PREPARATION AND CHARACTERIZATION OF PHASE INVERSION POLY (VINYL ALCOHOL)/ MULTI-WALLED CARBON NANOTUBES DYE REMOVAL ADSORBENTS

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BY

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LIST OF SYMBOLS

Symbols		Unit
C_e	Concentration of adsorbate at equilibrium	mg/L
C_o	Initial methylene blue dye concentration	mg/L
C_t	Concentration of adsorbate at time	mg/L
K_f	Empirical constant of Freundlich	$mg/g(L/mg)^{1/n}$
K_L	Equilibrium constant related to adsorption rate	L/mg
k_1	Rate constant of pseudo-first order	h^{-1}
k_2	Rate constant of pseudo-second order	g/h.mg
n	Intensity of adsorption constant Freundlich isotherm	-
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium	mg/g
q_t	Amount of adsorbate adsorbed per unit mass of adsorbent at time	mg/g
q_m	Maximum adsorption capacity of adsorbent	mg/g
V	Volume dye solution	L
W	Mass of adsorbent used	g

LIST OF ABBREVIATIONS

AC	Activated Carbon
BOD	Biochemical oxygen demand
CNTs	Carbon nanotubes
COD	Chemical oxygen demand
MB	Methylene blue
MWCNTs	Multi-walled carbon nanotubes
PVA	Polyvinyl alcohol
PVA/ MWCNTs	Polyvinyl alcohol/ Multi-walled carbon nanotubes
SDGs	Sustainable Development Goals
SWCNTs	Single wall carbon nanotubes
UV	Ultraviolet

PENYEDIAAN DAN PENCIRIAN POLI (VINIL ALKOHOL)/ NANOTUBE KARBON BERBILANG DINDING PENJERAP UNTUK PENYINGKIRAN PEWARNA

ABSTRAK

Industri tekstil menghasilkan banyak air sisa yang mengandungi sejumlah besar bahan pencemar, termasuk pewarna seperti metilena biru. Bahan adsorptif yang dijurutera mempunyai unsur-unsur bukan organik yang digabungkan dengan matriks polimerik memberikan kemungkinan penyingkiran pelbagai bahan pencemar. Dalam kajian ini, poli (vinil alkohol)/ nanotube karbon berbilang dinding telah disediakan melalui proses penyongsangan fasa. Penambahan nanotube karbon berbilang dinding yang merupakan bahan mesopori khas dengan diameter pori berpurata 3.4 nm ke penjerap poli (vinil alkohol) menghasilkan struktur mikropori dan asimetri untuk penjerapan dalam proses penyingkiran pewarna metilena biru. Kapasiti penjerapan sebanyak 0.068 mg/g dan kecekapan penyingkiran tertinggi sebanyak 56.21 % dicapai pada kepekatan metilena biru 2.00 mg/L dan masa penjerapan selama 4 jam diperolehi dengan menambahkan 1.00 g penjerap poli (vinil alkohol)/ nanotube karbon berbilang dinding. Data eksperimen sesuai diungkapan dengan model isoterm penjerapan Freundlich berbanding dengan model isoterm penjerapan Langmuir dan data kinetik penjerapan yang sesuai ialah dengan model urutan pseudo-kedua.

PREPARATION AND CHARACTERIZATION OF PHASE INVERSION POLY (VINYL ALCOHOL)/ MULTI-WALLED CARBON NANOTUBES DYE REMOVAL ADSORBENTS

ABSTRACT

Textile industries produce a lot of wastewater which contains a significant number of pollutants, including dyes such as methylene blue. Engineered adsorptive materials having inorganic constituent incorporated polymeric matrix provide the possibility of removing a wide range of pollutants. In this study, poly (vinyl alcohol)/ multi-walled carbon nanotubes adsorbents were prepared via phase inversion process. Adding multi-walled carbon nanotubes which is a typical mesoporous material with average pore diameter of 3.4 nm to the poly (vinyl alcohol) adsorbents provided a microporous and asymmetric structure for the adsorptive adsorbents in methylene blue dye removal. In order to find the optimum condition, the adsorption capacity was examined at various operating parameters, such as initial concentration, contact time and adsorbent dosage. The adsorption capacity of 0.068 mg/g and the highest removal efficiency of 56.21 % were obtained at initial dye concentration of 2.00 mg/L at 4 hours adsorption time by applying 1.00 g of poly (vinyl alcohol)/ multi-walled carbon nanotubes adsorbents. The experimental data were fitted well with the Freundlich adsorption isotherm model compared with the Langmuir adsorption isotherm model and the adsorption kinetic data verified the best fitting with the pseudo-second-order model.

CHAPTER 1
INTRODUCTION

Chapter 1 introduces the overview of this research and significance of dyes removal from water bodies. In general, this chapter summarizes the research background of dye removal using polymeric nanocomposite, problem statement and objectives of this final year project.

1.1   Research background

Industries used the various types of dyes in their manufactured products as colour agents. The problems associated with water contamination will arise from the disposal of these contaminants. This contributes to disrupt the photosynthetic mechanism, light penetration and dissolved oxygen which unfortunately leads to a reduction in the growth of aquatic organisms (Peng *et al.* 2015).

Water pollution is one of the main environmental issues that we are facing and it has been regarded as a global issue. Most of the world's supplies of drinking water indicate signs of significant pollution, especially from contaminants such as dyes, arsenic and phosphorus. Dyes have adverse effects on humans which can cause allergies reaction and increases risk of cancer. Besides, dyes also give impact on microorganism as they can interfere the growth of bacteria and other microorganism, simultaneously (Peng *et al.* 2015).

For the sake of solving this problem, various technologies are employed for the treatment of waters containing dyes such as ion exchange, coagulation, chemical oxidation, membrane separation, biological treatment, chemical oxidation and adsorption. Adsorption has been proven to be more beneficial than other approaches in terms of the versatility and simplicity of construction, initial expense, ease of operation and lack susceptibility to toxic

substances. In addition, it should not contribute to the creation of toxic compounds (Zare *et al.* 2018).

Activated carbon (AC) is typically used as an adsorbent to treat wastewater before it is discharged into the environment. However, carbon nanotubes (CNTs) have attracted much attention in the field of heavy metal ion removal because of their large specific surface area, small size, and hollow and layered structures (Naghizadeh 2015). On other hand, CNTs also have an excellent mechanical, electrical and thermal characteristics (Imani Yengejeh *et al.* 2017).

An appropriate choice has been found to remove the organic dyes from wastewater which is by incorporating an adsorbent into polymer by using phase inversion method. This method will produce microporous membrane that allows the adsorbent to effectively adsorb organic dyes from wastewater without worrying about the water pollution (Sattar *et al.* 2017).

1.2 Problem statement

In order to cure water pollution that comes from textile, leather, paper and plastic industries, an advanced technology is needed. Every removal technology has its benefits and drawbacks, respectively. Most dyes are non-biodegradable, stable to light and oxidation. Biological and chemical technology are both not suitable as they require higher operating cost and not effective for all dyes. Physical technology is proposed for this study due to its low production cost and most effective as compared to other technologies. In this study, adsorption will be used for removal of dyes from wastewater. Adsorption is the process in which a substance from its liquid or gaseous state is concentrated on a solid surface (Gupta and Suhas 2009).

AC is the current choice of adsorbent for wastewater treatment. AC has been discovered to be a versatile adsorbent that can remove wide range of pollutants including metal ions, as

well as has high capacity of adsorption and higher surface reactivity. However, AC will not able to make its application to a wider range because of its need of regeneration and the lack of carbon and productivity after regeneration (Gupta and Suhas 2009). Thus, researchers are exploring for better adsorbents to address water pollution. CNTs have been studied to substitute AC due to their unique chemical and physical properties. CNTs are more appealing in dyes removal compared to others because of their high selectivity, desirable physiochemical stability and large adsorption capability for organic dyes.

From previous study, CNTs are proven to be effective for dyes removal from wastewater. From the study of Hu et al. (2017), hyper-branched polyamine functionalized multi-walled carbon nanotubes (MWCNTs) composite displayed excellent adsorption ability for removing of organic dyes such as methyl violet, methylene blue (MB) and malachite green from wastewater. Poly (vinyl alcohol) (PVA) was chosen as the gel matrix material because of its simple preparation, stability at the atmosphere, low in cost, optical and transparency. In this study, PVA/ MWCNTs adsorbents in the form of nanocomposites will be used for MB dye removal. By the end of this study, phase inversion shows a good performance to produce these adsorbents due to its simplicity, low in cost production and less time consuming to form nanocomposites. The performances of the resultant adsorbents will be studied under various parameters.

1.3   Research Objectives

The objectives of this research are as follow:

1. To synthesis PVA and PVA/MWCNTs adsorbents via phase inversion method to produce asymmetric structure and microporous adsorbents.

2. To investigate the performance of adsorption of MB dye under the different conditions such as initial dye concentration, contact time and adsorbent dosage.

3. To determine the most suitable adsorption isotherm and kinetics for adsorption of MB dye on PVA and PVA/MWCNTs adsorbents.

CHAPTER 2
LITERATURE REVIEW

In the previous chapter, dyes in the effluents can cause one of the serious environmental issues which is water pollution and therefore, the need to remove these dyes and possible method used to remove them have been discussed. In the view of aforementioned observations, Chapter 2 presents the previous discoveries and reviews available from credible scientific records and references that are related to this final year project topic. This chapter covers the overview of dyes, methods to remove dye from wastewater, adsorption process and adsorbents available for removal of MB dye. Besides, this chapter also presents important information for adsorption isotherm.

2.1   Dyes classification

Dyes are complex unsaturated organic compound that are immune to multiple processes including light exposure. The discovery in 1856 of the first synthetic dye which was mauveine, marked the beginning of the period of synthetic and large-scale production of dyes (Forster *et al.* 2013). Synthetic dyes were first extracted from coal. Countless dye substances were later developed from coal tar and are continuously being enhanced in terms of color beauty and colorfastness. On the other hand, natural dyes usually obtained from plants and animals. Dyes are used by many industries such as textiles, plastics, leather, paper, cosmetics and printing to colour their goods while using a large quantities of water. There are several ways to classify dyes based on their chemical composition, ionic charge and method of application. Figure 2.1 illustrates that natural and synthetic dyes are graded as dyes. Natural coloring is derived from plant and animal sources.
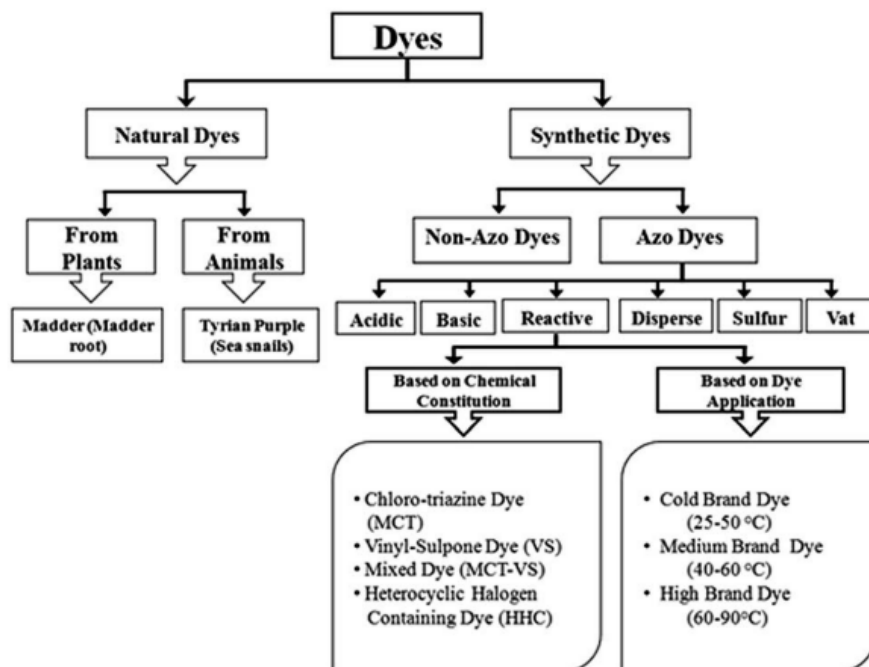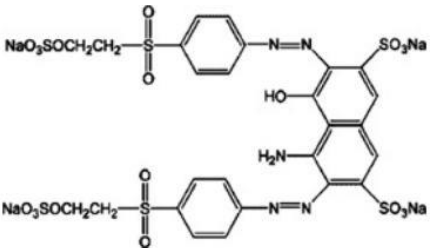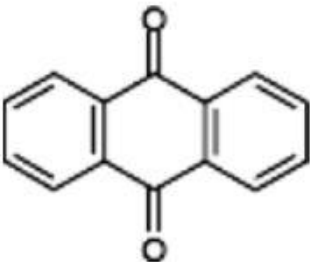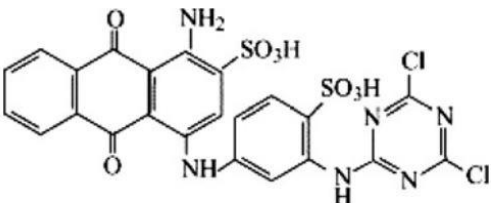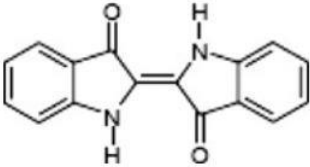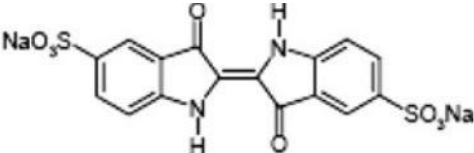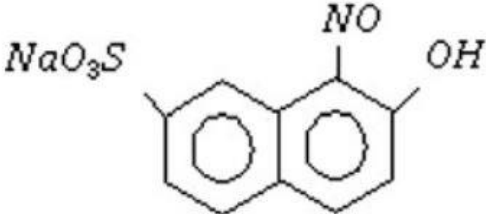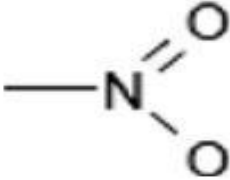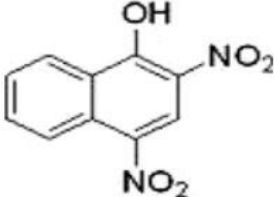
Figure 2.1: Categorization of dyes (Ajmal *et al.* 2014)

Azo dyes are more than 50% of all the dyes used in the manufacturing industry, making azo dyes as the dominant proportion of colorants. Dyes based on general composition can also be categorized as ionic and non-ionic dyes. Ionic dyes are further categorized into cationic dyes (basic dyes) and anionic dyes (acid dyes, reactive dyes and direct dyes). Meanwhile, non-ionic dyes are further categorized into vat dyes, sulphur dyes and disperse dyes. Dyes may also be classified by their chemical structure and method of applications. Table 2.1 shows the dye classification based on chemical structures. They are classified as azo dyes, anthraquinone dyes, indigoid dyes, nitroso dyes, nitro dyes and triarylmethane dyes. Table 2.2 shows the classification of dyes based on their application to the substrate. They are categorized according to the charge of the dyes as anionic, cationic and non-ionic.

Table 2.1: Classification of dyes based on chemical structure (Yagub *et al.* 2014)

Class	Chromospheres	Example
Azo dyes		Reactive Black 5
Anthraquinone dyes		Reactive Blue 4
Indigoid dyes		Acid Blue 71
Nitroso dyes		Acid green 1
Nitro dyes		Acid Yellow 24

Triarylmethane dyes

Basic Red 9
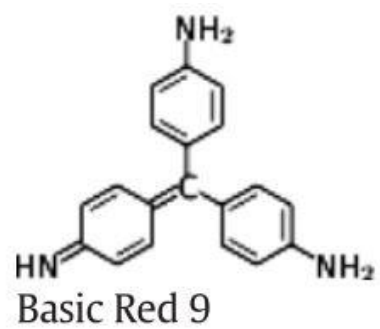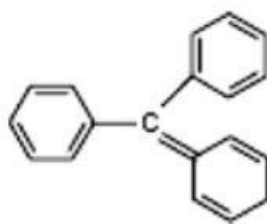
Table 2.2: Classification of dyes based on application to substrate (Yagub *et al.* 2014)

Class	Substrate	Method of Application	Chemical types
Acid	Wool, nylon, silk, inks, leather and paper	Generally from neutral to acidic bath	Anthraquinone, xanthene, azo (including, nitroso, 9remetallized), nitro, and triphenylmethane.
Basic	Inks, paper, polyacrylonitrile, treated nylon, and polyester	Applied from acidic dye baths	Hemicyanine, azo, cyanine, diazahemicyanine, azine diphenylmethane, xanthene, triarylmethane, acridine, anthraquinone and oxazine.
Direct	Nylon, rayon, paper, leather and cotton	Applied from neutral or a little alkaline bath containing additional electrolyte	Phthalocyanine, azo, oxazine, and stilbene.
Disperse	Polyamide, acrylic polyester, acetate, and plastics	Fine aqueous dispersions often applied by high temperature/ plastics pressure or lower temperature carrier methods; dye may be padded on cloth and thermo fixed	Benzodifuranone, azo, anthraquinone, nitro, and styryl.
Reactive	Wool, cotton, silk and nylon	Reactive site on dye reacts with functional group on	Anthraquinone, formazan,

		fibre to bind dye covalently under influence of heat and pH	phthalocyanine, azo, oxazine and basic.
Sulphur	Rayon and cotton	Aromatic substrate vatted with sodium sulphide and reoxidised to insoluble sulphur-containing products on fibre.	Indeterminate structures.
Vat	Wool and cotton	Water-insoluble dyes solubilised by dropping in sodium hydro- gen sulphite, then exhausted on reoxidised and fibre.	Indigoids and anthraquinone.

2.2   Dye toxicity

Colour is generally the first pollutant to be detected in wastewater, giving a simple sign of water being contaminated by the colour existing in dye effluents. The disposal of these dyes into the water bodies increase the degree of chemical oxygen demand (COD) level in the aquatic environments and decreasing the light penetration and therefore impacts the photosynthetic behaviours of flora, thereby badly disrupting the food supply of aquatic species. One of the most widely used classes of colours is azo dyes, a family of synthetic nitrogen based dyes that provide bright reds, oranges and yellows. They are poisonous or carcinogenic and pose significant threats to marine life (Peng *et al.* 2015). As seen most of dyes are carcinogenic and thus they can cause serious harm to human including renal dysfunction, reproductive system, liver, brain and central system.

2.3   Methylene blue (MB) dye

MB dye is classified as cationic dyes under ionic group. This dye is an aromatic heterocyclic used in a wide variety of applications as colouring and staining agent in the textile and pharmaceutical industries, respectively. However, excessive amount of MB dye entering into ecosystem can cause catastrophic effects on the environment and human health due to its high toxicity and concentration in the environment. High blood pressure, inflammation of the throat, mouth, oesophagus and stomach, diarrhoea, abdominal discomfort and dizziness are some common complications correlated with this dye (Miclescu and Wiklund 2010). Therefore, due to the toxicity of the MB dye, wastewater containing this colouring material must be treated effectively before it is released into the ecosystem. There are various chemical, physical and biological methods for the disposal of contaminated water have been developed

and used. An adsorption technique is one of the effective strategies for decreasing water contaminants.

2.4   Methods of dye removal from wastewater

There are various methods to treat dye effluents. The dye removal method can be classified into three categories which are biological, chemical and physical methods. Removing dyes from wastewater become very challenging as the dyes have very complex structure thus make the dyes resistant to aerobic digestion, stable to photo degradation and biodegradation.

2.4.1 Biological method

Biological methods are widely used for removing dyes from wastewater due to its low cost and optimal running time. It also known as the degradation of dyes with the biochemical phenomenon like bioremediation which is a sustainable method for removing dyes from textile waste (Ekambaram *et al.* 2016). Ali (2010) proposed application of certain microbial cultures in the biological technique such as fungi, bacteria, algae and yeasts which have the potential to absorb varieties of textile dyes. Senthilkumar et al. (2014) studied the ability of *Phanerocheate chrysosporium* to remove dyes by producing the extracellular enzymes like lignin peroxidase, manganese peroxidase and laccase-mediated. Some studies also reported that bacteria species such as *Bacillus subtilis*, *Enterobacter sp.* etc. had the potential to transform azo dyes to colourless amine (Sudha *et al.* 2018). In another research, algae species for example *Cystoseira barbatala* for MB, *Pithophora sp.* for malachite green, *Spirulina plantensis* for acid blue 9 have been identified pose the ability to degrade azo dyes into aromatic amine which is further catabolized into organic compound (Vasanth Kumar *et al.* 2005, Caparkaya and Cavas 2008, Dotto *et al.* 2012).

There are two type of biological method, which are aerobic and anaerobic process. Aerobic process is a process in which dyes in wastewater are stabilised by microorganisms in the presence of oxygen. It is mostly used as secondary treatment process following with an anaerobic stage. The anaerobic method can be used to convert organic matter (dyes) into biogas containing significant quantities of carbon dioxide and methane. Fungal, bacterial and algal are used as pre-treatment in the industries and they are effective for removing low quantities and concentration of dyes. However, the culture maintenance cost is high and it does not deal with the vast quantities of coloured effluents (Anjaneyulu *et al.* 2005).

2.4.2 Chemical method

Chemical methods use chemistry or its principles to achieve dye removal. Example of chemical dye removal methods are hydrogen peroxide (H_2O_2) oxidation, ozonation, Fenton's reagent and coagulation. Hydrogen peroxide (H_2O_2) or ozone (O_2) is typically the primary oxidising agent in the oxidative phase and has to be activated by UV-radiation. This oxidation method extracts dyes from the textile effluents by oxidation resulted in aromatic ring cleavage of the dyes molecules (Y.M. Slokar and A. Majcen Le 1998) . In 1970s, the use of ozone was first invented because of its extreme volatility relative, rendering it a better oxidising agent compared to chlorine and H_2O_2 (Thakur 2006). Ozonation is efficient for removing double bonded dyes molecules and it has potential to generate effluent wastewater that is ideal for discharge with no colour and low COD (Xu *et al.* 1999).

Fenton's reagent is an effective chemical method for the handling of waste water that is resistant to biological treatment or to living biomass (Y.M. Slokar and A. Majcen Le 1998). This chemical method is efficient for decolourising both soluble and insoluble dyes from textile effluents by using the action of sorption or bonding (Pak and Chang 1999). Meanwhile, coagulation uses alum, ferric chloride, etc. for producing an insoluble end product by chemical

reaction. Thus, this product can be used to eliminate dyes from the textile effluents (Yadav *et al.* 2012).

2.4.3 Physical method

Physical methods are usually achieved by the mass transfer mechanism. Example of physical dye removal methods are adsorption, membrane filtration and ion exchange. In the adsorption process, the selection of adsorbent depends on the form of contaminants. AC is the most widely used in the adsorption due to its ability to absorb cationic, acid dyes, dispersed, vat, pigment and reactive dyes (Rao *et al.* 1994). Silica gel is an excellent sorption for basic dyes, wood chips are effective for extracting acid dyes meanwhile peat is used to extract transition metals and polar organic compounds (Poots *et al.* 1976, Nigam *et al.* 2000). Ion exchange is suitable for removing both cation and anion dyes from textile effluents. Membrane filtration is capable of clarifying, concentrating and removing dyes from the effluents. It is very appropriate for water recycling within a textile dye facility if the effluents contain minimal concentration of dyes (Xu *et al.* 1999).

Table 2.3 shows numerous example of biological, chemical and physical dye removal methods along with advantages and disadvantages.

Table 2.3: Various example of dye removal technologies along with advantages and disadvantages (Yazdani 2018)

Biological treatment	Advantages	Disadvantages
Aerobic	Low running costs and non-toxic end products of complete mineralization	Synthetic dyes are not uniformly decolorized, many dyes are recalcitrant to biological breakdown and non-transferable under aerobic conditions
Anaerobic	Inexpensive, well-established degradation of variety of synthetic dyes, no foaming problems with surfactants, and cheap removal of biochemical oxygen demand (BOD)	Insufficient BOD removal, dyes and other refractory organics are not mineralized, nutrients (N, P) are not removed, and transformation of sulphates to sulphide
Chemical treatment		
Hydrogen peroxide (H_2O_2) oxidation	Simplicity of application	pH dependency, and sludge production
Ozonation	Gaseous state of ozone reagent, no increase in water volume, and no sludge production	Short half-life (20 min)
Fenton's reagent	Efficient decolourization of soluble/insoluble dyes, effective reduction of COD, total organic carbon and toxicity, and applicable even with high-suspended solid concentration	Sludge production, effectiveness within narrow pH range, and longer reaction time
Coagulation	Economically feasible, and satisfactory removal of disperse, sulphur, and vat dyes	Large quantities of concentrated sludge, pH dependency, and unsatisfactory removal for highly

		soluble dyes; azo, reactive, acid and basic dyes
Physical treatment		
Adsorption	High quality treated water, effective for variety of dyes	Expensive, need of regeneration otherwise disposal of the concentrates has to be considered, and reduced performance after regeneration/re-use
Membrane filtration	Effective for all dye types, resistance to: temperature, adverse chemical environment and microbial attack, and high-quality treated effluent	High working pressure, significant energy consumption, high cost, relatively short membrane life, and frequent clogging
Ion exchange	No weight loss in regeneration reclamation of solvent after use, and effective for soluble dyes	Not effective for all dyes: not effective for disperse dyes, high cost, and expensive organic solvents
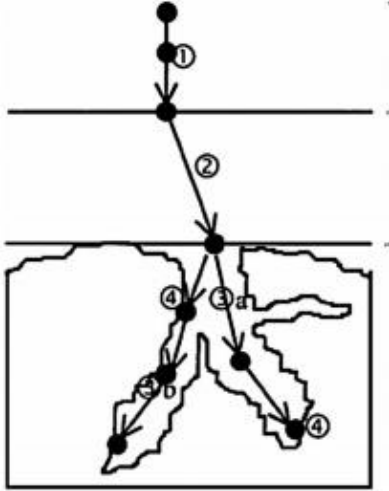
2.5 Adsorption

Adsorption is a mechanism of mass transfer by which materials like ions or molecules are transported to the surface of a solid phase from the solvent phase. Thus, they can be completely extracted from the solvent. Commonly, adsorption can be defined as an extraction of chemical compounds from a solvent phase on the surface of a solid. The material that is transported to the surface is known as an adsorbate and the solid in which the adsorbate accumulates is known as an adsorbent.

The mechanism of adsorption typically consists of four steps. The first step is transportation of adsorbate particle from bulk solution to the boundary layer. Then, the second step is transportation of adsorbate particle via the boundary layer to the outer surface of adsorbent (film diffusion). In third step, the adsorbate particle is transported within the pores of the adsorbent which occurs on the exterior surface (intra-particle diffusion or pore diffusion) and the last one is the adsorption of the adsorbate particle on the inner surfaces of the pores and capillary spaces of the adsorbent (Kalavathy *et al.* 2005). The diffusion mechanism involved in the adsorption process is shown in Table 2.4. The second and third steps differ in their dependency on the hydrodynamic parameters especially the stirring velocity in batch reactor and flow velocity in fixed bed model. The rate of film diffusion increase with increasing stirring or flow velocity due to the reduction of the boundary layer thickness. Surface region and diffusion pathway for film and intra-particle diffusion in the third step are influenced by the size of adsorptive molecules. (Dąbrowski 2001).

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Table 2.4: Diffusion mechanism involved in the adsorption process (Viegas *et al.* 2014)

Position	Phenomenon
Bulk of solution	**1**
	Diffusion/Convection
Outer layer	**2**
	External mass transfer
Particle	**3a**
	Porous diffusion
	3b
	Surface diffusion
	4
	Adsorption

In addition, adsorption process can be categorized into two type which are physisorption and chemisorption. In physisorption, the adsorbate attaches to the surface via weak Van der Waals force, hydrogen bonding or electrostatic attraction and it is observed to be reversible with low interaction energy. Meanwhile, chemisorption is achieved by chemical reaction between adsorbate and the surface site via covalent bonding and thus this bonds is known to be irreversible with high energy (Králik 2014). Table 2.5 shows the difference between chemisorption and physisorption.

Table 2.5: Difference between chemisorption and physisorption (Králik 2014)

Property	Physisorption	Chemisorption
Type of bonding forces	Van der Waals	Chemicals bonds
Adsorption heat	Low, 10-40 kJ mol^{-1}	High, 20-400 kJ mol^{-1}
Chemical change of adsorptive	None	Formation of a surface compound
Reversibility	Fully reversible, i.e. desorption of adsorbate occurs by decreasing the activity of the adsorptive in the fluid surrounding the surface.	The process is irreversible; "desorbed compounds" are different from the adsorbed ones.
Activation energy	Very low (close to zero)	High, similar to a chemical reaction
Effect of temperature	Negative	In some extent of temperatures positive; so called activated adsorption.
Specificity of adsorbate-adsorbent interactions	Very low	High
Formation of multilayers	Yes, in gas phase adsorption usually accompanied by liquefaction in micro and mesopores	Monolayer

2.6   Carbon nanotube as adsorbents

There are many types of materials have been used as adsorbents in treating wastewater for example AC, magnetic and polymeric materials, clays and others. New carbon materials have been developed such as CNTs, carbon nanofibers and graphene. The first CNTs were identified by Iijima in 1991. CNTs have been widely used among carbon-based materials as an

effective polymer composite reinforcements (Imani Yengejeh *et al.* 2017). CNTs are cylindrical macromolecules where the carbon atoms are structured in the shape of a hexagonal lattice in the partitions of the tubes and at the end sides are covered with half of fullerene (Iijima 1991). These are generally categorised on the basis of the carbon atom hybridization in the CNT layers. There are two type of CNTs which are single wall carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs).

CNTs adsorbents provide many advantages including extremely high specific surface area and associated sorption sites, short intra-particle diffusion distance, and adjustable pore size and surface chemistry. Furthermore, CNTs have been proven as promising adsorbents for adsorption due to their large adsorption capacity for synthetic dyes. CNTs strongly adsorb many of polar organic compounds because of the diverse contaminant–CNT interactions including hydrophobic effect, π-π interactions, hydrogen bonding, covalent bonding and electrostatic interactions (Zare *et al.* 2015). Indeed, MWCNTs have demonstrated to be effective in removing MB dye from aqueous solutions (Shahryari *et al.* 2010).

There are three techniques usually used to produce CNTs which arc discharge, laser ablation and chemical vapour deposition (Strickland and Shaffer 1971, Sugihara *et al.* 1990, Kong *et al.* 1998). The key components for the production of nanotubes are catalyst and an appropriate amount of energy. The common characteristic of these techniques is addition of energy to a carbon source to obtain particles that can recombined to generate CNTs. To enhance adsorption performance, CNTs can be functionalized by oxidation treatment, open the closed points or apply any metal oxides to their surface (Tamburri *et al.* 2005, Hu *et al.* 2006). These would improve the dispersion and reaction of the CNTs for the sustainable ecosystem application. Functionalized CNTs exhibit better mechanical and electrical properties and can boost nanotubes contact with other entities as well.

2.7 Poly (Vinyl Alcohol)

PVA is a vinyl material that can be manufactured in bulk inexpensively. Besides, PVA is a well-known polymer that used to synthesis polymeric membranes due to its high durability, biocompatibility, good tensile strength, degradability and better film forming properties (Rashidzadeh and Olad 2013). In addition, some studies reported PVA as an effective adsorbent for removing heavy metal ions, anionic and cationic dyes due to the abundance of free hydroxyl and acetate groups existing on the PVA polymeric chains (Wu *et al.* 2010, Sandeman *et al.* 2011). PVA also can easily form membrane via phase inversion without any chemical cross linkers that can contribute to toxicity. Figure 2.2 slows the structure of PVA
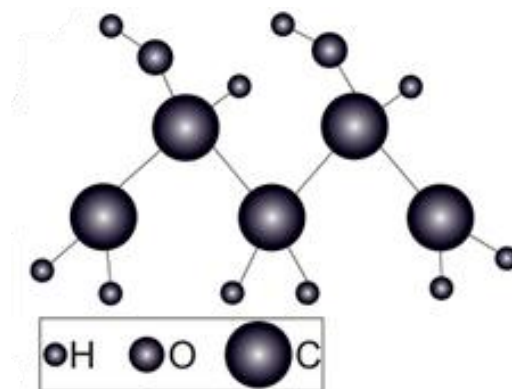
Figure 2.2: PVA structure (Aslam *et al.* 2018)

2.8 PVA/ MWCNTs nanocomposite

Mansor *et al.* (2020) reported that cellulose acetate/PVA blended membrane prepared by phase inversion method and this membrane could effectively remove the cationic dyes from aqueous textile solution due to its unique adsorption behaviours, better flux and high rejection efficiency. Meanwhile, Mallakpour & Rashidimoghadam (2019) reported that by applying PVA/Vitamin C multi-walled carbon nanotubes (VC-MWCNTs), 97% of MB dye can be

separated from aqueous solution. Therefore, in this study phase inversion method have been chosen to prepare PVA/ MWCNTs adsorbents using water as the solvent and acetone as the non-solvent to investigate their potential applications for removing of MB dye.

Phase inversion, also called demixing or precipitation, may be induced by immersion precipitation, controlled evaporation, thermal precipitation and precipitation from the vapour phase. Immersion precipitation is chosen as it is the most common technique to produce asymmetric structure and microporous membrane. Phase inversion can be generally described as the process by which a homogeneous polymer solution becomes thermodynamically unstable because of the exchange of solvent (in the polymer solution) and non-solvent (in a coagulant bath). As a result, the solution separates into two phases which is polymer rich phase and polymer poor phase. When the solution solidifies after phase separation, the polymer poor phase manifests as pores distributed throughout the polymer rich phase. Generally, the homogeneous polymer solution is casted in the appropriate support and then immersed in a non-solvent bath, resulting in the immediate solid membrane formation (Sapalidis 2020).

2.9   Adsorption isotherm

Adsorption isotherm can be expressed via curve as relationship between the quantity of adsorbate adsorbed on the adsorbent's surface and in liquid phase at constant temperature when equilibrium phase is accomplished. It is defined via constants such as functions of surface properties, affinity and adsorption ability (Aksu and Tezer 2000). Isotherm method was evaluated by exposing a known quantity of adsorptive substances in a constant volume of solution with varying adsorbate concentrations. Once equilibrium phase is completed, the aqueous concentration of the adsorbate is determined and the adsorption equilibrium capacity is estimated by using Equation 1:

$$q_e = \frac{(C_o - C_e).V}{W} \qquad (1)$$

$$R(\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (2)$$

where q_e represents amount of adsorbate absorbed per unit mass of adsorbent at equilibrium (mg/g), C_o is the initial concentration of adsorbate (mg/L), C_e is the final concentration (at time t or at equilibrium) (mg/L), V is the volume of the solution (L), W is the mass of the adsorbent used (g) and R is the percentage of dyes removal (%).

Langmuir and Freundlich isotherm models are commonly used to study the adsorption process. The equilibrium between solid surface and solution is defined by Langmuir isotherm as reversible chemical equilibrium. The surface consists of fixed individual adsorptive sites in which the adsorbate could be chemically bound. The adsorption has constant free energy change for all sites due to its homogeneous surface. It is a monolayer adsorption because every site has potential to attach at most with one molecule of adsorbate (Langmuir 1917). Freundlich

model is characterised as non-ideal and reversible adsorption where not limited to monolayer development. It describes as multilayer adsorption onto the surface of heterogeneous sites with different bond energy. This isotherm is widely used as standard equation to describe adsorption mechanism from aqueous solution (Mallakpour and Rashidimoghadam 2019). Model equations for both Langmuir and Freundlich isotherm are shown in Table 2.6.

Table 2.6: Langmuir and Freundlich isotherm models in this study (Langmuir 1917, Mallakpour and Rashidimoghadam 2019)

Isotherm	Non-linear form	Linear form	Linear plot	Factors
Langmuir	$q_e = \dfrac{q_m K_L C_e}{1 + K_L C_e}$	$\dfrac{C_e}{q_e} = \dfrac{1}{q_m K_L} + \dfrac{C_e}{q_m}$	$\dfrac{1}{q_e}$ vs. $\dfrac{1}{C_e}$	K_L and q_m
Freundlich	$q_e = K_F C_e^{1/n_f}$	$\log q_e = \log K_F + \dfrac{1}{n} \log C_e$	$\log q_e$ vs. $\log C_e$	K_F and n_f

q_e: Amount of adsorbate absorbed per unit mass of adsorbent at equilibrium (mg/g),

q_m: Maximum adsorption capacity of adsorbent

C_e: Equilibrium adsorbate concentration (mg/L),

K_L: Equilibrium constant related to adsorption rate (L/mg), n: adsorption intensity,

K_F: Empirical constant of Freundlich $[(mg/g)(L/mg)^{1/n}]$