
R_z	Average Third Highest Peak to Third Lowest Valley Height
RAFT	Reversible Addition-Fragmentation Chain Transfer Polymerisation
RhB	Rhodamine B

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rGO	Reduced Graphene Oxide
RO	Reverse Osmosis
S	Sulphur
SBMA	PMMA-r-sulfobetaine Methacrylate
SB2VP	PMMA-r-sulfobetaine-2-vinyl-pyvidine
SDS	Sodium Dodecyl Sulphate
SEM	Scanning Electron Microscopy
s-GO	Sulfonated-Graphene Oxide
SiO_2	Silicon Dioxide
SO_2	Sulfone Group
t	Time
T_g	Glass Transition Temperature
T_m	Melting Point
TC14	Sodium 1,4-Bis(Neopentyloxy)-3-(Neopentyloxycarbonyl)-1,4-Dioxobutane-2-Sulphonate
TEP	Triethyl Phosphate
THF	Tetrahydrofuran
Ti	Titanium
TiO_2	Titanium Dioxide
TIPS	Thermally Induced Phase Separation
TMC	Trimesoyl Chloride
TMP	Trans Membrane Pressure
UF	Ultrafiltration
UV-Vis	Ultraviolet-Visible
V	Voltage

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V	Volume
VIPS	Vapor Induced Phase Separation
W	Weight
wt%	Weight Percentage
XRD	X-ray Diffraction
ZnO	Zinc Oxide
ZnS	Zinc Sulfide
1 – D	One Dimensional
2 – D	Two Dimensional
ε	Membrane Porosity
ρ_w	Density of Water
ρ_p	Polymer Density
λ	Wavelength
θ	Angle

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CHAPTER 1

INTRODUCTION

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1.1 Introduction

This chapter discusses the research background of graphene oxide (GO)- and reduced GO (rGO)-based membrane by utilising polyvinylidene fluoride (PVDF) and polyethersulfone (PES) as main polymer for water treatment application. The research problem, objectives, scope and limitation of this study are also described in this chapter. This chapter is ended with a description of the thesis organisation.

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1.2 Research Background

In this modern era, depletion of clean water turns out to be the finest topic to be discussed due to dye contamination. The dyes usage increases in textile, printing inks, paper and paints industries on account of the rapid growth of industrialisation. Commonly, about 2 % of all produced dyes are discharged directly into water (Peydayesh, Mohammadi & Bakhtiari, 2017). Synthetic dyes are toxic and carcinogenic to aquatic living organism (K. Wang et al., 2019). In addition, featuring as high solubility in water and molecularly stable to oxidising agent, aerobic digestion, light and heat makes this problem more severe since there are huge discharge amounts of dyes into water directly (Amiri, Asghari, Vatanpour & Rajabi, 2020).

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Water treatment technologies have come up with various applicable methods to reduce or remove the existing contaminations in wastewater including biological treatment, adsorption, membrane separation technologies and chemical degradation. Among these methods, membrane separation is considered as a versatile and good selection for dye removal with many significant advantages including simple in operation, low energy consumption and no phase change (Abdulkarem et al., 2020; Makhetha & Moutloali, 2018; Méricq et al., 2015). According to their properties and separation principles, membrane processes have been classified into four categories which were microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Among them, NF membrane was widely exploited in dye removal due to their advantages such as high permeation flux at relatively low operating pressure (4 - 20 MPa) and its ability to separate organic dyes with the molecular weight ranging from 200 to 1000 Da from aqueous solution (Peydayesh et al., 2017).

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Various polymers with their own properties are available for membrane separation processes, such as PVDF, PES, poly(methyl methacrylate) (PMMA), polyamide (PA) and polyacrylonitrile (PAN). Commonly, these polymers can be categorised based on their hydrophilic or hydrophobic characteristics. Both of hydrophilic and hydrophobic polymers can be utilised as the main polymer to fabricate membrane since high level and stable filtration can be achieved. However, hydrophobic polymer has been extensively used due to their high mechanical strength and chemical resistance over a long period as compared to hydrophilic polymer (Alenazi, Hussein, Alamry & Asiri, 2017).

PVDF and PES have been substantially used in water treatment processes due to its outstanding thermal stability, good mechanical properties and chemical resistance (Bagheripour, Moghadassi, Parvizian, Hosseini & Van der Bruggen, 2019; Mahmoudi, Ng, Ang, Teow & Mohammad, 2020). Unfortunately, these two pristine polymers commonly confront major limitation of hydrophobic nature which resulted in membrane fouling (Bagheripour, Moghandasi, Hosseini & Van der Bruggen, 2018; Hosseini et al., 2019; Zinadini & Gholami, 2016) and shorter lifespan (Oulad, Zinadini, Zinatizadeh & Derakhshan, 2020). The fouling phenomenon is caused by the deposition of feed components on the membrane surface which caused flux decline or permeate rate decrement during the filtration process (R. Zhang et al., 2016). Commonly, fouling formation on membrane surface is influenced by surface properties (hydrophilic or hydrophobic) (Behboudi, Jafarzadeh & Yegani, 2016; She, Wang, Fane & Tang, 2016). However, tendency of hydrophobic surface to foul is higher than hydrophilic surface.

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Various approaches have been carried out to render hydrophilic properties to these two membranes including surface coating, surface modification by blending with hydrophilic organic or inorganic material (Alenazi et al., 2017; Liu, Huang, Zhang & Zhao, 2018; Mahmoudi et al., 2020; Otitoju et al., 2018) and plasma treatment. Among various mentioned approaches, blending with organic or inorganic materials into the polymer matrix has been widely used to enhance membrane hydrophilicity due to its advantage of facile preparation method through phase inversion. Recently, different inorganic nanomaterials including titanium dioxide (TiO_2) (Guo & Kim, 2017; Livari, Aroujalian, Raisi & Fathizadeh, 2012; G. Wu, Gan, Cui & Xu, 2008), silicon dioxide (SiO_2) (Faneer, Rohani & Mohammad, 2016), zinc oxide (ZnO) (A. L. Ahmad, Abdulkarim, Ismail & Ooi, 2015; Abdul Latif Ahmad, Sugumaran & Shoparwe, 2018), carbon nanotubes (CNTs) (Ghaemi et al., 2015), GO (Abdel-Karim et al., 2018; Igbinigun, Fennell, Malaisamy, Jones & Morris, 2016) and rGO (H. H. Huang, Joshi, De Silva, Badam & Yoshimura, 2019; Peng et al., 2018; P. Zhang et al., 2019) have been utilised to fabricate NF membrane with excellent properties of antifouling effect, permeability and membrane selectivity.

TiO_2 is a potential candidate to effectively reinforce PVDF and PES polymeric materials due to its excellent properties such as hydrophilicity, large surface area, chemical stability, commercial availability and low toxicity (Park et al., 2018). TiO_2 is considered as the best metal oxide to overcome the fouling issues by increasing the membrane hydrophilicity (Liu et al., 2018; L. Wu, Zhang, Wang, Du & Yang, 2019). Several reports have demonstrated that incorporation of TiO_2 could improve the fouling resistance (Guo & Kim, 2017; Li et al., 2019; Xie, Li, Sun, Dong & Dong, 2021). In addition, it also showed that the membrane structure, hydrophilicity properties and

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permeability were improved when TiO_2 nanoparticle was used as an additive for membrane fabrication.

Guo and Kim (2017) showed that hydrophilicity of the fabricated membrane measured by contact angle was improved from 68 to 57° for pristine PES and PES/TiO_2, respectively. PES/TiO_2 membrane also showed higher Bovine Serum Albumin (BSA) rejection of 99 % compared to the pristine PES membrane (96.5 %). In addition, Ahmad et al. (2019) agreed that TiO_2 can act as excellent additive to enhance surface hydrophilicity and increased the membrane performance. They reported that the incorporation of 1 wt % of TiO_2 resulted the membrane with lower contact angle (67°) and higher water flux of 27. 262 L/m^2h as compared to pristine PES membrane (72° and 21.196 L/m^2h, respectively).

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On the other hand, polyvinyl alcohol (PVA) is commonly blended with PVDF or PES in order to modify the membrane surface. PVA possesses excellent hydrophilicity, good cohesion, biodegradability and biocompatibility (Prasad et al., 2019; Sakarkar, Muthukumaran & Jegatheesan, 2020). In addition, PVA can minimise the fouling rate due to its oleophobic nature. Several reports have shown that PVA can enhance water flux and dye rejection of the fabricated membrane. Jie Zhang et al. (2017) proved that by embedding PVA into PVDF, there is a strong compatibility correlation with solution stability thus resulted in deterioration of casting solution stability. The obtained result by Sakarkar et al. (2020) also showed an improvement in membrane hydrophilicity shown by the decrement of contact angle value (62.68 - 42.68°) and better tensile strength (52.3 - 81.22 MPa) with the increasing loading of PVA (1 - 12 wt%).

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Polyvinylpyrrolidone (PVP), also known as amphiphilic polymer is commonly blended with main polymer to improve membrane hydrophilicity. PVP also act as a pore former during the membrane fabrication (Kourde-Hanafi et al., 2017). PVP possesses excellent solubility in polar solvents, high chemical stability and nontoxicity. In addition, PVP also exhibits good water solubility and can increase surface hydrophilicity. Several reports have shown that PVP can enhance the water flux and dye rejection of the fabricated membrane. Kourde-Hanafi et al. (2017) proved that PES membrane with addition of 4 wt% PVP showed a higher pure water permeability (170 L/m^2hMPa) than pristine PES (1.5 L/m^2hMPa). The result obtained by Hosseini et al. (2019) also proved that by embedding PVP in PES membrane, higher water flux (9.96 L/m^2h) was achieved compared to pristine PES membrane (3.14 L/m^2h).

PMMA is an interesting polymer material to be utilised as additive due to its compatibility with other polymer by simultaneous precipitation in a water bath all over the concentration range (Benhabiles et al., 2019). Therefore, the hydrophilicity and water permeation flux of the fabricated membrane can be easily tailored. PMMA introduction into the composite membrane can also improve the crystalline and mechanical properties of the fabricated membrane. In addition, PMMA is used in various industrial application due to its excellent properties of good chemical resistance and high transparency (Aid et al., 2019). Bussi, Golan, Dosoretz and Eisen (2018) has prepared a membrane by blending the PMMA into polystyrene via phase inversion method. The fabricated membrane possesses good mechanical and chemical stability with high fluxes. Meanwhile, Fu et al. (2018) figured out that PMMA melts partly in the PVDF/PMMA/SiO_2 membrane via scanning electron microscopy (SEM) test and enhance the mechanical properties of the fabricated membrane. Benhabiles et al. (2019)

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showed that PVDF/PMMA/TiO_2 possessed a porous and sponge-like structure along the cross-section and also presented higher methylene blue (MB) dye removal (~99%).

Multi-walled CNTs (MWCNTs) is one of the potential materials that can be utilised to enhance PVDF and PES membrane properties. It has been reported that CNTs possessed higher surface to volume ratio, low density and high strength (Mavukkandy, Zaib & Arafat, 2018; J. Wang, Lang, Xu, Zhang & Guo, 2015). With the aim to study the effect of dual-layer casting on membrane characteristic, Mavukkandy et al. (2018) immobilised CNTs on the PVDF membrane surface. They also blended PVP into the polymer dope solution to maintain the hydrophilicity of membrane surface since pristine CNTs are generally hydrophobic. Although the CNTs are hydrophobic in nature, the water contact angle of composite membrane decreased to 20° than that of pristine membrane (around 70°). In another study, Yuan et al. (2020) has prepared PVDF/oxidised MWCNTs (OMWCNTs)/GO by phase inversion method to study the simultaneous pollutant filtering with real-time filtering detection. The results showed that PVDF/OMWCNTs/GO composite membrane presented better surface pore structures, high hydrophilicity and excellent antifouling properties. Higher water flux was achieved (125.6 L/m^2h) compared to pristine PVDF membrane (75.5 L/m^2h).

GO has been known as a promising inorganic material to be utilised as an additive to fabricate hydrophilic membrane. GO as an additive has many advantages for water treatment due to its large surface area (calculated up to 2630 m^2/g) (X. Huang, Qi, Boey & Zhang, 2012), good chemical stability and high mechanical strength (Young modulus ~ 1TPa) (Lee, Wei, Kysar & Hone, 2008). As exfoliated GO contains the considerable

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number of oxygen functional groups, such as carboxyl, carbonyl, epoxy and hydroxyl groups, GO are highly hydrophilic (Miao et al., 2017; Jiguo Zhang et al., 2013). Plenty attempts have been made to develop extensive and low-cost procedures for high quality and quantity GO production such as Staudenmaier, Hummers' and improved Hummers' method. However, there are several limitations associated with all of these routes since it is often required long time production and hazardous solvents/reagents (Abdelkader, Cooper, Dryfar & Kinloch, 2015; Zaaba et al., 2017). These unfavourable conditions will require relatively high cost associated with the industrial scale-up of the procedures. In addition, these methods usually resulted poisonous gases and hazardous waste (S. Yang, Lohe, Mullen & Feng, 2016).

In contrast to the mentioned methods, electrochemical exfoliation method has drawn an attention over the last few years as a reliable option to synthesise GO. This method has offered advantages that are simple, greener and low-cost GO production (Suriani et al., 2015, 2019). The utilisation of harsh chemical by the previous mentioned methods then can be avoided by manipulating electrochemical activation thus results in a simpler product purification step (Yu, Lowe, Simon & Zhong, 2015). Moreover, it is a potential scalable method to produce high yield of GO in the solution form through a single synthesis process (Yu et al., 2015). Many reports of GO-incorporated membranes for wastewater treatment systems have also successfully removed different heavy metal ions (lead, cadmium, copper and chromium) (Kochameshki, Marjani, Mahmoudian & Farhadi, 2017) and dye pollutant (MB, methylene orange (MO) and Rhodamine B (RhB)) (Safarpour, Vatanpour & Khataee, 2016; M. Yang, Zhao, Zhang, Li & Hou, 2017; Zhu et al., 2017).

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Igbinigun et al. (2016) found that the GO addition could improve the hydrophilicity of PES membrane shown by the decrement of water contact angle from 77 ± 5 to $55 \pm 5°$. As a consequence, the PES/GO membrane exhibited excellent antifouling properties with higher flux recovery than commercial PES membrane using a humid acid (HA) feed solution. In addition, Abdel-Karim et al. (2018) reported that the pore size, pure water flux, hydrophilicity and antifouling properties of PES membrane were improved by introducing GO. They found that by embedding 0.5 wt% of GO into the membrane matrix, higher pure water flux of 13 L/m^2h was obtained compared to the pristine PES membrane (2 L/m^2h). In addition, a rejection of 97 % BSA was achieved by using PES/GO membrane.

Nonetheless, the agglomeration of GO is the major drawback in the development of GO-based membrane, which can reduce its performance. In order to prevent GO from agglomeration, the utilisation of surfactant for better dispersion of GO in the polymer matrix is essentially needed. The previous study conducted by Mohamed et al. (2014) showed better dispersion of CNTs by utilising the triple-tail sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulphonate (TC14) surfactant as compared to single- sodium dodecyl sulphate (SDS) or double-tail sodium bis(3,5,5-trimethyl-1- hexyl) sulphosuccinate (AOT4)) surfactant.

Suriani et al. (2016) also proved that the utilisation of triple-tail TC14 has presented smooth surface with low GO agglomeration when the synthesised GO was intermixed with natural rubber latex. The triple-tail surfactant offers triple interaction during electrochemical exfoliation which resulted higher dispersion of GO. On the other hand, the incorporation of the triple-tail TC14 surfactant in the thin film fabrication had

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resulted higher dye sensitized solar cell (DSSCs) efficiency as compared to the single-tail surfactant (Suriani, Fatiatun, et al., 2018; Suriani, Muqoyyanah, et al., 2018). These results confirmed that the surfactant's tail number influenced the quality of the synthesised GO. In addition, previous report has proved that the direct GO synthesis utilising single-tail SDS surfactant and N,N-dimethylacetamide (DMAC) as solvent was successfully achieved and can be used to fabricate PVDF membrane which resulted high dye rejection of 92.76 % (Suriani et al., 2019).

Recent research also suggests that rGO has been viewed as one of additive material candidate due to their smaller lattice parameter (~ 0.34 nm) and graphene-like properties which can theoretically filtrated the unwanted material based on size exclusion (H. H. Huang et al., 2019). Abdel-Karim et al. (2019) have prepared PVDF membrane incorporated with rGO and have been employed for water purification of aqueous solutions containing sodium chloride via air gap membrane distillation (AGMD). The significant finding from this study is that membranes containing just 0.5 wt% of rGO showed an increment of water flux (7.0 L/m^2h) compared to the pure PVDF membrane (2.6 L/m^2h). In another study, H. H. Huang et al. (2019) have studied the influence of rGO on the performance of PVDF/rGO membrane. Their results showed that PVDF/rGO has a potential to block salt ions as small as Na^+ with high precision.

On the other hand, the appropriate solvent selection plays a crucial role in the membrane formation characteristics (Wahab, Muchtar, Arahman, Mulyati & Riza, 2019). This was due to the asymmetric membrane formation was influenced by the solvent selection. There are various kinds of solvent used for membrane fabrication, such as DMAC, dimethylformamide (DMF), N-methyl-pyrrolidinone (NMP) and triethyl

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phosphate (TEP). It was found that the utilisation of DMAC as solvent possesses higher porosity of the fabricated membrane than other solvents (Fahrina et al., 2018). This result was in a good agreement with Méricq et al. (2015) where a dense structure was obtained when incorporating DMAC as a solvent compared to NMP which then lead to higher porosity and water permeability.

1.3 Problem Statement

PVDF and PES have been utilised as polymeric material in membrane separation process for dye rejection application since they possessed an outstanding physical and chemical properties. However, PVDF- and PES-based membrane imperfections are prevalent issues in the membrane development. Despites its excellent properties, these two polymeric materials endure from hydrophobicity problem. This problem then led to a major problem with lower separation efficiency due to the serious membrane fouling. Therefore, it would decrease the lifespan of membrane and concurrently increase the production cost. The membrane performance and efficiency could be critically affected if these issues are not be figured out.

The incorporation of additives such as TiO_2, GO, rGO, MWCNTs, PVA, PVP and PMMA are believed could enhance membrane properties and its performance by increasing membrane permeability and selectivity, hydrophilicity and antifouling properties. These additives are well-known as highly hydrophilic materials. Nonetheless, GO agglomeration in the GO-based composite membrane development is a primary stumbling block. The electrochemical exfoliation method then presents a

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simpler GO synthesis process as compared to other method such as Hummers' method which utilised hazardous chemicals and complex synthesis procedures. Furthermore, more fabrication step can be hindered by performing the direct electrochemical exfoliation method. The DMAC_based-GO solution can be obtained from a single step without the requirement of dispersing GO powder into the solvent which obviously needed in other methods.

On the other hand, chemical reduction process utilising hydrazine hydrate would also result thin and fine rGO layer. Therefore, rGO could uniformly dispersed in the composite membrane. The customised triple-tail surfactants, 1-butyl-3-imidazolium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl) 1,4-dioxobutane-2-sulphate (BMIM-TC14) and TC14, have also proved its effectiveness for better exfoliation as compared to the commercially available single- and double-tail surfactants for adsorption application (Jamaluddin et al., 2020, 2021). To date, the effect of single- and double-tail surfactant's compound for better GO dispersion in the polymeric membrane has also been proven in the previous study (Suriani et al., 2019). It is believed that the tail of these surfactants provided supplementary chain to interconnect between the polymeric polymer (PVDF and PES) and GO and resulted better performance of the NF composite membrane (Suriani et al., 2019).

The major concern of this study is to determine these issues by improving the membrane performance with separation efficiency enhancement. Hence, in this work, GO is synthesised by electrochemical exfoliation method with the assistance of different surfactants (customised triple-tail BMIM-TC14 and TC14). Meanwhile, the rGO is produced via chemical reduction by utilising hydrazine hydrate as reducing agent. The

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synthesised DMAC_based-GO and -rGO, TiO_2, MWCNTs, PMMA, PVA and PVP are utilised as the additives for GO- and rGO-based composite NF membrane fabrication for further membrane modification. To the best of our knowledge, the novelty of this study lies on the utilisation of triple-tail BMIM-TC14 and TC14 surfactants to assist the GO and rGO production during exfoliation and chemical reduction process, respectively and its hybridisation with TiO_2, MWCNTs, PVA, PVP and PMMA as the additives for NF membrane fabrication which further used for dye rejection application. It is believed that the utilisation of these surfactants in the GO- and rGO-based composite NF membrane fabrication will increase the hydrophilicity, water flux, dye rejection and antifouling performance.

1.4 Research Objectives

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The objectives of this study are:

i. To fabricate various GO- and rGO-based composites NF membrane by utilising nonsolvent induced phase separation (NIPS) method for dye rejection application.
ii. To optimise the performance of GO- and rGO-based composite NF membrane by utilising different types of additives.
iii. To investigate the physico-chemical properties of the fabricated GO- and rGO-based composite NF membrane.
iv. To investigate the separation mechanism of GO- and rGO-based composite NF membrane.

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1.5 Scope and Limitation

There are four major scopes in this study; synthesis of GO and rGO solution, fabrication of GO- and rGO-based composite NF membrane, optimisation of GO (or) rGO-based composite NF membrane and characterisation of the fabricated GO- and rGO-based composite NF membrane.

In the stage of GO solution synthesis, a low-cost and simpler electrochemical exfoliation method is applied by utilising graphite rod as carbon precursor instead of other graphitic materials. The utilisation of surfactants for GO synthesis is also limited to the customised triple-tail BMIM-TC14 and TC14 surfactants. Meanwhile, the rGO production is performed via chemical reduction process by incorporating hydrazine hydrate instead of other processes and reducing agents. Next, NIPS method is applied to fabricate the GO- and rGO-based composite NF membrane by utilising DMAC as a solvent. Meanwhile the utilisation of additives for the membrane fabrication are limited to GO, rGO, MWCNTs, TiO_2, PVA, PVP and PMMA. The parameters of experimental design were then focused on the optimisation of GO- and rGO-based composite NF membrane which include the effect of different surfactants, polymeric material, incorporation of different carbon-based additives and different polymeric additives for dye rejection analysis towards the membrane performance.

The GO- and rGO-based composite NF membranes are then characterised using several instrumentations. The morphological and elemental compound of various fabricated GO-based composite NF membranes are determined using field emission SEM (FESEM), energy dispersive X-ray (EDX) and atomic force

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microscopy (AFM). Meanwhile, the spectroscopy and crystallinity of composite NF membrane is analysed through micro-Raman spectroscopy, X-ray diffraction (XRD) and Fourier transform infrared (FTIR). Next, ultraviolet visible (UV-Vis) spectroscopy, drop shape analyser and dead-end filtration are used to investigate the properties and performances of the fabricated composite NF membrane.

1.6 Thesis Organisation

This work is focused on the water treatment applications based on GO- and rGO-based material. The dye rejection improvement and antifouling performance by utilising two type of surfactants are done for membrane separation. Chapter 1 consists of research background, research problem, research objective and scope and limitations of the study. Meanwhile, Chapter 2 presents the brief description of previous study and theories about membrane separation. A general introduction to the materials and methods carried out in the study are discussed in Chapter 3. Specific details on the fabrication method and its characterisation techniques also are given in this chapter. Chapter 4 explains the results and discussion including the morphological, structural and performance on dye removal for membrane separation process. Finally, Chapter 5 covers the conclusion and suggestion for future work.

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