ADSORPTION OF METHYLENE BLUE DYE FROM LIQUID PHASE BY CARBON NANOTUBE-INFUSED POLY (VINYL) ALCOHOL MEMBRANE

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2018

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by

NG ZHI HENG

Thesis submitted in partial fulfilment of the requirement for the degree of Bachelor of Chemical Engineering

June 2018

ACKNOWLEDGEMENT

First and foremost, I would like to convey my sincere gratitude to my supervisor, Associate Proffesor Dr. Tan Soon Huat for his precious encouragement, guidance and generous support throughout this work.

I would also extend my gratitude towards all the MSc and PhD students for their kindness cooperation and helping hands in guiding me carrying out the lab experiment. They are willing to sacrifice their time in guiding and helping me throughout the experiment besides sharing their valuable knowledge.

Apart from that, I would also like to thank all SCE staffs for their kindness cooperation and helping hands. Indeed their willingness in sharing ideas, knowledge and skills are deeply appreciated. I would like to express my deepest gratitude to my beloved parents, Ng Chee Keong for his continuous love and support.

Once again, I would like to thank all the people, including those whom I might have missed out and my friends who have helped me to the accomplishment of this project. Thank you very much.

Ng Zhi Heng

June 2018

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LIST OF SYMBOL

Symbol	Description	Unit
n_a	Amount of dye adsorbed	mg
$(P)_T$	Equilibrium pressure at constant temperature	atm
q_m	Langmuir constant corresponding to dye removal capacity (maximum adsorption capacity)	mg/g
K	Langmuir constant corresponding to adsorption energy	L/mg
q_e	Amount of methylene blue adsorbed at equilibrium	mg/g
q_t	Amount of methylene blue adsorbed at time	mg/g
C_e	Equilibrium concentration of methylene blue solution	mg/L
C_0	Initial concentration of methylene blue solution	mg/L
wt. %	Mass fraction in percentage	%
vol. %	Volume fraction in percentage	%
W	Weight of adsorbent used	g
V	Volume of methylene blue solution	L
k_1	Rate constant of pseudo-second-order adsorption	min^{-1}&hr^{-1}
k_2	Rate constant of pseudo-second-order adsorption	g/mg.min & g/mg.hr
C	Intercept of intraparticle diffusion model	mg/g
k_i	Intraparticle diffusion rate constant	mg/g $min^{1/2}$
k_f	Adsorption capacity related to Freundlich isotherm	$(mg\ g^{-1})\ (mg\ L^{-1})^{-1/n}$
k_H	Halsey isotherm constant	(L/g)

n	Dimensionless constant	-
t	Time	hr
R^2	Correction coefficient value	-
$q_{e,exp}$	Experimental value of adsorption capacity at equilibrium	mg/g
$q_{e,cal}$	Calculated value of adsorption capacity at equilibrium	mg/g

LIST OF ABBREVIATIONS

PVA	Poly(vinyl alcohol)
CNT & CNTs	Carbon nanotubes
MWCNT & MWCNTs	Multi walled Carbon nanotubes
SWCNT & SWCNTs	Single walled Carbon nanotubes
MWCNT-SH	Multi walled Carbon nanotubes with thiol group
MB	Methylene blue dye
GA	Glutaraldehyde
HCL	Hydrochloric acid

PENYERAPAN METILENA BIRU DARIPADA FASA CECAIR OLEH MEMBRAN POLIVINIL ALKOHOL DIGABUNG DENGAN TIUB NANO-KARBON

ABSTRAK

Membran PVA dan PVA yang digabungkan dengan tiub nano karbon membran nanokomposit (PVA/MWCNT) digunakan sebagai penyerap untuk menghilangkan metilena biru dari air berair. Beberapa kondisi penjerapan seperti masa kenalan, suhu dan kepekatan awal metilena biru (MB) juga disiasat untuk menentukan keadaan yang optima untuk penjerapan ini. Selepas 4 jam, tidak ada perubahan yang jelas dalam penyerapan pewarna MB pada permukaan membran PVA dan membran nanokmposit PVA/MWCNT. Kapasiti penjerapan pada keseimbangan untuk membran PVA adalah 0.102 mg/g manakala membran nanokomposit PVA/MWCNT adalah 0.146 mg/g pada 20 ℃. 4 jam adalah masa optima untuk proses penjerapan ini dan masa penjerapan untuk mengkaji kesan kondisi penjerapan lain ditetapkan kepada 4 jam. Ia juga mendapati bahawa kapasiti penjerapan membran PVA menurun sementara kapasiti penjerapan membran nanokomposit PVA/MWCNT meningkat dengan peningkatan kepekatan permulaan MB pewarna dari 1.0 mg /L hingga 4.0 mg /L. Selain itu, kapasiti penjerapan membran PVA menurun manakala kapasiti penjerapan membran nanokomposit PVA/MWCNT meningkat dengan peningkatan suhu dari 25 ℃ hingga 40 ℃. Sebaliknya, data keseimbangan adsorpsi untuk membran PVA didapati selari dengan model isotherma Langmuir jenis I manakala untuk membran nanokomposit PVA / MWCNT didapati selari dengan model isoterma Langmuir jenis I and II. Kinetik adsorpsi penyingkiran perwana MB menggunakan membran PVA dan membran nanokomposit PVA / MWCNT juga baik diterangkan oleh model pseudo tertib kedua.

ABSORPTION OF METHYLENE BLUE DYE FROM LIQUID PHASE BY CARBON NANOTUBE- INFUSED POLYVINYL ALCOHOL NANOCOMPOSITE MEMBRANE

ABSTRACT

The PVA membrane and PVA incorporated with carbon nanotube (PVA/MWCNT) nanocomposite membrane were used as adsorbent to remove methylene blue from aqueous water. Several conditions of adsorption such as contact time, temperature and initial concentration of methylene blue were also investigated to determine the optimum condition of the adsorption. After 4 hours, there was no visible change in the removal of methylene blue (MB) dye on PVA membrane and PVA/MWCNT nanocomposite membrane surface. The adsorption capacity at equilibrium for PVA membrane was 0.102 mg/g while PVA/MWCNT nanocomposite membrane was 0.146 mg/g at 20℃. It was found that 4 hours is the optimized contact time for the adsorption process. The adsorption capacity of PVA membrane decreases while adsorption capacity of PVA/MWCNT nanocomposite membrane increases with increase in the initial concentration of MB dye from 1.0 mg/L to 4.0 mg/L. Besides, the adsorption capacity of PVA membrane decreases while adsorption capacity of PVA/MWCNT nanocomposite membrane increases with increase in the temperature from 25℃ to 40℃. On the other hand, the adsorption equilibrium data for PVA membrane was found to be well fitted with the type I of the Langmuir isotherm model while for PVA/MWCNT nanocomposite membrane it was found to be well fitted with both type I and type II of Langmuir isotherm model. Adsorption kinetics of MB dye removal using PVA membrane and PVA/MWCNT nanocomposite membrane was better described by pseudo-second order model.

CHAPTER 1

INTRODUCTION

1.1. Research background

Manufacture and use of synthesis dyes for fabric dyeing has become massive industry nowadays due to dyes provide a wide range of colour. The presence of dye in wastewater can cause severe environmental problem due the most dyes are toxic. Few decades earlier the dye selection, application and uses of dyes were no given a major consideration and half of the chemical composition of dyes used was unknown. In the 80s, with the growing of health concerns, people started to pay more attention in the dye waste (Gupta and Suhas, 2009).

The amount of dyes produced in the world is estimated to be more than 10,000 tons per years and amount of dyes discharged in the environment is estimated 1-2% loss in production and 1-10% loss in use (Forgacs *et al.*, 2004). Synthesis dye can cause considerable environmental pollution due to their large scale of production and extensive application. Dye can cause serious environment pollution even at low concentration, giving undesirable colour to the water and adsorption and reflection of sunlight by dyes ultimately affect the aquatic life. The colour is the contaminant of water which can easily to be recognised by naked eyes and the public perception of water quality is highly influenced by the water colour .Dye concentration in textile industry wastewater is about 10-200 ppm while most dyes are visible at concentration below 1 ppm, hence, the efficient removal of dye in wastewater is required (Pandey *et al.*, 2007). The choice of dye removal treatment is depended on the effluent characteristics such as concentration of dye, the economic involves flow, volume and social factor (Goel *et al.*, 2005). Separation of dye has become one of the most import studies of environmental analysis due to their large distribution in the ecological environment.

1.2. Problem statement

One of the major environment pollution problems in Malaysia comes from textile, leather, paper and plastic industries (Pang and Abdullah, 2013). Those industries use dye and require substantial volume of water, as a result, a considerable amount of coloured wastewater is generated. The presence of dyes in effluents from those industries is a major concern because of their adverse effects to many forms of life.

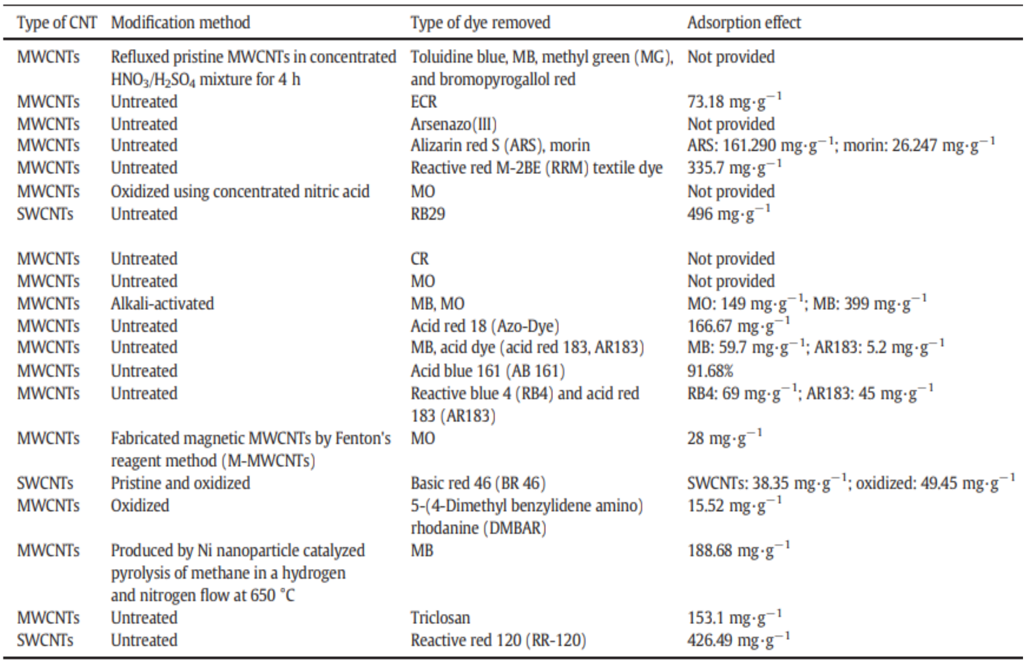
Efficient removal of dye has become a challenging task nowadays. Adsorption, biological degradation, Fenton-like reaction and photo catalysis (Osuolale and Zhang, 2017) are used to treat dye effluents. Every removal technique has its advantages and disadvantages, respectively. Most dyes are non-biodegradable, stable to light and oxidation. Traditional chemical or biological process is not very effective for removal of dye in the wastewater. In this project, adsorption had been chosen to study the removal of dye from aqueous water due to the simplicity of design, ease of operation and insensitive to toxic substances (Pathania et al., 2017). Adsorption is the process where a material is concentrated at a solid surface from its liquid or gaseous surrounding (Mishra et al., 2012) and it is a popular choice of dye removal treatment among the chemical and physical methods (Alam et al., 2007).

One of the most popular adsorbents was activated carbon and normally used for removing heavy metals and dyes from wastewater (Babel and Kurniawan, 2003). However, the regeneration cost of activated carbon is very expensive (Robinson et al., 2001).

Carbon nanotubes (CNTs) have been studied to replace the current adsorbent due to their unique chemical-physical properties and low production cost. CNTs are more attractive in dye removal compared with activated carbon due to their high selectivity, favourable physiochemical stability and large adsorption capacity for organic dyes. Multi walled carbon nanotubes (MWCNTs) have been reported to have better adsorption of safranine O (SO) from wastewater compared to cadmium hydroxide nanowire-loaded activated carbon (Ghaedi et al., 2012). Currently, CNTs are used directly in removal of dye without any further treatment (Ghaedi et al., 2011). Table 1.1 shows the modification methods of MWCNTs and single walled carbon nanotubes (SWCNTs) to remove different organic dyes. Most CNTs are untreated and directly used in dye removal. Yao et al. (2010) found that the adsorption capacity of MB dye of SWCNTs at 333K is 41.63mg/g while Shahryari et al. (2010) found that the adsorption capacity of MWCNTs is 132.6 mg/g at 310K.

Currently, most researches removed dyes using MWCNTs by dissolving the MWCNTs powder in the solution containing dye and the mixtures are agitated on shakers continuously for certain period of time. Then, MWCNTs are filtered using a centrifuge and the concentration of dye in the filtrates are analysed (Shahryari et al., 2010). The reuse and regeneration of MWCNTs is difficult due to MWCNTs is in suspension form and filtration is required to collect the used MWCNTs. In this report, PVA/ MWCNTs nanocomposite was prepared as adsorbent so that the adsorbent can be easily collected from solution without filtration because the adsorbent is in solid membrane form. Hence, the regeneration and reuse of adsorbent will become easier.

Table 1.1: Removal of dyes using SWCNTs and MWCNTs (Yu *et al.*, 2014)



Type of CNT	Modification method	Type of dye removed	Adsorption effect
MWCNTs	Refluxed pristine MWCNTs in concentrated HNO_3/H_2SO_4 mixture for 4 h	Toluidine blue, MB, methyl green (MG), and bromopyrogallol red	Not provided
MWCNTs	Untreated	ECR	$73.18\ mg \cdot g^{-1}$
MWCNTs	Untreated	Arsenazo(III)	Not provided
MWCNTs	Untreated	Alizarin red S (ARS), morin	ARS: $161.290\ mg \cdot g^{-1}$; morin: $26.247\ mg \cdot g^{-1}$
MWCNTs	Untreated	Reactive red M-2BE (RRM) textile dye	$335.7\ mg \cdot g^{-1}$
MWCNTs	Oxidized using concentrated nitric acid	MO	Not provided
SWCNTs	Untreated	RB29	$496\ mg \cdot g^{-1}$
MWCNTs	Untreated	CR	Not provided
MWCNTs	Untreated	MO	Not provided
MWCNTs	Alkali-activated	MB, MO	MO: $149\ mg \cdot g^{-1}$; MB: $399\ mg \cdot g^{-1}$
MWCNTs	Untreated	Acid red 18 (Azo-Dye)	$166.67\ mg \cdot g^{-1}$
MWCNTs	Untreated	MB, acid dye (acid red 183, AR183)	MB: $59.7\ mg \cdot g^{-1}$; AR183: $5.2\ mg \cdot g^{-1}$
MWCNTs	Untreated	Acid blue 161 (AB 161)	91.68%
MWCNTs	Untreated	Reactive blue 4 (RB4) and acid red 183 (AR183)	RB4: $69\ mg \cdot g^{-1}$; AR183: $45\ mg \cdot g^{-1}$
MWCNTs	Fabricated magnetic MWCNTs by Fenton's reagent method (M-MWCNTs)	MO	$28\ mg \cdot g^{-1}$
SWCNTs	Pristine and oxidized	Basic red 46 (BR 46)	SWCNTs: $38.35\ mg \cdot g^{-1}$; oxidized: $49.45\ mg \cdot g^{-1}$
MWCNTs	Oxidized	5-(4-Dimethyl benzylidene amino) rhodanine (DMBAR)	$15.52\ mg \cdot g^{-1}$
MWCNTs	Produced by Ni nanoparticle catalyzed pyrolysis of methane in a hydrogen and nitrogen flow at 650 °C	MB	$188.68\ mg \cdot g^{-1}$
MWCNTs	Untreated	Triclosan	$153.1\ mg \cdot g^{-1}$
SWCNTs	Untreated	Reactive red 120 (RR-120)	$426.49\ mg \cdot g^{-1}$

1.3. Research objectives

- To synthesis nanocomposite membrane of PVA incorporated with MWCNTs via solution casting method.
- To study the performance of adsorption of dye under the different conditions such as contact time, temperature and initial concentration of MB dye solution.
- To determine the most appropriate adsorption isotherm for adsorption of MB dye on PVA membrane and PVA/MWCNTs nanocomposite membrane surface.
- To study the kinetic model of adsorption of MB dye on PVA membrane and PVA/MWCNTs nanocomposite membrane surface.

CHAPTER 2

LITERATURE REVIEW

2.1. Dye classification

Dye can be classified in many ways such as their application, colour and structure. The classification based on application is often favourable due to the complexities of colour nomenclature from the chemical structure system (Yagub *et al.*, 2014). The ionic categorization of dyes influences the efficiency of dye removal (Tan *et al.*, 2015).

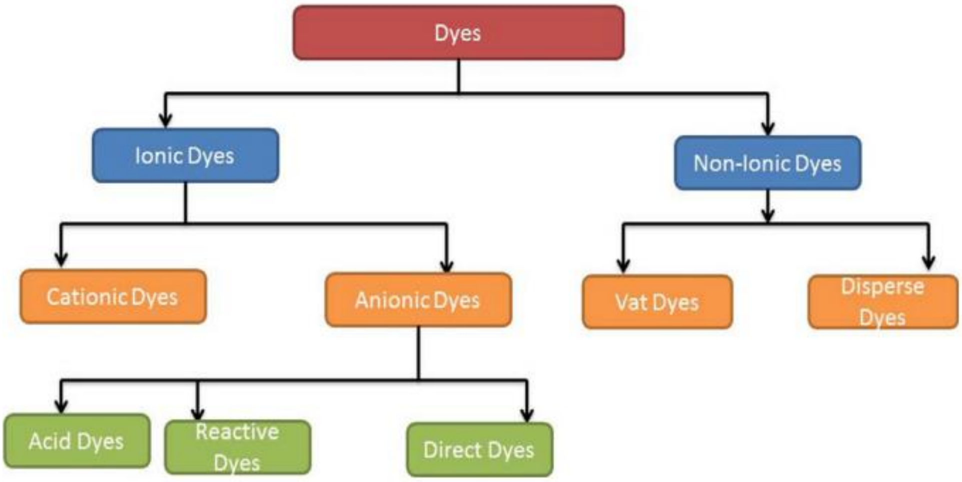


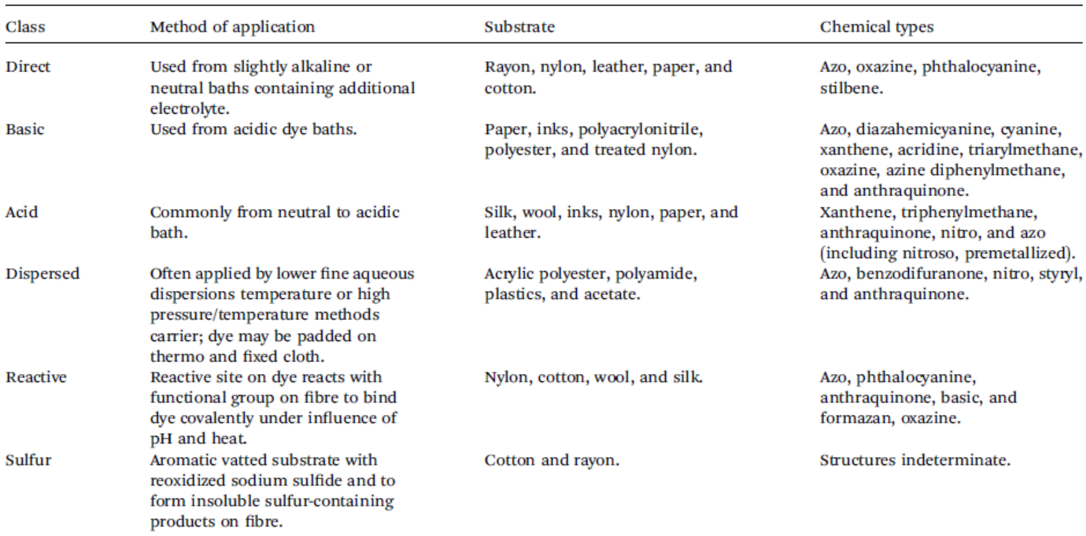
Figure 2.1: Categorization of dye based on ionic charge (Tan *et al.*, 2015)

Figure 2.1 shows that dyes are categorized into ionic and non-ionic dyes. Ionic dyes are further categorized into cationic dyes and anionic dyes. Cationic dyes are cationic salts of coloured organic bases containing imino and amino groups, combined with sulphuric or hydrochloric acid. They are basic dye and used for paper, polyarcylonitrite, modified polyester, nylons and to some extent for medicine. Anionic dyes carry anionic charge and they can be further categorized into acid dyes, reactive dyes and direct dyes. Acid dye is a salt of a carboxylic, sulfonic or phenol organic acid. They are normally made up from large aromatic molecules consisting of many linked rings and water is used as medium for dyeing to occur. They are used for nylon, wool and also to some extent for leather, paper, food, ink and cosmetic. Direct dyes are water soluble anionic dyes and form aqueous solutions when dyed in the presence of electrolytes. They are used for dyeing of cotton and rayon, leather, paper and to some extent of nylon. Reactive dyes contain chromophoric groups and have simple chemical structures. They are able to form covalent bond with fiber and used for cotton and small extent on wool and nylon.

Non-ionic dyes are further categorized into vat dyes and disperse dyes. Vat dyes are oldest dyes and insoluble in the water. They are incapable of dyeing fibers directly. They are mainly used for cotton, rayon and wool. Disperse dyes are insoluble non-ionic dyes containing styryl, azo, nitro, anthraquinone and benzodifuranone groups. They are used for mainly on polyester and to some extent on nylon and cellulose.

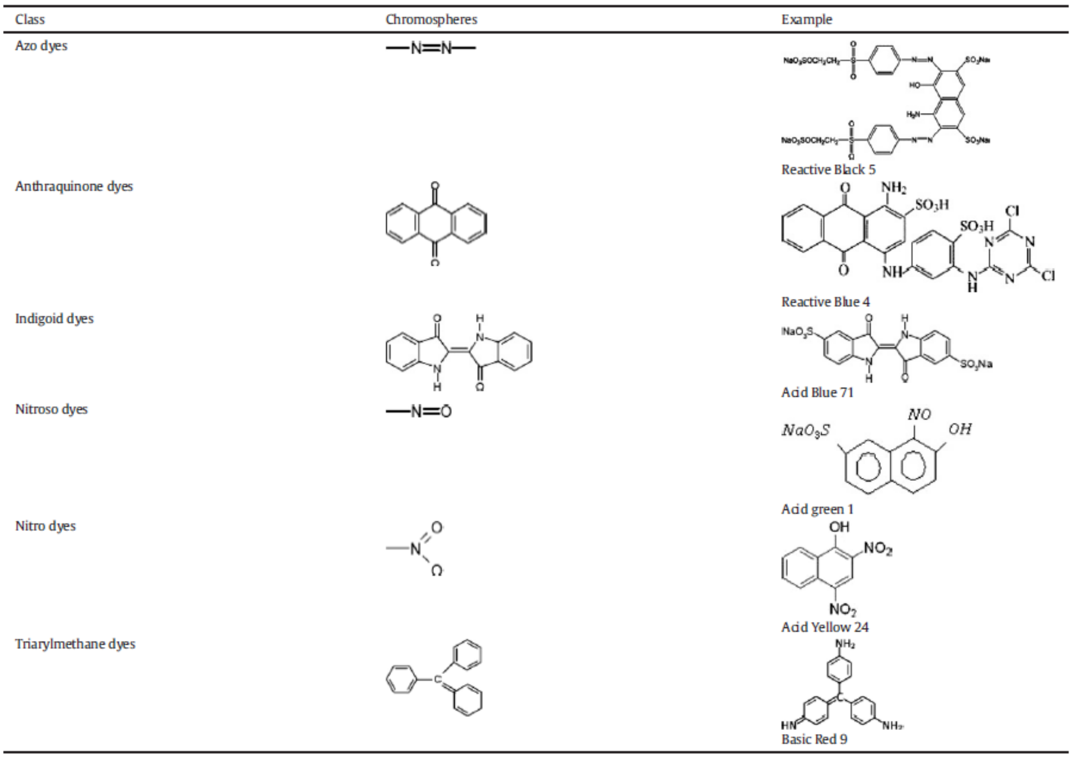
Table 2.1 shows dye classification based on their application and those dyes are classified according to the charge of the dyes such as anionic, cationic and non-ionic (Yagub *et al.*, 2014). Table 2.2 shows the dye classification based on chemical structures. They are classified as nitro dyes, azo dyes, indigoid dyes, anthraquinone dyes, triarylmethane dyes and nitroso dyes (Yagub *et al.*, 2014).

Table 2.1: Dye classification based on their chemical application (Yagub *et al.*, 2014)



Class	Method of application	Substrate	Chemical types
Direct	Used from slightly alkaline or neutral baths containing additional electrolyte.	Rayon, nylon, leather, paper, and cotton.	Azo, oxazine, phthalocyanine, stilbene.
Basic	Used from acidic dye baths.	Paper, inks, polyacrylonitrile, polyester, and treated nylon.	Azo, diazahemicyanine, cyanine, xanthene, acridine, triarylmethane, oxazine, azine diphenylmethane, and anthraquinone.
Acid	Commonly from neutral to acidic bath.	Silk, wool, inks, nylon, paper, and leather.	Xanthene, triphenylmethane, anthraquinone, nitro, and azo (including nitroso, premetallized).
Dispersed	Often applied by lower fine aqueous dispersions temperature or high pressure/temperature methods carrier; dye may be padded on thermo and fixed cloth.	Acrylic polyester, polyamide, plastics, and acetate.	Azo, benzodifuranone, nitro, styryl, and anthraquinone.
Reactive	Reactive site on dye reacts with functional group on fibre to bind dye covalently under influence of pH and heat.	Nylon, cotton, wool, and silk.	Azo, phthalocyanine, anthraquinone, basic, and formazan, oxazine.
Sulfur	Aromatic vatted substrate with reoxidized sodium sulfide and to form insoluble sulfur-containing products on fibre.	Cotton and rayon.	Structures indeterminate.

Table 2.2: Dye classification based on their chemical structure (Yagub *et al.*, 2014)



Class	Chromospheres	Example
Azo dyes	—N=N—	Reactive Black 5
Anthraquinone dyes		Reactive Blue 4
Indigoid dyes		Acid Blue 71
Nitroso dyes	—N=O	Acid green 1
Nitro dyes		Acid Yellow 24
Triarylmethane dyes		Basic Red 9

2.2. Dye toxicity

One of the major factors that dyes must be removed from wastewater is due to most dyes are toxic. Complex dyes always contain chromium, which is carcinogenic (Clarke and Anliker, 1980). Many dyes are resistant against heat,optical oxidizing agents and biodegradable due to the presence of of many aromatic compound in dye compounds that form stable complexes (Ryan, 2000). Reactive dyes are hard to be removed from wastewater due to they are water soluble and they will give a high coloured effluent causing serious trouble in the environment. Besides, conventional wastewater treatment hardly to remove reactive dyes due to their non-biodegrable and being chemically stable (Rajabi *et al.*, 2016). Dyes are also teratogenic, mutagenic or carcinogenic in various microbiological species of fish (Rajabi *et al.*, 2017). Dyes also can affect photosynthesis activity of aquatic life since they can absorb and reflex sunlight from penetrating through the water. Hence, the elimination of dyes in the wastewater is very important.

2.3. Methylene blue (MB) dye

MB dye is cationic dye and it is widely used for dyeing wood, cotton and silk (Robati *et al.*, 2016). Even though MB is not highly venomous dye, it still will cause increased heart rate, vomiting shock, Heinz body formation, cyanosis, jaundice, quandriplegia, diarrhea and tissue necrosis in humans (Khodaie *et al.*, 2013). There are a lot of methods to remove MB dye from wastewater such as physical, biological and chemical processes. Adsorption is one of the most simple and economical methods to remove the dyes from wastewater (Tehrani-Bagha *et al.*, 2011).

2.4. Methods to remove dye from wastewater

Removal of dyes from wastewater is complicated due to the complexity and variety of dyes. Besides, dyes also might react with other chemical reactants in the wastewater. Several general methods are applied to remove the dye such as chemical, biological and physical methods.

2.4.1. Chemical method

In chemical methods, dye is oxidised by using hydrogen peroxide (H_2O_2) or ozone (O_3) or dye is decomposed by photochemical reaction under UV treatment in the presence of hydrogen peroxide (H_2O_2) (Ai *et al.*, 2014). Fentons reagent (H_2O_2-Fe^{2+}) is often used to treat the dyes which are not biodegradable or are poisonous to live biomass (Slokar and Majcen Le Marechal, 1998). Fentons reagent can effectively decolourise both soluble and insoluble dyes but the major problem in using Fentons reagent is the sludge generation (Robinson *et al.*, 2001). The sludge contains concentrated impurities requires disposal and it has been conventional incinerated which is not environmentally friendly. Besides, the resulting floc from the reaction is in poor quality and does not settle well (Yerramilli *et al.*, 2005).

Ozonation is effective for azodye removal and it is able to produce effluent wastewater with no colour and low chemical oxygen demand (COD) which is suitable for discharging (Xu *et al.*, 1999) but it is not suitable for dispersed dyes and will releases aromatic amines which is cancerogenic (Yerramilli *et al.*, 2005).

2.4.2. Biological method

Biological method used microorganisms to biochemically decompose the dye in wastewater and stabilize the end product. In biological method, certain microbial culture such as white-rot fungi is used to decolourise the dyes in both aerobic and anaerobic process. A wide variety of microorganisms are able to decolourise the dye.

White-rot fungi are the most efficient mircoorganism to break down the dyes because of their ability to produce non-specific extracellular lignin-degrading enzymes (Daâssi *et al.*, 2013). Other fungi such as *Aspergillus niger* (Fu and Viraraghavan, 1999), *Rhizopus oryae* (Gallagher *et al.*, 1997), *Rizopus oryzae* also can decolorize and biosorb dyes. Fungi have proved to be able to remove dye and suitable for the treatment of textile effluent. Fungal mycelia are able to solubilise the insoluble substrates by producing extracellular enzyme. Due to the extracellular nature of the fungal enzyme, fungi are able to tolerate high concentration of toxicants (Kaushik and Malik, 2009).

Algae is also able to decolorize and remove dye (Tarlan *et al.*, 2002). Commonly available green algae- *Spirogya* was studied and has potential to remove synthetic azo dye from wastewater. Their performance of colour removal is depended both on the dye concentration and algal biomass (Venkata Mohan *et al.*, 2002).

Certain bacteria such as *Bacillus subtilis* (Horitsu *et al.*, 1977), *Bacillus cereus* (Wuhrmann *et al.*, 1980), *Mycabacterium avium* (Jones and Falkinham, 2003) are found to be able to biodegrade azo dyes.

There are two type of biological method, which are aerobic and anaerobic process. Aerobic process is used as main treatment for distillery, brewery, pulp and paper and sugar industries. Anaerobic process can be used for wide variety of complex dyes and the bio gas produced from the treatment can be used for steam generation (Yerramilli *et al.*, 2005). Fungal, algal and bacterial are used as post treatment in any industry and they are efficient for low volumes and concentration of dyes removal. However, the culture maintenance cost is expensive and cannot cope with large volume of coloured effluents (Yerramilli *et al.*, 2005).

2.4.3. Physical method

In physical method, suitable adsorbent is used to remove pollutants. The choice of adsorbent is depended on the type of pollutants. Physical method is often preferred over other methods due to the lower process costs and easier to recover and able to reuse of adsorbent without additional materials required (Altmann *et al.*, 2014).

Silica gel is effective for basic dye removal but the side reaction prevent commercial application (Robinson *et al.*, 2001). Peat is used in post or pretreatment in any industry and it is effective due to cellular structure and no activation required but its surface area is lower than activated carbon (Yerramilli *et al.*, 2005). Wood chips are good sorption for acid dyes but required larger contact times and huge quantities (Robinson *et al.*, 2001; Yerramilli *et al.*, 2005). Activated carbon is effective for removal of acid dyes, pigment and reactive dyes (Vuono *et al.*, 2017). However, the regeneration cost is expensive and is limited to particular dye removal treatments and ineffective in another (Robinson *et al.*, 2001). Ion-exchange is also one type of physical method and the major advantages are able to regenerate with low loss of adsorbent but not effective for all dyes and is limited to specific application (Robinson *et al.*, 2001).

2.5. Adsorption Process

Adsorption is a process in which a gas or liquid solute is attached to the surface of a solid adsorbent, forming an atomic or molecular film through chemical or physical bond (Sasaki *et al.*, 2014). The molecules or atoms removed from liquid phase and being accumulated on the solid surface are called adsorbate while adsorbent is the component that providing the solid surface for adsorbate.

Dye adsorption consists of four consecutive steps (Al-Qodah, 2000). First step is the diffusion or convection of dye molecules through the bulk of solution. Second step is the diffusion of dye molecules through a diffusional boundary layer. Third step is the diffusion of dye molecule from the surface into interior of adsorbent materials. Last step is the attachment of dye molecule to the surface of materials through molecular interaction. Second step is depended on the agitation force and dye concentration. Adsorption of dye molecule on the surface is depended on third step and the last step is depended on the chemical natural of dye such as anionic, cationic and nonionic. Third step can be divided into two type of diffusion, which are porous diffusion and surface diffusion. Porous diffusion is the process in which adsorbate first diffuse into the liquid phase to fill up the pores and then only is adsorbed while surface diffusion is the process in which adsorbate is first adsorbed then diffuse from one place to another place (Noroozi and Sorial, 2013).

Adsorption process can be classified into two type which are physisorption and chemisorption (Králik, 2014). Physisorption is adsorption in which adsorbate is attached to the absorbent surface by van der Waals forces between molecules or/and atoms on the adsorbent surface. Chemisorption is adsorption in which adsorbate is attached to the absorbent surface by the formation of a chemical bond.

2.6. Carbon nanotube (CNTs) as adsorbent

CNTs have gained a lot of interest among researches and are selected by many researchers to develop nanocomposite membranes due to their extraordinary mechanical, electrical and thermal properties. CNTs are one of the potential adsorbents for dyes due to their large surface area, defined cylindrical hollow structure, high ration respect, easy modification and hydrophobic wall surfaces (Pathania *et al.*, 2017). CNTs also contain easily functionalizable surface which make them becoming one of the most potential adsorbent. CNTs are made up from carbon and having diameter measuring on nanometer scale. CNTs can have different structures, lengths and number of layers. CNTs consist of graphitic sheets, which have been rolled up into graphitic sheets and their characteristics are depending on how the graphitic sheet has rolled up to form tube. SWCNTs consist of one layer of graphitic sheet while MWCNTs consist of two or more layer of graphitic sheet. SWCNTs have outer diameters in the range of 1-3 nm, with inner diameters of 0.4-2.4 nm while MWCNTs have outer diameters in the range from 2 nm to 10 nm (Yen *et al.*, 2012). There are three main synthetic methods of CNTs such as arc discharge, laser ablation and chemical vapour deposition. For arc discharge, carbon nanotube is produced by evaporating carbon by electric arc discharge generated between two graphite electrodes under an inert atmosphere of helium (Saito *et al.*, 1996). For laser ablation, CNTs are produced by direct laser vaporization of graphite composite rods in the condensing vapour in a heated flow tube (Guo *et al.*, 1995). For chemical vapour deposition, substrate dispersed with small metal catalysts such as iron particle and is decomposed in an oven under constant flow of hydrocarbon and argon mixture gas (Guo *et al.*, 1995).

MWCNTs offers better adsorption performance than SWCNTs due to their structural configuration as MWCNTs has high amount of structural defects which are potential active sites for adsorption. The porous nature of MWCNTs formed by interaction between the SWCNTs via van der Waals forces also help to enhance the performance of adsorption (Vuono *et al.*, 2017).

Functionalization of CNTs can change their properties such as specific surface area and total pore volume. Modification of oxygen content such as hydroxide group, carbonyl group and carboxylic group on chemical surface of CNTs influences the maximum adsorption capacity on CNTs. The possible function group on CNTs is depended on the synthetic procedure and purification steps or it could be generated by oxidation with acid, plasma, ozone or removed by thermal treatment under 2200℃ (Kayiran *et al.*, 2004; Pan and Xing, 2008). Ability of CNTs to adsorb aromatic compounds through π- π interactions can be increased by moderate oxidation of CNTs while strong oxidation will reduces the availability sites for π- π interactions due to the formation of amorphous carbon (Chin *et al.*, 2010). CNTs with high oxygen content can cause lower adsorption capacity due to decrease of availability adsorption site or lead to hydrogen bonding, dispersive and electrostatic interaction (Chin *et al.*, 2010; Kayiran *et al.*, 2004). Presence of catalyst particle on CNTs also can directly influences the adsorption on the outer surface of carbon nanotube (Agnihotri *et al.*, 2005). Due to the versatility and lower cost of production of carbon nanotube, CNTs become one of the potential adsorbents to replace other types of adsorbents such as activated carbon which is very expensive and difficult to regenerate.

The mechanisms of adsorption of different dye compounds by CNTs depend on the types of dyes, whether the dyes are cationic or anionic. There are various possible interactions between CNTs and dyes such as hydrophobic interaction, van der Waals forces, π- π stacking, hydrogen bonding and electrostatic interactions.

2.7. Adsorption isotherm of dye on carbon nanotubes

The relationship between the equilibrium pressure $(P)_T$ in constant temperature and the amounts of dye adsorbed, n_s is important to study dye adsorption isotherm on CNTs (Yao *et al.*, 2010) :

$$n_a = F(P)_T \tag{2.1}$$

There are two types of isotherm equations which are commonly used to describe the adsorption equation, there are Langmuir and Freundlich isorthems models. Most appropriate correction of curve of adsorption equilibrium is important for optimizing the dye adsorption system design. (Yao *et al.*, 2010) found that equilibrium data of adsorption of methylene blue dye using CNTs fitted very with Langmuir isorthem. Langmuir isotherm model can be linearized in at least four different types which are expressed as (Rajabi *et al.*, 2017):

$$\text{Type (I)}: \frac{C_e}{q_e} = \frac{1}{KQ_m} + \frac{C_e}{Q_m} \tag{2.2}$$

$$\text{Type (II)}: \frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{KQ_mC_e} \tag{2.3}$$

$$\text{Type (III)}: q_e = Q_m - \frac{q_e}{KC_e} \tag{2.4}$$

$$\text{Type (IV)}: \frac{q_e}{C_e} = KQ_m - Kq_e \tag{2.5}$$

Where Q_m (mg/g) is Langmuir constant corresponding to dye removal capacity, K (L/mg) is Langmuir constant corresponding to adsorption energy, q_e (mg/g) is the amount of MB adsorbed at equilibrium, C_e (mg/L) is equilibrium concentration of MB. Table 2.3 shows an example of the adsorption capacity of CNTs on MB.

Table 2.3: Adsorption capacity of CNTs on MB, adapted from (Rajabi *et al.*, 2017)

Adsorbent	q(mg/g)	Time	Temperature (K)	pH
MWCNT-SH	166.7	60 mins	298	6
MWCNT	100	60 mins	298	6
CNTs	35.4	45 mins	273	7
CNTs	46.2	45 mins	298	7
CNTs	64.7	45 mins	333	7
CNTs	103.62	120 mins	290	7
CNTs	109.31	120 mins	300	7
CNTs	119.7	120 mins	310	7
CNTs	188.68	5 hours	298	6

2.8. Kinetic analyses

In order to determine the rate at which dye is removed from solution, kinetic analysis must be done. Pseudo-first and second-order models and intraparticle diffusion model are commonly used to describe the sorption of dyes using solid adsorbent (Yao *et al.*, 2010). One of the most widely used of adsorption rate equations is the Lagergren rate equations which is shown below:

Pseudo-first-order kinetic model of Lagergren (Yao *et al.*, 2010):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.6}$$

Pseudo-second-order equation corresponding to adsorption equilibrium capacity (Yao *et al.*, 2010):

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{2.7}$$

Where q_e (mg/g) is the amount of MB adsorbed at equilibrium, q_t (mg/g) is the amount of MB adsorbed at time, k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption, k_2 (g/mg.min) is rate constant of pseudo-second-order adsorption.

Intraparticle diffusion model (Kavitha and Namasivayam, 2007):

$$q_t = k_i t^{\frac{1}{2}} + C \tag{2.8}$$

Where C is intercept, t (min) is time and k_i is intraparticle diffusion rate constant (mg/g $min^{1/2}$).

2.9. PVA membrane

PVA has been widely used to fabricate polymeric membranes due to their environmentally friendly properties (Dong *et al.*, 2011). PVA polymer is a hydrophilic polymer with excellent water perm-selective properties and it is commonly used to enhance the hydrophilic properties in the membrane (Kim and Lee, 2009). PVA has high mechanical strength, high thermal resistance and pH stability (Zhang *et al.*, 2006), hence the PVA based membrane can be used in wastewater treatment of variety characteristics either acidic or alkaline wastewater.

Although, PVA membrane exhibit high degree of swelling in water. This problem can be minimised by cross-liking PVA membrane with glutaraldehyde (GA). The reaction of cross-linked PVA with GA is shown as Figure 2.2.

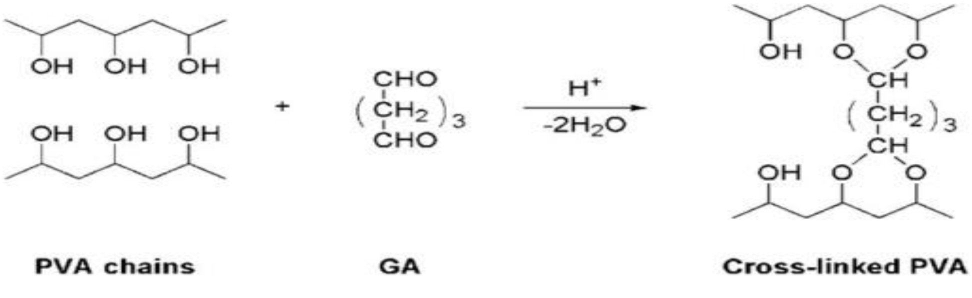


Figure 2.2: Gelation of PVA membrane by GA (Jikihara *et al.*, 2013)

The extent of swelling of PVA membrane is depended on the pH, salts, light, electric field and temperature (Marcombe *et al.*, 2010). The cross-link content, ionic content and hydrophilic content control the swelling process of a hydrogel (a network of polymer chain that are hydrophilic) (S.Matty *et al.*, 2015).

The swelling of PVA membrane is decreased with the increasing of concentration of GA, this is because crosslinking agent prevent the dissolution of hydrogel. By increasing the concentration of GA, the space between copolymer chains is decreased and therefore the structure is highly rigid and can hold a large quantity of water (Peppas and Simons, 2004). Hence, the regeneration of adsorbent will be easier.

Besides, PVA membrane is able to be cross-linked by exposing PVA solution to repeated cycle of freezing and thawing, as a result the formation of crystallites. The intermolecular interaction among the chain may produce crystallites when the temperature of PVA solution decreases below room temperature due to the formation of hydrogen bonds. The crystallites proceed further when the cooling time increases, as a result high mechanical strength of PVA membrane without chemical cross-links. On the other hand, thermal cross-linking is possible for PVA membrane. Lima *et al.* (2011) cross-linked PVA membrane by heating at about 120℃ using a ventilated oven.

2.10. PVA/MWCNT nanocomposite membrane

PVA/MWCNT nanocomposite membrane was prepared by ultrasonification method using dimethylformamide (DMF) and deionized water as solvent. Jagadish *et al.* (2016) found PVA/MWCNT nanocomposite membrane is an effective adsorbent to remove dye in a very short duration via single step reaction as shown as Figure 2.3.

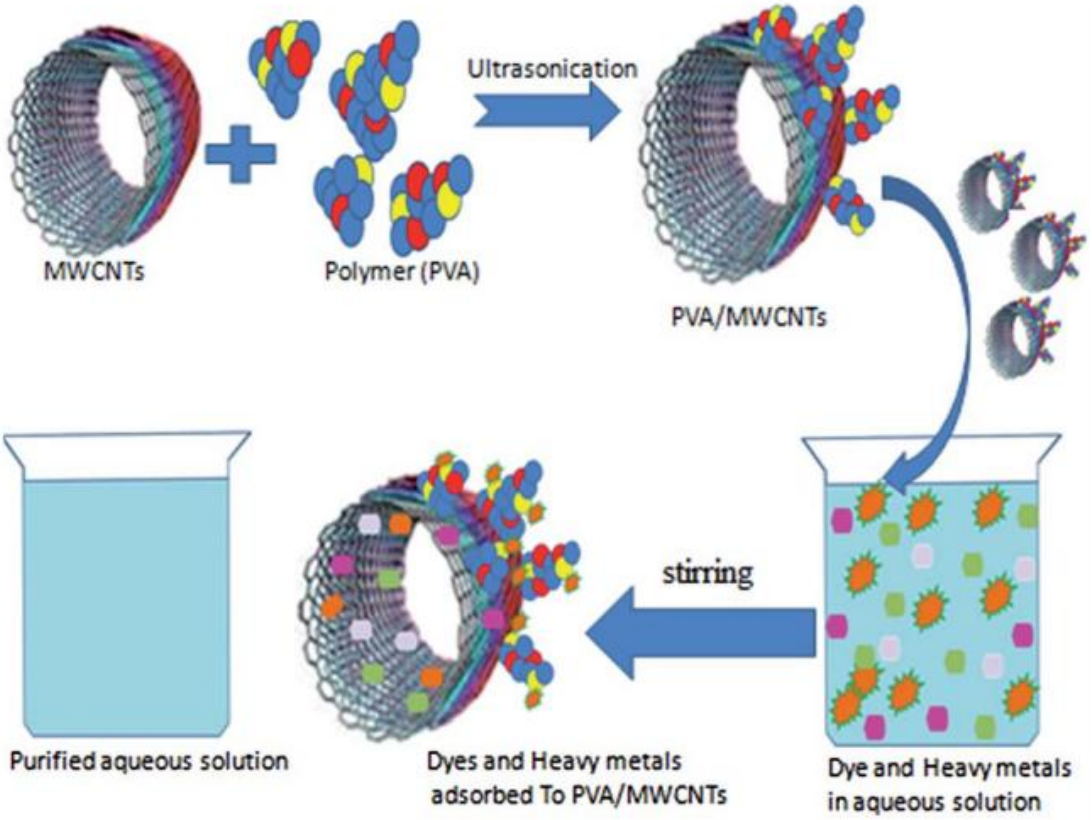


Figure 2.3: Preparation of PVA/MWCNT nanocomposite membrane by ultrasonification and purification of effluent aqueous solution (Jagadish *et al.*, 2016)

2.11. Solution casting

A small scale of polymer membrane is able to prepare by solution casting method. There are three key characteristics of raw materials so that the polymer membrane is able to form via solution casting method (Siemann, 2005). Firstly, the polymer is soluble in water or a volatile solvent. Secondly, reasonable minimum solid content and thirdly, homogenous film must be able to form and able to release from the casting support. Solution casting does not require convectional extrusion or injection molding technologies. The polymer solution is casted on a glass plate with a casting knife and then the spread thin film is left for evaporation to produce solid membrane.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

Table 3.1 shows the materials used for the experiment.

Table 3.1: Materials for experiment

Material	Specifications	Supplier
MWCNT	>95 wt. % of purity 2.56 wt. % of COOH content 5-15 nm of outer diameter 50 µm of length < 1.5 wt. % of ash content	Timesnano
PVA	96 % hydrolyzed	Acros Organics
GA	Formula weight : 100.12 Pentanedial Glutaral : 24 % to 26.5 %	Fisher Chemical
Acetone	99.5 wt. % of purity Molecular weight : 58.08 0.790 g/cm^3 of density	Fisher Chemical
HCl	Fuming : 36 % Molecular weight : 36.45	R&M Chemicals
MB	Molecular weight : 355.89 Absorption maximum lambda max : 660-665 nm Specific absorptivity A1%/1 cm : 2250-2750 Assay (spectrophotometrically) : > 82 %	Sigma Aldrich
Deionized Water	N/A	Produced in lab
Distilled Water	N/A	Produced in lab

3.2. Preparation of PVA membrane

5 wt. % of PVA solution was prepared by dissolving 5 g of PVA powder into 95 g of deionised water. The solution was kept stirring at 90℃ overnight to form a homogenous solution. 5 mL of PVA solution was casted on the petri dish. The casted solution was allowed to dry under ambient condition up to 4 days to make sure that the form membranes are fully dried. PVA membrane was then peeled off and stored in zip plastic bag.

3.3. Preparation of PVA/ MWCNT nanocomposite membrane

The PVA/MWCNT nanocomposite membrane was prepared by adding 0.18 g of MWCNT powder into 17.82 g of 5 wt. % of PVA solution that was prepared earlier to form 1 wt. % of the MWCNTs fillers in the PVA/MWCNT nanocomposite membrane. In order to facilitate the dispersion of MWCNTs in PVA solution, the solution was sonicated for 20 minutes using an ultrasonic water bath. The solution was then stirred overnight to ensure the even distribution of MWCNTs powder. The casted solution was allowed to dry under ambient condition up to 4 days to make sure the form membranes are fully dried. The PVA/MWCNT nanocomposite membrane was then peeled off and stored in a zip plastic bag.

3.4. Cross-link PVA membrane with GA

Cross-linking of PVA membrane with GA was carried according to the method reported by P. Kusumocahyo and Sudoh (2000). The resultant PVA membrane was immersed into a solution containing 5 vol. % of GA solution, 0.12 vol. % of HCl and 94.88 vol. % of 0.96 mol/L of acetone solution at 40 ℃. In a typical experiment, 100 mL of cross-linked solution was prepared, where 0.96 mol/L of acetone solution was prepared by diluting 6.70 mL of acetone solution (density: 0.790 g/cm^3) into 88.18 mL of deionised water. The diluted solution was then mixed into 5.0 mL of GA solution then adding 0.12 mL of HCl solution. Subsequently, 5.0 mL of cross-linked solution was put on the top of PVA membrane for 3 hours at 40 ℃ in an oven. After 3 hours, the membrane was then immersed into distilled water for 1 day at 40℃ in the oven to remove residue on the surface of membrane.

3.5. Preparation of MB dye and calibration curve of dye concentration

0.5 mg/L, 1.0 mg/L, 1.5 mg/L, 2.0 mg/L, 2.5 mg/L, 3.0 mg/L, 3.5 mg/L and 4.0 mg/L of MB solutions were prepared by dilution. Then, a double-beam UV-Visible spectrometer (Model Shimadzu UV-1800, Japan) was used to measure the absorbance of dye solution with dye concentration of 0 mg/L, 0.5 mg/L, 1.0 mg/L, 1.5 mg/L, 2.0 mg/L, 2.5 mg/L, 3.0 mg/L, 3.5 mg/L and 4.0 mg/L, respectively. The wavelength of MB was set to 665 nm. The measurement of absorbance was repeated 3 times to get the average reading. Calibration curve was plotted for MB dye by plotting a graph of absorbance against concentration of dye solution. The calibration curve obtained can be used to measure the concentration of dye solution after the adsorption of dye from solution using PVA membrane and PVA/MWCNT nanocomposite membrane.

3.6. Study the effect of contact time on the removal of MB dye

In order to optimise the contact time of adsorption of MB dye on PVA membrane and PVA/MWCNT nanocomposite membrane, various contact time of removal of MB dye were conducted. The PVA membrane was immersed into 30 ml of methylene blue dye solution with dye concentration of 3 mg/L at 20℃. Similarly, the PVA/MWCNT nanocomposite membranes also immersed into another 30 mL of MB dye solution with same dye concentration at 20℃ in order to compare the performance of adsorption using PVA membrane. After 1 hour, the remaining concentration of MB dye in the samples was determined by using UV-Visible spectrometer. The experiments were repeated at various time 2 hours, 3 hours and 4 hours. If the amount of removal of MB was not changed after a specific time, the time was selected as optimum time for studying effect of parameters.

3.7. Study the effect of initial MB dye concentration on the adsorption process

PVA membrane was immersed into 30 mL of MB dye solution with dye concentration of 1.0 mg/L, 2.0 mg/L, 3.0 mg/L and 4.0 mg/L, respectively at 20 ℃. The experiment was conducted in 100 mL of conical flasks. After optimum time (found in section 3.6), the remaining concentration of MB dye in the samples were determined by using UV-Visible spectrometer. The experiment was repeated by using PVA/MWCNT nanocomposite membrane as adsorbent.

3.8. Study the effect of temperature on the adsorption

PVA membrane was immersed into 30 ml of MB dye solution with dye concentration of 3 mg/L at 25℃. Similarly, PVA/MWCNT nanocomposite membrane was immersed into another 30 mL of MB dye solution with similar dye concentration at 25℃ in order to compare the performance of adsorption using pure PVA membrane. After optimum time, the remaining concentration of MB dye in the samples were determined by using UV-Visible spectrometer. The experiment was repeated under different temperature of samples which are 25℃, 30℃, 35℃ and 40℃.

3.9. Adsorption rate of MB dye

The absorbance values measured by double-beam UV-Visible spectrometer for untreated (before adsorption) and treated (after adsorption) of dye solution were recorded into a table. The samples must be stirred to ensure the dye was distributed evenly before measuring by spectrometer. The adsorption rate and adsorption amount of MB concentration in the samples before and after adsorption was calculated using the below equation (Robati *et al.*, 2016):

$$q_e = \frac{C_0 - C_e}{W} x\, V \tag{3.1}$$

Where q_e is amount of MB dye adsorbed at equilibrium (mg/g), C_0 is the MB dye concentration in the sample before adsorption (mg/L), C_e is the equilibrium concentrations of MB concentration in the sample (mg/L), W is weight of adsorbent used (g), V is the volume of MB solution (L). Figures 3.1 shows the overall layout of research flow diagram.