

POLYVINYLIDENE FLUORIDE/MULTIWALLED CARBON

NANOTUBES MEMBRANE FOR METHYLENE BLUE DYE

REMOVAL VIA ADSORPTION

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by

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LIST OF SYMBOLS

Symbol	Description	Unit
P	Pressure	mm Hg
T	Temperature	°C
MW	Molecular weight	g/mol
OD	Outer diameter	mm
wt%	Mass fraction in percentage	%

LIST OF ABBREVIATIONS

pH	Potential of hydrogen
CNT	Carbon nanotube
SWCNT	Single-walled Carbon Nanotube
MWCNT	Multi-walled Carbon Nanotube
MB	Methylene Blue
MFG Code	Manufacturing code
DMF	Dimethylformamide
R ²	Correlation coefficient
R _L	Separation factor
hr	Hour (unit for time)
min	Minute (unit for time)
g	Gram (unit for mass)
mg	Milligram (unit for mass)
ml	Milliliter (unit for volume)
cm	Centimeter (unit for length)
mm	Millimeter (unit for length)

MEMBRAN POLIVINILIDIN FLUORIDA/KARBON NANO TIUB MULTI-DINDING UNTUK PENYINGKIRAN METILENA BIRU MELALUI PENJERAPAN

ABSTRAK

Membran polivinilidina fluorida (PVDF) dihasilkan melalui kaedah penyongsang fasa untuk penjerapan pewarna metilena biru dari larutannya. Karbon tiub nano multi-dinding (MWCNT) mengandungi kumpulan fungsi karboksilik (-COOH) dimasukkan ke dalam membran PVDF untuk meningkatkan kekuatan mekanikal serta sifat penjerapan membran. MWCNT bertindak sebagai jambatan yang akan memberikan lebih banyak tapak penjerapan kosong berbanding dengan membran PVDF dengan sendirinya untuk membantu dalam penjerapan pewarna metilena biru. Proses penjerapan kemudian diuji dengan 3 faktor yang berbeza iaitu suhu, masa dan kepekatan permulaan larutan pewarna metilena biru (MB) untuk melihat faktor-faktor yang mempengaruhi PVDF serta membran PVDF/MWCNT. Kajian tentang kesan suhu menunjukkan bahawa kecekapan penjerapan menurun apabila suhu di sekitarnya meningkat. Ini membawa kepada kesimpulan bahawa proses penjerapan antara PVDF dan PVDF/MWCNT dan pewarna MB adalah proses endotermik. Kajian masa hubungan antara membran dan pewarna MB menunjukkan bahawa proses bermula dengan cepat apabila kepekatan larutan turun sebanyak 5.66% dalam jam pertama dan perlahan-lahan berkurang apabila kepekatan larutan hanya berkurang sebanyak 2% dalam 3 jam seterusnya kerana tapak penjerapan kosong yang sedang diisi penuh oleh larutan pewarna MB. Kajian kepekatan permulaan penyelesaian pewarna MB menunjukkan bahawa kedua-dua membran PVDF dan PVDF/MWCNT dapat menampung larutan pewarna MB 1-2 mg/l tanpa kehilangan kecekapan. Membran PVDF mula kehilangan kecekapan pada kepekatan pewarna MB 3 mg/l sedangkan membran PVDF/MWCNT mula kehilangan kecekapan pada kepekatan pewarna MB 4 mg/l. Kajian isotherm penjerapan menunjukkan bahawa isotherm yang paling berkaitan adalah isotherm Langmuir.

POLYVINYLIDENE FLUORIDE/MULTIWALLED CARBON NANOTUBES MEMBRANE FOR METHYLENE BLUE DYE REMOVAL VIA ADSORPTION

ABSTRACT

The polyvinylidene fluoride (PVDF) membrane is fabricated by phase inversion method for the adsorption of methylene blue dye from its solution. The functionalized multiwalled carbon nanotubes (MWCNTs) containing carboxylic groups (-COOH) functional groups are incorporated into the PVDF membrane to improve the mechanical strength as well as the adsorption qualities of the membrane. The MWCNTs act as a bridge that would provide more vacant adsorption sites compared to PVDF membrane by itself to assist in the adsorption of the methylene blue dye. The adsorption process is then tested with 3 different factors which are temperature, contact time and the initial concentration of the methylene blue (MB) dye solution to observe which factors affect the PVDF as well as the PVDF/MWCNT membrane most. The study of the effect of temperature showed that the efficiency of the adsorption decreases as the temperature of the mixture increases. This leads to the conclusion that the adsorption process between PVDF as well as PVDF/MWCNT and the MB dye is an endothermic process. The study of the contact time between the membrane and the MB dye showed that the process begins rapidly when the concentration of the solution decreases by 5.66% in the first hour and slowly reduces in efficiency when the concentration only reduced about 2% over the next 3 hours due to the vacant adsorption sites being filled. The study of the initial concentration of MB dye solution revealed that both PVDF and PVDF/MWCNT membrane is able to accommodate MB dye solution of 1-2 mg/l without loss of efficiency. The PVDF membrane starts losing efficiency at MB dye concentration of 3 mg/l whereas PVDF/MWCNT membrane starts losing efficiency at MB dye concentration of 4 mg/l. The study of the adsorption isotherms showed that the best fit isotherm for the adsorption process between the PVDF and PVDF/MWCNT membrane with the methylene blue solution would be the Langmuir isotherm.

CHAPTER 1: INTRODUCTION

1.1 Research background

Adsorption has been used as one of the primary treatment procedures for the removal of different pollutants primarily organic pollutants such as dyes from industrial waste water. Adsorption can be defined as the adhesion of gas, liquid or a dissolved solid onto a solid surface. The occurrence of adsorption is considered a surface phenomena where it mainly utilizes surface forces. The process can occur when a solution with adsorbable solute, called adsorbate, comes into contact with a solid, called the adsorbent, with highly porous surface structure liquid-liquid intermolecular forces of attraction causing the solute to attach to the solid surface. Adsorbents can be formed from many different commonly found items. Some of the common sources of adsorbents are zeolites, charcoal, clays, ore and other waste resources. Adsorbents can be prepared from many different waste resources such as coconut shell, rice husk, petroleum wastes, tannin-rich materials, sawdust, scrap tyres, fruit wastes and many more (Cameselle et al., 2013).

Common adsorbent characteristics are that they usually have high abrasion resistance, high thermal stability and small pore diameters which results in higher exposed surface area and hence provide a high capacity for adsorption to occur. The efficiency of using adsorption as the method to remove dye depends on the physical and chemical properties of the adsorbent and the adsorbate, their cost, availability, ease of operation, surface area and least toxicity (Kausar et al., 2018). Polyvinylidene fluoride (PVDF) has been a suitable membrane material due to its alkali resistance, corrosion resistance, chemical stability, thermal stability and its long service life. Hydrophilic modifications of the PVDF membrane has been topic of many researches due to the surface hydrophobicity of the PVDF.

Through the years, there have been researches for nanoadditives to improve the hydrophilicity of PVDF membrane (Zhu et al., 2017). Since carbon nanotubes (CNTs) has proven to be an excellent material for many applications due to its characteristics like light-weight, high surface area, chemical and electrochemical stability, thermal and electrical conductivities and mechanical strength (Tabrizi and Yavari, 2015). These characteristics have introduced CNTs as promising choices for environmentally safe applications in sorption, filtration and separation processes (Kuo et al., 2008, Ai et al., 2011, Machado et al., 2014). The use of CNTs for sorption processes are good but the recovery of the CNTs prove to be difficult due to its very small size. Thus its extraction from the solution after the adsorption process is tough. The support provided by the PVDF membrane would prove to be essential in the feasibility and reusability of the membrane after every adsorption cycle. Thus combining PVDF and CNTs as a nanocomposite membrane would prove to be ideal to study for the adsorption of methylene blue dye.

1.2 Problem Statement

Textiles, printing, rubber, cosmetics, plastics and leather industries uses dyes as coloured compounds to colour their products. As a result, there is large generation of coloured wastewater. Dyes are mainly characterized into anionic, cationic and non-ionic dyes. Dyes can be defined as chemical compounds that attach itself to fabric or other surfaces to colour it. This are usually used as decoration purposes in food, clothing, labelling and many other sectors in the industry. The three main removal techniques of dyes consist of physical, chemical and biological methods. The various removal methods consist of biological degradation, ion exchange, chemical precipitation, reverse osmosis coagulation, flocculation and flocculation. However, these removal methods all had their significant disadvantages compared to the adsorption process such as high cost and generation of toxic sludge. Thus adsorption has become the most preferred method of dye removal (Seow and Lim, 2016).

The biggest issue in the removal of dye from wastewater is due to the high cost of the process to remove the dye. Chemical coagulation which is a common treatment method requires an extra step to destroy the large amount of sludge generated thus leading to a high cost (Sala and Gutiérrez-Bouzán, 2012). In general, the materials used as adsorbents lacks mechanical strength and the option to be recovered successfully after its usage as adsorbents. Thus, polymeric and nanocomposite membranes are introduced as an efficient way to remove the dye and for the material to be extracted from the solution easily.

In this study, MWCNT will be introduced into PVDF membrane using the phase inversion method. This membrane will then be tested as an adsorption material to determine its viability as an adsorbent for methylene blue dye. The optimal conditions to use the membrane will be determined by studying the factors that affect adsorption which is the initial dye concentration, temperature of the process and time that the membrane is left to adsorb the dye.

1.3 Research Objectives

The objective for this research,

- i. To synthesize composite membrane of PVDF with and without MWCNTs as fillers
- ii. To characterize composite membrane of PVDF incorporated with and without MWCNTs via adsorption test with methylene blue dye as the adsorbate
- iii. To study the equilibrium isotherm and kinetic of MB adsorption on the resultant membrane

CHAPTER 2: LITERATURE REVIEW

2.1 Adsorption

Adsorption is the adhesion of atoms, ions, molecules of gas, liquid, or dissolved solids to a surface. A film of adsorbate (the molecules that are being collected) will form on the surface of the adsorbent. This process differs from the absorption process where a fluid permeates or is dissolved by a liquid or a solid. Adsorption occurs due to a consequence of the surface energy similar to surface tension. The bonding materials (ionic, covalent or metallic) of the respective atoms of the material are filled by the other atoms in the material for bulk material. However, atoms on the surface of the adsorbent are not surrounded by other adsorbent atoms. This gives space for adsorbate material to be adsorbed onto the adsorbent surface. The natures of the bonds depend on the material involved. Generally, the adsorption process is usually classified as a physisorption (as a results of Van der Waals forces) or chemisorption (as a result of covalent forces). There are many processes that have been used for removal of dye from waste water through the years such as precipitation, flocculation, electro-kinetic coagulation, membrane filtration, irradiation and ozonation. However, this processes have been proven to be quite costly and thus cannot be effectively done by small industries to treat the wastewater. Thus, through the years adsorption has been preferred as a treatment of wastewater due to its cheapness, simple design, less energy usage, no toxic effect while still being highly effective in the treatment of the wastewater (Seow and Lim, 2016). Over the past few years, many researches have been done to improve the treatment of wastewater with adsorption. The adsorption process is either used as a stage of integrated physical-chemical-biological process for the treatment of the wastewater (Morawe et al., 1995, Geenens et al., 2001), or biological process simultaneously (Kargi and Yunus Pamukoglu, 2003). There are four consecutive steps that occur in the dye removal by

adsorption process (Al-Qodah, 2000). Firstly, the dye molecules will diffuse through the bulk of solution. Secondly, diffusion of the dye molecules will occur through a diffusional boundary layer (film diffusion). Thirdly, the dye molecules will diffuse from the surface into the interior of the adsorbent materials. Lastly, the dye molecules will attach to the surface of the materials through molecular interactions. The factors that affect the adsorption of dye are the initial concentrations of dye, the pH of the solution, the dosage of adsorbent, temperature of the solution as well as the duration of the adsorption process (Seow and Lim, 2016).

2.1.1 Adsorption Kinetics

There are two models that can apply to an adsorption study. The adsorption reaction models as well as the adsorption diffusion models (Piergiovanni, 2014). Adsorption reaction models are based on the chemical kinetics of the process and are considered pseudo first-order system. The rate of dye adsorption based on the adsorption capacity can be modelled as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2.1)$$

where q_t (mg dye/g adsorbent) represents the quantity of dye adsorbed at time t , q_e (mg dye/g adsorbent) is the quantity of dye adsorbed at equilibrium and k_1 is the average value of the rate constant. When initial condition is set that $q_t = 0$ at $t = 0$, the equation above will yield

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2.2)$$

The second model which is based on the adsorption diffusion consist of three steps where first the dye will diffuse across the external film surrounding the adsorbent, then

diffuses into the pores, and then finally will be adsorbed onto the active site. This process is modelled as a pseudo second-order model:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2.3)$$

Solving above equation with initial condition $q_t = 0$ at $t = 0$ results in

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (2.4)$$

which can then be rearranged to become

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \quad (2.5)$$

This form of the equation can be plotted without an estimation of q_e .

2.1.2 Adsorption Isotherms

The study of adsorption includes the study of the of the equilibrium nature of the adsorption process. The process can be studied through graphs called the adsorption isotherms. These represents the basic adsorption isotherm as shown in Figure 2.1:

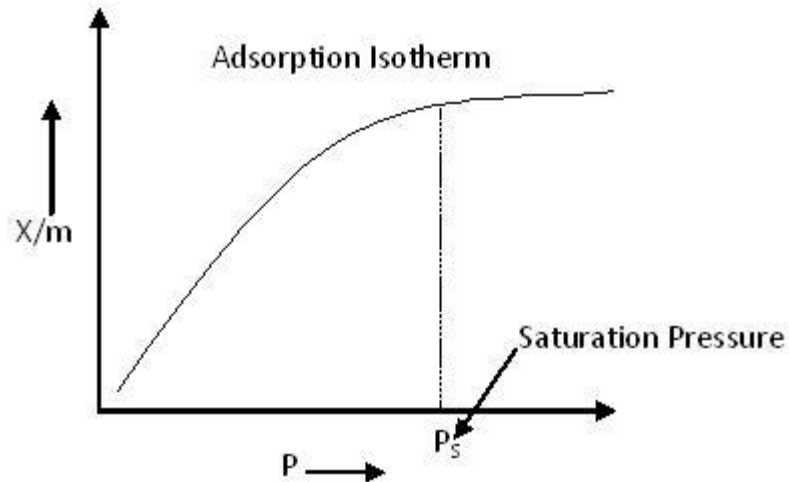


Figure 2.1 Basic Adsorption Isotherm

X/m represents the adsorption per gram of adsorbent which is obtained by dividing the amount of adsorbate used (X) by the weight of the adsorbent (m). From the graph above, it can be predicted that adsorption will not occur anymore after the saturation pressure P_s . This occurs since there are only a limited numbers of vacancies on the surface of the adsorbent. A stage is reached when all the sites are occupied at high pressure and further increases in the pressure will not result in any change. There are five different type of adsorptions namely the Type I, Type II, Type III, Type IV and Type V adsorption isotherms.

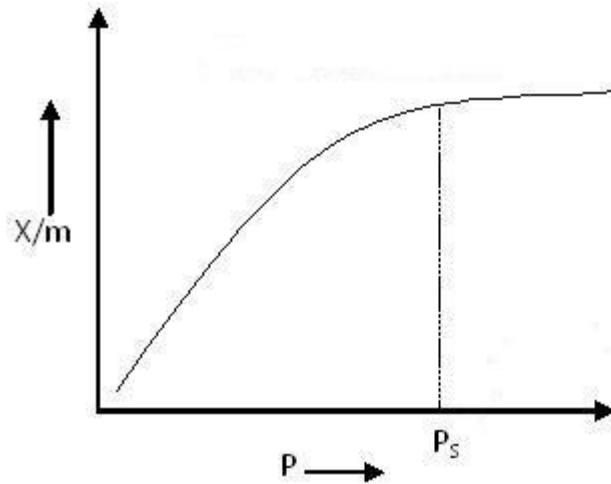


Figure 2.2 Type 1 Adsorption Isotherm

The above graph represents monolayer adsorption and can be explained using the Langmuir Adsorption Isotherm. Examples of Type I adsorption are the adsorption of nitrogen or hydrogen on charcoal.

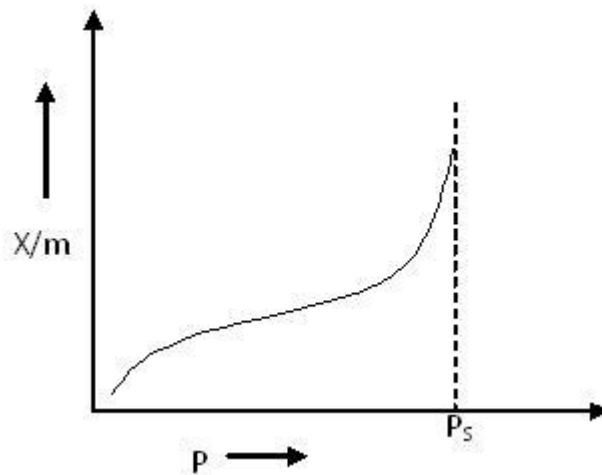


Figure 2.3 Type 2 Adsorption Isotherm

Type II adsorption isotherm differs a lot from the Langmuir model of adsorption which will be explained later. Monolayer formation is depicted by the intermediate flat region in the isotherm. Examples of Type II adsorption are the nitrogen adsorbed at -1950°C on iron catalyst and nitrogen adsorbed at -1950°C on silica gel.

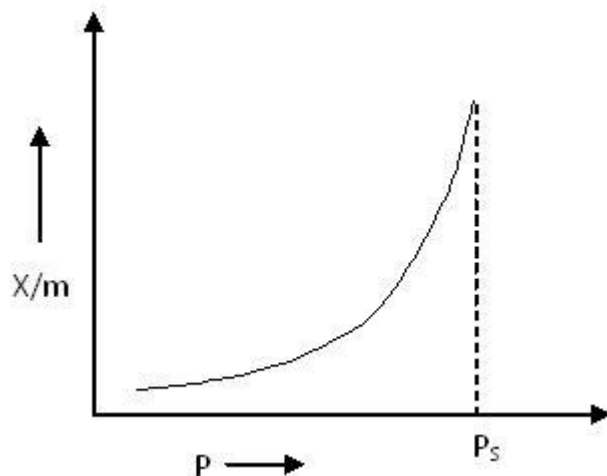


Figure 2.4 Type 3 Adsorption Isotherm

Type III adsorption isotherm also largely deviates from the Langmuir adsorption isotherm model. The isotherm explains the formation of multilayer on the surface of the adsorbent in the adsorption process, Since, there is no flat region, this indicates that there is no monolayer formation. Examples of Type III adsorption isotherm are bromine at 790°C on silica gel or iodine at 790°C on silica gel as well.

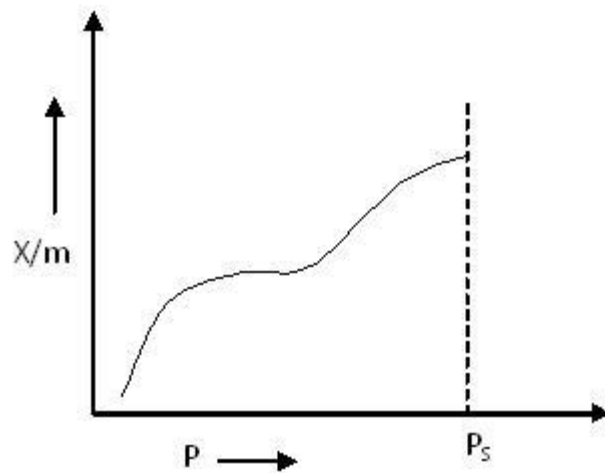


Figure 2.5 Type 4 Adsorption Isotherm

At lower pressures, the adsorption model is very similar to the type II adsorption isotherm model. The graph shows a formation of monolayer followed by multilayer formation. The saturation level reaches at pressures below the saturation vapour pressure. This is due to the possibility of gases being condensed in the tiny capillary pores of adsorbent at pressure below the saturation pressure of the gas. Examples of Type IV adsorption isotherm are the adsorption of benzene on iron oxide at 500 °C and adsorption of benzene on silica gel at 500 °C.

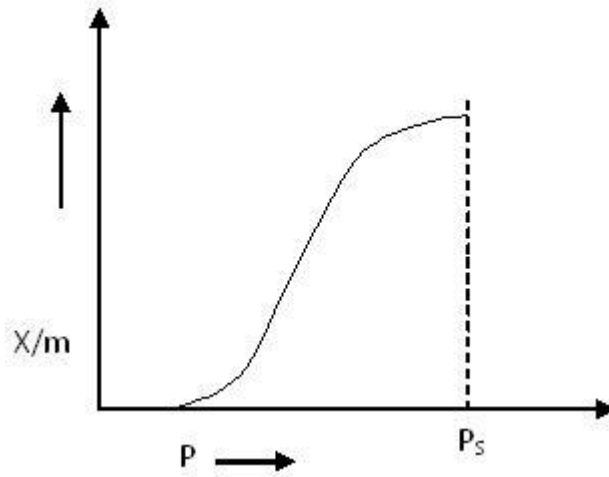


Figure 2.6 Type 5 Adsorption Isotherm

Type V adsorption isotherm is very similar to the type IV adsorption isotherm. Thus the explanation of the graph is similar to the type IV adsorption isotherm. Examples of type V adsorption isotherm is the adsorption of water at 1000 °C on charcoal.

There are two main adsorption isotherms that are most common and can be compared to most of the nature of the adsorption isotherm. They are the Freundlich adsorption isotherm and the Langmuir adsorption isotherm. The Freundlich equation represents the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as the Freundlich Isotherm.

$$\frac{x}{m} = kP^{\frac{1}{n}} \quad (2.6)$$

where, x/m = adsorption per gram of adsorbent, P is pressure, k and n are constants where values depend on the adsorbent and gas at the particular temperature. Freundlich isotherm is

able to correctly establish the adsorption relationship at lower pressures, but is unable to predict the values of adsorption at higher pressures.

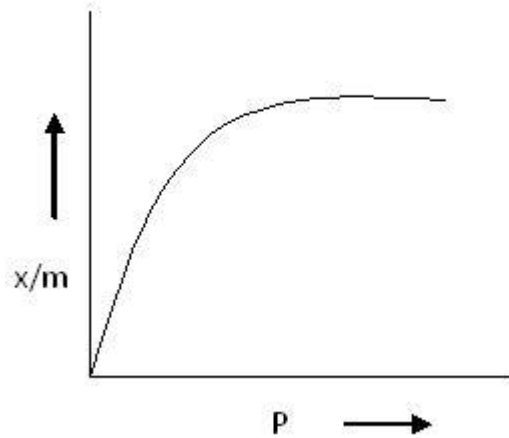


Figure 2.7 Freundlich Adsorption Isotherm

Taking the logarithms of the above equation,

$$\frac{\log(x)}{m} = \log k + \frac{1}{n} \log P \quad (2.7)$$

Langmuir isotherm model is a model that represents the new model isotherm for gases adsorbed to solids which comes from a proposed kinetic mechanism. This isotherm model is based on several assumptions where dynamic equilibrium exists between the adsorbed gas molecules and the free gas molecules. It is based on four assumptions:

1. The surface of the adsorbent is uniform where all the adsorption sites are equivalent.
2. Adsorbed molecules do not interact.
3. All adsorption occurs through the same mechanism.

4. At maximum adsorption, only a monolayer is formed.

Langmuir suggests that adsorption takes place through this mechanism:



where,

A(g) = Unadsorbed gaseous molecule

B(s) = Unoccupied metal surface

AB = Adsorbed gaseous molecule,

Based on this theory, a relationship is formed between the number of active sites of the surface undergoing adsorption and pressure called the Langmuir equation:

$$\theta = \frac{KP}{1 + KP} \quad (2.9)$$

where,

Θ = Number of sites of the surface which are covered with gaseous molecule

P = Pressure

K = Equilibrium constant for distribution of adsorbate between the surface and the gas phase

However, the limitation of the Langmuir adsorption model is that it is valid at low pressure only. At lower pressure KP is so small, thus making the factor (1+KP) to be ignored. Thus the equation will then reduce to

$$\theta = KP \quad (2.10)$$

At high pressure, the KP value will be very large, thus leading the factor (1+KP) in the denominator to be nearly equal to KP thus the equation will reduce to unity.

$$\theta = \frac{KP}{KP} = 1 \quad (2.11)$$

2.2 Adsorbents

Adsorbents are the material at which the adsorption takes place. One of the most common material that has been used as adsorbents are activated carbon. Since activated carbon can be made from many different sources, the source of material is also much diversified. Adsorbents usually are in shape of moldings, rods, monoliths or spherical pellets with hydrodynamic diameter between 0.5 and 10 mm. High surface capacity is a major requirement for adsorbents. This can be achieved by material with small pore diameters. Since they will be released into the solution freely, it is required that the adsorbents also have high abrasion resistance and thermal stability. Mass transport is an important phenomenon that will occur throughout the surface of the adsorbents. Thus adsorbents with unique and efficient pore structures that enables fast transport of the gaseous vapors is really effective to be chosen as adsorbents (Yang, 2003b)

As mentioned earlier, there are many sources of different adsorbents that can be used for different purposes. Researchers have been done to use adsorption in almost all fields due to low cost, and easily found materials as adsorbents. These adsorbents can be characterized into three classes namely the oxygen containing compound, carbon based compound and the

polymer-based compound. Oxygen containing compounds are usually hydrophilic and polar such as silica gel and zeolites. Carbon based compounds are usually hydrophobic and non-polar that include materials such as activated carbon and graphite. Polymer based compounds are polar or non-functional groups that exist on a porous polymer matrix.

Activated carbon is most commonly used as adsorbents for organic substances as well as waste gas. It is used widely due to its chemical properties such as the surface group and physical properties such as pore size distribution and surface area can be adjusted to the specific ones that's needed as good adsorbents. Activated carbon has several advantages to its name but further research and studies need to be done to overcome the disadvantages that activated carbon brings when it is used as a adsorbent. The disadvantage include that activated carbon usually have a short service life. Once the adsorption sites are filled, the activated carbon has to be replaced with new activated carbon. Besides, the activated carbon adsorbents is known to further deteriorate in its adsorption capacity as the number of cycles increases (Yang, 2003a). This would lead to increased purchase costs in the industry. Besides the effectiveness of the activated carbon adsorbents depend a lot on the contact time between the adsorbate and adsorbent. This results in processes that flow fast or have less contact time with the activated carbon adsorbent has poor adsorption effectiveness. The recovery of the product after undergoing adsorption with activated carbon as adsorbents might require further distillation or extraction process. The spent activated carbon adsorbents are also considered hazardous waste in some cases.

2.2.1 Polyvinylidene fluoride

PVDF has been known as a polymer membrane with excellent properties such as inertness, high thermal and mechanical strength, high hydrophobicity, compared to other commercialized polymeric materials (Gopal et al., 2007, Liu et al., 2011). It has been used extensively in ultrafiltration and microfiltration processes for general separation purposes. Since they are so extensively used, current researchers are looking forward to use the membrane in applications of contactor and membrane distillation. Several studies have been done in the development of PVDF as membranes (Uragami et al., 1981, Munari et al., 1983). The PVDF membranes are able to reach high performances for their applications in membrane distillation, membrane contactor as well as in wastewater treatment. The reason that allow PVDF to be the chosen membrane over other polymers is due to its ability to dissolve in common organic solvents. As a result, porous PVDF membranes can be formed from via phase inversion method by a simple immersion precipitation process. Since it has high mechanical strength and high chemical stability, it makes it suitable to be used in wastewater treatment systems. The adsorption qualities of the PVDF membrane can be improved with the surface modification of PVDF membranes such as surface coating or surface grafting (Liu et al., 2011).

2.2.2 Carbon Nanotubes

Carbon nanotubes (CNTs) have attracted special attraction due to its superior separation performances. CNTs are tubular graphic sheets rolled-up along a central axis with a diameter within nanometer range. The efficiency of the CNTs depends on the effective dispersion into the polymer matrix. The enhanced sorption-desorption phenomenon and

faster transport over the CNTs surface make it fit to be used in the adsorption process (Skoulidas et al., 2002). CNTs can be classified as single-walled carbon nanotubes (SWCNT) and multiwalled carbon nanotubes (MWCNT). MWCNTs exhibit better performances than SWCNTs in terms of its adsorption applications. This is due to its structural configuration (Szabó et al., 2010, Serp et al., 2003). In MWCNTs the porous quality of the material can be described as inner hollow cavities of small diameter and aggregated pores, formed through the interaction between single CNTs from Van der Waals forces. The oxygen content on CNTs influences the maximum adsorption capacity and can depend on the synthesis or purification steps or generated by oxidation with acids, plasma, ozoned or removed by thermal treatment (Kayiran et al., 2004). Vuono et al. (2017) studies on CNTs show that it is more effective than activated carbon in the removal of dye from wastewater. The study also shows that the efficiency of recovery of dyes on CNTs is near to unity in the investigated conditions. This allows the reusability of the dyes to be an option for the industries.

2.3 Membrane Fabrication Method

There are many different methods involved in the fabrication of membranes such as solution casting, in situ polymerization and phase inversion (Ismail et al., 2015). Phase inversion method has proven itself to be successful in producing well-functioning membranes Phase inversion is capable to produce membranes that can achieve certain characteristics in its membrane such as being more porous. Different membrane characteristics would significantly effect in different ways. Phase inversion casting method is known to produce membranes with porous characteristics.

2.3.1 Phase Inversion

Phase inversion is a process where the polymer transformation is controlled from a liquid phase to a solid phase (Ladewig and Al-Shaeli, 2017). There are four basic techniques that is used to create phase inversion membranes that is the precipitation from vapor phase, precipitation by controlled evaporation, thermally induced phase separation, and immersion precipitation. Immersion precipitation is the most widely used method for preparing polymer membrane and thus is used in most researches producing PVDF membrane (Ladewig and Al-Shaeli, 2017). Since CNTs are inert material, the material can be added into the PVDF without any changes to the phase inversion process. Precipitation from the vapor phase happens by placing a solvent-polymer mixture is cast on the film, and placed in a vapor atmosphere that contains nonsolvent saturated with the same solvent. Membrane forms by the diffusion of nonsolvent into the cast film thus resulting in a porous membrane. Precipitation by controlled evaporation is achieved by dissolving the polymer in a solvent and nonsolvent mixture. The evaporation of the solvent will occur and the concentration of the nonsolvent and the polymer will increase. The polymer will precipitate and form a skinned membrane. Thermally induced phase separation is achieved by cooling down a mixed or single solvent polymer. The solvent evaporation allows membrane formation and is often used to prepare microfiltration membranes. Immersion precipitation is achieved when a polymer plus solvent solution is cast on a proper supporting layer and then submerged in a coagulation bath containing the nonsolvent. The exchange between the solvent and nonsolvent allows membrane formation. This method forms porous membrane and it utilized in the formation of PVDF membranes widely.

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials

Table 3.1 List of material used and specifications

Material	Specifications	Supplier
PVDF Pellets	Average MW ~ 180,000 by GPC	Sigma Aldrich
Dimethylformamide (DMF)	Anhydrous, 99.8%	Sigma Aldrich
MWCNT	OD ~ 8-15 nm -COOH Content ~ 2.56wt% Length ~ 50 μ m Purity ~ >95 wt% Ash ~ <1.5 wt% SSA ~ <233 m ² /g EC ~ >10 ² s/cm MFG Code ~ MC2/21224	Timesnano
Methylene Blue	Average MW ~ 355.89 g/mol Adsorption maximum lambda ~ 660-665 nm	Sigma Aldrich
Non-woven cloth	N/A	-
Distilled water	N/A	Produced in lab
Deionized water	N/A	Produced in lab

3.2 Membrane Preparation

In this study, only one method of preparing the membrane is used and that is the phase inversion via immersion precipitation method. This method is used to form pure PVDF membrane as well as the PVDF membrane with MWCNTs as fillers forming nanocomposite membranes.

3.2.1 Preparation of PVDF and PVDF/MWCNTs Solutions

PVDF solution is prepared by dissolving 15 wt% of the PVDF pellets into the DMF solvent. The solution is then stirred overnight using a magnetic stirrer at 85 °C. While for the PVDF-MWCNT solution, the MWCNT are added to the previously prepared PVDF solution with a composition of 1 wt% of MWCNT. The PVDF-MWCNT suspension is then sonicated for 15 minutes and stirred overnight to ensure the MWCNTs are distributed homogeneously in the solution.

3.2.2 Phase Inversion via Immersion Precipitation method

The phase inversion method used is based on the method reported by Zhu et al. (2017). The solutions prepared earlier are cast onto a non-woven cloth that is fixed to the glass plate. A glass rod is used to flatten the solution onto the glass plate to ensure equal thickness throughout the film. The resultant glass plate is then immersed into a coagulation bath consisting of deionized water at 25 °C for 15 minutes. The porous PVDF layer is left overnight in fresh distilled water to extract the remaining solvent entrapped in the PVDF membrane. The membrane is then allowed to dry in room temperature.

3.3 Adsorption Test

In this study, three parameters which are initial dye concentration, temperature of adsorbate and the duration of adsorption will be investigated in order to find the optimal conditions for the adsorption of methylene blue dye by the membrane. The methylene blue dye solution stocks are prepared according to the concentrations needed by the experiment which consists of 1, 2, 3 and 4 mg/l, respectively of methylene blue dye solution. The

absorbance of the stock solutions are then obtained by its absorbance in a cuvette through the Spectro Gen 20 Vis-Thermo Scientific spectrophotometer equipment. Pour 50 ml of the 1mg/l stock solution into a beaker. Ensure the solution temperature is maintained at about 25 °C using the oven provided in the laboratory. The membrane is then left in the solution for 3 hours. At the end of the experiment, a sample of the dye solution is collected in a cuvette to obtain its absorbance with the Spectro Gen 20 Vis-Thermo Scientific. The dye removal (D_e) is then calculated using the formula:

$$D_e(\%) = \frac{1 - C}{C_0} \times 100 \quad (3.1)$$

where,

C = Concentration of dye after adsorption

C_0 = Initial concentration of dye

The experiment was then repeated using the following conditions:

Table 3.2 List of parameter conditions for the study

Parameter	Initial Dye Concentration	Temperature	Duration of adsorption
Manipulating Variable	1, 2, 3, 4 mg/l methylene blue dye solutions	25°C, 30°C, 35°C, 40°C	1 hr, 2 hr, 3 hr, 4 hr
Constant Variable	25 °C 3 hr	3 mg/l methylene blue dye solution 3 hr	25 °C 3 mg/l methylene blue dye solution

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Adsorption of MB Dye Test Results

The adsorption experiment is then conducted according to the steps and variables decided in the previous section. The results are recorded by the adsorbance values of methylene blue dye solution. Firstly, a calibration curve was performed then it will be used to calculate the concentrations of the dye solution after the adsorption experiment has been carried out with different factors. The table below represents the results of the calibration curve.

Table 4.1 Calibration curve results

Concentration (mg/l)	Adsorbance			
	Reading 1	Reading 2	Reading 3	Average
0	0	0	0	0
0.5	0.106	0.103	0.101	0.103
1	0.174	0.172	0.17	0.172
1.5	0.273	0.27	0.272	0.272
2	0.336	0.334	0.333	0.334
2.5	0.443	0.441	0.44	0.441
3	0.578	0.576	0.58	0.578
3.5	0.713	0.709	0.71	0.711
4	0.805	0.802	0.796	0.801