SYNTHESIS OF PET/MWCNTs ELECTROSPUN NANOFIBER WITH POLYESTER FIBER SUPPORT FOR METHYLENE BLUE REMOVAL

STEVEN LING GUANG HU

UNIVERSITI SAINS MALAYSIA

2021

SYNTHESIS OF PET/MWCNTs ELECTROSPUN NANOFIBER WITH POLYESTER FIBER SUPPORT FOR METHYLENE BLUE REMOVAL

by

STEVEN LING GUANG HU

Project proposal submitted in partial fulfilment of the requirement for the degree of

Bachelor of Chemical Engineering

2021

ACKNOWLEDGEMENT

Praise to Lord for the wisdom bestowed upon me and good health in completing this final year project. First of all, I would like to deliver my appreciation to the supervisor, Associate Professor Dr. Tan Soon Huat, who guided me through this final year project. Despite this COVID-19 pandemic, he is willing to guide me on the project and share his knowledge through email or social media. I deeply appreciate his support and guidance throughout the whole process to completion of this final year project.

Next, I would express my gratitude to Ng Wei Lin, a postgraduate student for his generous aid for guiding me to use chemicals and the equipment involved in this final year project. Next, I also thank the assistance from the laboratory technicians of the School of Chemical Engineering, Universiti Sains Malaysia who are Nor Zalilah Ahmad and Yusnaida Mohd. Yusof. They are willing to assist me in providing required facilities so that my experiments could be conducted in the limited time.

Moreover, I also thanks to my family members and my friends for their encouragement and support. Once again, thank you to those who helped me along the progress of this final year project. I appreciate your contributions deeply throughout the completion of this project.

STEVEN LING GUANG HU

June 2021

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOLS

Symbol		Unit
B_T	Temkin constant related to heat of adsorption	J/mol
C	Constant related to the thickness of the boundary layer	mg/g
C_e	Equilibrium dye concentration in aqueous solution	mg/L
C_o	Initial or highest dye concentration	mg/L
C_t	Concentration of dye solution at any time	mg/L
k_1	Adsorption rate constants of pseudo-first-order kinetic model	min^{-1}
k_2	Adsorption rate constants of pseudo-second-order kinetic model	g/mg.min
K_F	Freundlich adsorption constant	$(mg/g(L/mg)^{1/n})$
K_L	Langmuir adsorption constant	L/mg
$K_T \times 10^5$	Equilibrium binding constant	L/mg
M	Mass of adsorbent	g
n	Intensity of adsorption	-
Q_{calc}	Calculated value of adsorption capacity at equilibrium	mg/g
q_e	Equilibrium adsorbed quantity	mg/g
Q_{exp}	Experimental value of adsorption capacity at equilibrium	mg/g
Q_m	Theoretical maximum adsorption capacity	mg/g
q_t	Amount of dye adsorbed at specific time	mg/g
R^2	Correlation coefficient	-
R_L	Separation factor or equilibrium constant	-
t	Time	min
V	Volume of aqueous solution	L

LIST OF ABBREVIATIONS

AB 25	Acid red 25
ARS	Alizarin red S
CNT	Carbon nanotube
ECR	Eriochrome Cyanine R
HFIP	Hexafluoro-2-propanol
MB	Methylene blue
MWCNTs	Multiwalled carbon nanotubes
PET	Polyethylene terephthalate
PES	Polyester fiber
RB 29	Reactive blue 29
RR 120	Reactive red 120
RRM	Reactive red M-2BE
UV	Ultraviolet
SWCNTs	Single walled carbon nanotubes

SINTESIS POLIETILENA TEREFTALAT/NANOTIUB KARBON BERBILANG DINDING NANOSERAT DENGAN SOKONGAN GENTIAN POLIESTER UNTUK PENYERAPAN METILENA BIRU

ABSTRAK

Kejadian pencemaran air termasuk pencemaran pewarna dan logam berat menyebabkan kualiti air menurun dengan ketara. Salah satu pewarna utama yang terdapat di dalam air sisa ialah metilena biru (MB). Tujuan kajian ini adalah untuk mensintesis polietilena tereftalat/nanotiub karbon berbilang dinding (PET / MWCNTs) terpejam elektrik nanoserat dengan sokongan gentian poliester (PES) dan mengaji prestasi penjerapannya untuk MB. Kaedah untuk mensintesis PET-MWCNTs/PES terpejam elektrik nanofiber ialah melalui kaedah pejaman elektrik proses. Terdapat tiga parameter utama termasuk masa hubungan, dos adsorben dan kepekatan pewarna awal yang harus diselidiki melalui eksperimen mod berkala. Masa hubungan optimum yang diperoleh untuk penjerapan ialah 1440 minit. Kapasiti penyerapan dan kecekapan penyingkiran PET-MWCNTs/PES ialah 0.3398 mg/g dan 13.63% yang mempunyai prestasi yang lebih baik berbanding dengan PES yang mempunyai nilai kapasiti penyerapan 0.2529 mg/g dan nilai kecekapan penyingkiran 11.62%. Kapasiti penyerapan menunjukkan tren kecenderungan dan peratusan penyingkiran MB menunjukkan tren meningkat apabila dos penjerap meningkat. Namun, terdapat peningkatan pada kapasiti penjerapan dan tren penurunan pada peratusan penyingkiran MB ketika kepekatan pewarna awal meningkat. Untuk isoterm penjerapan, daripada data eksperimen didapati bahawa model isoterm Langmuir lebih sesuai berbanding dengan model isoterm Freundlich dan Temkin. Model kinetik pseudo-urutan-kedua lebih sesuai dalam menggambarkan kajian kinetik dalam penjerapan MB. Oleh demikian, PET-MWCNTs/PES

pusingan elektro nanoserat boleh menjadi penyerap yang berpotensi dalam menyah pewarna MB dari air sisa.

SYNTHESIS OF PET/MWCNTS ELECTROSPUN NANOFIBER WITH POLYESTER FIBER SUPPORT FOR METHYLENE BLUE REMOVAL

ABSTRACT

Occurrence of water pollution including contamination of dyes and heavy metals causes the quality of water to decrease significantly. One of the major dyes found in the wastewater is methylene blue (MB). The purposes of this study were to synthesis polyethylene terephthalate/multi-walled carbon nanotubes (PET/MWCNTs) electrospun nanofiber with polyester fibers (PES) as support and to investigate its adsorption performance on MB. The method to synthesis PET/MWCNTs electrospun nanofiber was using electrospinning process method. There are three major parameters such as contact time, adsorbent dosage and initial dye concentration were to be evaluated through batch mode experiment. The optimum contact time obtained for adsorption was 1440 minutes. PES+PET/MWCNTs had adsorption capacity of 0.3398 mg/g and removal efficiency of 13.63% which had better performance as compared to PES having adsorption capacity of 0.2529 mg/g and removal efficiency of 11.62%. The adsorption capacity showed a decreasing trend and the MB removal percentage showed an increasing trend when the adsorbent dosage increased. However, there was an increment in adsorption capacity and a reducing trend in MB removal percentage when the initial dye concentration increased. For adsorption isotherm, it was found that Langmuir isotherm model is relevant with the experimental data as compared to Freundlich and Temkin isotherm model. Pseudo-second-order kinetic model was more favourable in providing the details of the kinetic studies in MB adsorption. Thus, PET/MWCNTs electrospun nanofiber can be a potential adsorbent in removing MB dye from wastewater.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Water is an essential for humans' daily lives as water is used for a variety of purposes such as cleaning, drinking, manufacturing and so forth. It is important to maintain the quality of water so that water supply can be sustainable in a very long term. However, the occurrence of water pollution including contamination of dyes and heavy metals causes the quality of water to decrease significantly. According to the World Health Organization, there were 785 million people, including 144 million people who relied on surface water as a basic drinking-water supply (*Drinking-Water*, 2019).

Adsorption is an economical and effective method in water treatment such as dye removal. Adsorption is a process in which the ions, atoms or molecules adhere on the surface of a solid material called adsorbent. Application of nanotechnology is beneficial in the improvement of water quality. Nano-adsorbent can be classified into several types such as carbonaceous nanomaterials, nanofibers, polymer-based nanomaterials and aerogels (Khajeh et al., 2013). Carbon nanotubes (CNTs) and multiwalled carbon nanotubes (MWCNTs) which are carbonaceous nanomaterials considered as good alternatives in dealing with dye removal in recent years. The study on adsorption of dye using carbonaceous nanomaterial is required to understand its adsorption efficiency and adsorption kinetic.

Other than dye, polyethylene terephthalate (PET) is also another source which leads to environmental pollution. PET is a type of polyester which is formed by esterification reaction between terephthalic acid and ethylene glycol. At present, PET is introduced in many applications including packaging for food, drinks and pharmaceutical products (Mallakpour & Behranvand,

2017). However, PET had caused environmental pollution due to poor management of waste instead of being a commercial packaging material due to its high toughness, easy method of manufacturing and low fabrication cost. Several problems have emerged due to extensive production and usage of PET including immense generation of waste, requirement of non-renewable fossil fuel precursors and carbon dioxide emissions related to production and disposal of PET products (Cano et al., 2020).

In this project, the PET-MWCNT nanofibers would first electrospinning onto the PES support, then the resultant nanofibers (PET-MWCNT/PES) would be uses for removing of methylene blue dye via adsorption process. Three aspects will be studied on the electrospun nanofibers such as the effect of contact time, adsorbent dosage and initial dye concentration. Subsequently, the study on the adsorption kinetic and isotherm of methylene dye removal will be conducted by using adsorption isotherms.

1.2 Problem Statement

Water disruption has been one of the issues in the world including Malaysia. A news on 8th December 2020 reported that more than 850 areas in Klang Valley were affected by water shortage due to detection of raw water pollution in Sungai Selangor (Chung, 2020). Dye is one of the industrial wastes which leads to water pollution. It is widely used in several fields of advanced technology including textile, food processing, cosmetics, textile, etc. In the dyeing process, about 10 to 15% of the dyes used are being released into the wastewater which causes the quality of water to be highly affected (Samchetshabam et al., 2017). There are five major industries which contributed to the emission of dye effluent to the environment such as textile (54%), dyeing (21%), paper and pulp (10%), tannery and paint (8%) as well as dye manufacturers (7%) (Katheresan et al., 2018a). Although dye serves several purposes, but dyes are toxic, hazardous and can be

potential carcinogens which are harmful to the living organisms and the environment if treatment of dye is not applied. Partial degradation or transformation of azo dyes could occur in anoxic sediments, leads to reduction of azo-type compounds thus forming hazardous aromatic amines (Ito et al., 2016). Aquatic ecosystem will be affected through long term exposure of these carcinogenic compounds as well as human health through drinking water. Hence, a suitable method on treatment of dyes is using adsorption method.

Adsorbents are used as a media to adsorb components in adsorption method. One of adsorbents is activated carbon. It has a complex mechanism in the adsorption process of organic pollutants where there is existence of difficulties in adsorption. These difficulties cause by variables such as electrostatic, dispersive and chemical interactions, intrinsic properties of adsorbent (pore size distribution) as well as system temperature (Lellis et al., 2019). Another adsorbent is carbon nanotubes (CNTs). CNTs can be classified into two types which are single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). CNTs are good adsorbents as they provide high adsorption capacity, high tensile strength, good thermal and electrical conductivity. However, it is hard to recover back the powder form adsorbents as they suffer from agglomeration at the end of adsorption process. Necessary studies on MWCNTs nanofibers are needed to understand their performance in different conditions and their adsorption kinetics.

In 2014, 41 million tonnes of PET were produced approximately throughout worldwide, where the method used in majority is the polycondensation of bis(hydroxyethyl)terephthalate. There is an increment in global production of PET up to 56 million tonnes in 2016 and more than 70 million tonnes of PET has been forecasted to be produced annually (Sang et al., 2020). This massive production of PET leads to uncontrollable water pollution. Improper disposal of PET

waste bottles generates wastes will also lead to pollution. Thus, researchers considered to implement the usage of PET as a potential adsorbent by fabricating MWCNTs on its surface. As PET is collected from polluted water source, it can be recycled to be synthesized as PET/MWCNTs nanocomposite. If the amount of dyes left in water source is at minimum after adsorbed by PET/MWCNT nanocomposite, this will indeed reduce wastage and protect the environment from dye contamination. So, understanding the properties and adsorption mechanism of the PET/MWCNTs electrospun nanofibers is crucial and important for better efficiency of dye removal.

1.3 Objectives

1. To study the effect of contact time, adsorbent dosage and initial dye concentration on the adsorption of methylene blue dye.

2. To identify the adsorption isotherm of the PES and PET-MWCNT/PES electrospun nanofibers for methylene blue dye removal.

3. To identify the adsorption kinetics of the PES and PET-MWCNT/PES electrospun nanofibers for methylene blue dye removal.

CHAPTER 2

LITERATURE REVIEW

2.1 Classification of Dyes

Dye is a synthetic or natural substance used to apply colour on materials. It provides colour due to several reasons like absorption of light in visible spectrum (between 400 and 700 nm), presence of at least one chromophore which is a colour-bearing group, existence of conjugated system (example like alternating single and double bonds) as well as resonance of electrons which is a stabilizing force in organic compounds. Auxochromes known as colour helpers are also present in most of the dyes. The auxochromes does not involve in providing colour but they can shift the colour of the colourant and influence dye solubility (Abrahart, 1977).

Generally, natural dyes and synthetic dyes are two types of dye available. The original source for natural dyes are obtained from minerlas, plants and animals whereas synthetic dyes are being processed from chemical plant through chemical reactions in large production. Dyes are not just applied in textile and painting, but also used in applications with advanced technology such as electronics, medical field and printing industries and (Hunger, 2002). Dyes can be classified in a more specific way such as their structures, colour and application method (Clarke & Anliker, 1980). Some of the main classes of dyes are acid dye, basic dye, direct dye, reactive dye and solvent dye. They are being classified under application or principal substrates, method of application and chemical types. The general classification of dyes is summarized and stated in Table 2.1.

Table 2.1: Classification of dyes by chemical type and application

Class	Type	Application Method	Chemical types	Example	Reference
Acid	Nylon, wool, silk, paper, inks, leather	Usually from neutral to acidic dye baths	Azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro, nitroso	Acid Yellow 36	(Hunger, 2002; Katheresan et al., 2018b)
Basic (Cationic)	Paper, polyacrylonitrile, modified nylon, polyester, inks	Applied from dye baths in acidic condition	Cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triarylmethane, azo, azine, xanthene, acridine, oxazine, anthraquinone	Methylene Blue	(Hunger, 2002; Katheresan et al., 2018a)
Direct	Cotton, rayon, paper, leather, nylon	Applied from neutral or slightly alkaline dye baths with additional electrolyte	Azo, phthalocyanine, stilbene, oxazine	Direct Orange 36	(Hunger, 2002; Katheresan et al., 2018b)
Disperse	Polyester, polyamide, acetate, acrylic, plastics	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carrier methods	Azo, anthraquinone, styryl, nitro, benzodifuranone	Disperse Blue 27, Disperse Red 4, Disperse Yellow 3	(Hunger, 2002; Katheresan et al., 2018b)

Reactive	Cotton, wool, silk, nylon	Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)	Azo, anthraquinone, phthalocyanine, formazan, oxazine, basic	Reactive Blue 3	(Hunger, 2002; Katheresan et al., 2018b)
Solvent	Plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils, waxes	Dissolution in the substrate	Azo, triphenylmethane, anthraquinone, phthalocyanine	Solvent Red 26, Solvent Blue 35, Solvent Black 1	(Hunger, 2002; Katheresan et al., 2018b)
Sulfur	Cotton, rayon	Aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur-containing products on fiber	Indeterminate structures	Sulphur Black 1	(Hunger, 2002; Katheresan et al., 2018b)
Vat	Cotton, rayon, wool	Water-insoluble dyes solubilized by reducing with sodium hydrogensulfite, then exhausted on fiber and reoxidized	Anthraquinone (including polycyclic quinones), indigoids	Vat Blue 4 (indanthrene)	(Hunger, 2002; Katheresan et al., 2018b)

2.2 Methylene Blue

Methylene blue is a synthetic cationic thiazine dye. It is commonly used in the medical field to cure illness and disorders. The chemical formula of methylene blue is $C_{16}H_{18}N_3SCl$ and its chemical structure is shown in Figure 1 (Doˇ et al., 2009). The chemical name for methylene blue is 3, 7-bis (Dimethylamino)-phenaza-thionium chloride or simplified as tetramethylthionine chloride. In oxidized state, the dye will present in deep blue colour whereas it will be colourless under reduced form as leucomethylene blue (Pentru et al., 2010).

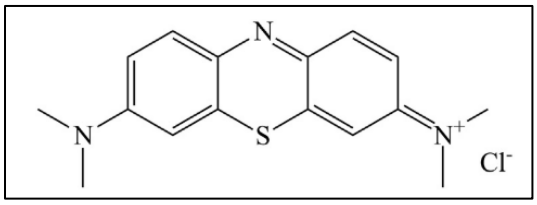

Figure 2.1: Chemical structure of methylene blue (Doˇ et al., 2009)

Methylene blue is a commonly used dye in most of the applications and it has discovered in 1876 by Heinrich Caro (Lo et al., 2014). The wide application of this dye has caused high risks and adverse effects towards the living and non-living organisms. In the long-term exposure of methylene blue, humans will tend to face several illnesses including dizziness, headache, vomiting, diarrhoea, abdominal pain and others. Hence, necessary actions should be taken to remove methylene blue from the wastewater, rivers and oceans.

2.3 Method of Dye Removal

Dyes usually are non-biodegradable in natural condition and can be seen clearly through eye vision. Thus, removal of dyes should be applied in reducing dye contamination in the water sources.

There are three types of dye removal method such as biological method, chemical method and physical method. For biological method, living organisms like enzymes are used to remove the dyes. The process should be handled with care as the growth rate of organism can be affected easily. For chemical method, utilization of chemicals and through the chemical reactions the dyes are being removed. Specific equipment might be needed and the overall cost for the treatment could be costly. As for physical method, it is considered to be quite straightforward and common by using mass transfer mechanism. Examples with description for the three types of dye removal method are listed in Table 2.2.

Table 2.2: Examples for the biological, chemical and physical methods with description (Katheresan et al., 2018b)

Method	**Example**	**Description**
Biological	Aerobic-anaerobic combination	Break down of complex dye molecules by using a prepared sludge
	Enzyme degradation	Dye molecules are degraded by extracted enzymes
	Microbial cultures	Dye particles are removed by mixture of bacteria and chemicals
Chemical	Advanced oxidation process	Dye particles are removed by multiple oxidation process
	Electrochemical destruction	Dye molecules are eaten up by electro-coagularion or non-soluble anodes
	Photochemical	Removal of dye molecules is done using Fenton reaction coupled with ultraviolet light (UV)

Physical	Adsorption	Dye molecules are adsorbed by adsorbents with high adsorption capacity
	Ion exchange	Ions from dye wastewaters are exchanged with similar ions attached to a stationary solid surface
	Reverse osmosis	Pressure driven system is used where water passed through an extremely thin membrane results in contaminants on one side and water on the other side

2.4 Adsorption

Adsorption is a method where adsorbents with high adsorption capacity are considered in removing the dye molecules. In adsorption process, dyes and pigments will be accumulated at the surface of the adsorbent thus forming an interface between two phases, either liquid-solid surface or gas-solid surface. The process is also described as physisorption or chemisorption based on the strength of the interaction between the substrate and adsorbate (Sims et al., 2019). For physisorption, the surface of the adsorbent caused the target molecules to attract towards it by van der Waals forces. For chemisorption, covalent chemical reaction will be undergone by the target molecules so that the binding site of adsorbent will bind by them. Figure 2.2 shows the general idea of interaction for physisorption and chemisorption of substance.

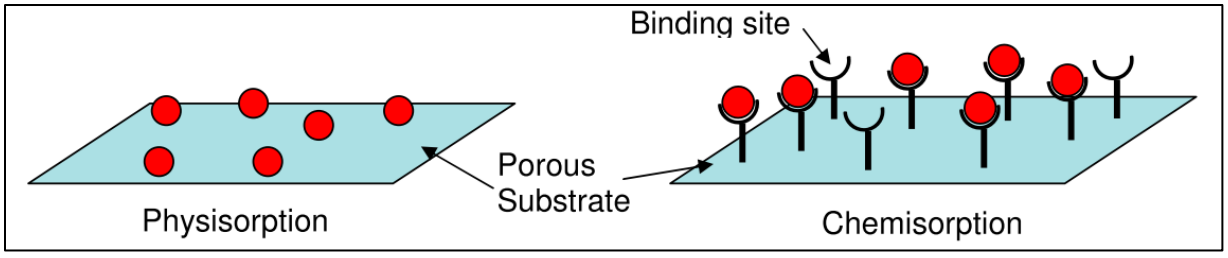

Figure 2.2: Interaction for physisorption and chemisorption (Berger & Bhown, 2011)

The advantages of this method are well adsorption performance in wide variety of dyes and ability to regenerate by adsorbents. There are other advantages of adsorption (physical) including simple design, easier to operate, high availability, able to biodegrade, less sensitive or insensitive to toxic substances and ability to treat highly concentrated dyes. However, the method will be costly due to highly priced adsorbents (Mishra et al., 2010). As the adsorbents can be recovered and reused for further removal of dye, it is still considered to be reasonable.

2.5 Adsorption Isotherm

In general, adsorption isotherms are used to describe the adsorbate quantity on the surface as a function of its pressure at constant temperature. The interaction mechanisms between the adsorbent and the adsorbate can be described by adsorption isotherm models with consideration of the equilibrium data and adsorption properties of the adsorbent and adsorbate (Sims et al., 2019). There are common adsorption isotherm models which are applicable with the experimental data to identify the type of interaction between substances including Langmuir, Freundlich and Temkin isotherm. Proper analysis of the adsorption isotherm helps in design purpose through improving the performance and efficiency of the adsorption process.

According to Langmuir theory, this isotherm is an empirical model assuming that one molecule is the thickness of adsorbed layer, known as monolayer adsorption, where equivalent definite localized and identical sites involved in adsorption process. Lateral interaction and steric hindrance are absent including at adjacent sites in between the adsorbed molecules (Al-Ghouti & Da'ana, 2020; Vijayaraghavan et al., 2006). For Freundlich isotherm model, it describes the reversible and non-ideal adsorption process. It does not restrict to monolayer adsorption but also applied to multilayer adsorption. There is no requirement for uniform distribution of the adsorption heat and affinities on the heterogeneous surface in this isotherm model (Adamson, 1997). In

Temkin isotherm model, interactions between the adsorbent and the adsorbate are to be considered. Assumption is made that a linear decrement is noticed for every molecules' heat of adsorption in the layer instead of logarithmic with certain extent by ignoring the extremely small and large value of concentrations (Aharoni & Ungarish, 1977; Foo & Hameed, 2010).

The isotherm constant parameters for each adsorption isotherm model are stated in Table 3 where C_e represents equilibrium dye concentration in aqueous solution (mg L^{-1}) and q_e represents equilibrium adsorbed quantity (mg/g).

Table 2.3: List of adsorption isotherm models

Isotherm	Equation	Plot	Parameter	Reference
Langmuir	$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{K_L Q_m C_e}$	$1/q_e$ vs $1/C_e$ (Linear), with $1/(K_L Q_m)$ as gradient and $1/Q_m$ as y - intercept	Q_m (mg/g) is the theoretical maximum adsorption capacity, K_L (L/mg) is the Langmuir adsorption constant	(Al-Ghouti & Da'ana, 2020; Mehrorang Ghaedi & Kokhdan, 2012a)
Freundlich	$lnq_e = lnK_F + \frac{1}{n} lnC_e$	ln q_e vs ln C_e (Linear), with gradient of 1/n and y-intercept of ln K_F	1/n is the intensity of the adsorption, K_F (L/mg) is the Freundlich adsorption constant	(Al-Ghouti & Da'ana, 2020; Ayawei et al., 2017; Mehrorang Ghaedi & Kokhdan, 2012a)
Temkin	$q_e = \frac{RT}{b_T} lnK_T + \frac{RT}{b_T} lnC_e$	q_e vs ln C_e (Linear), with RT/b_T as gradient and (RT/b_T) ln K_T as y - intercept	b_T (J/mol) is the Temkin constant relating heat of adsorption, K_T (L/g) is the Temkin isotherm constant, T (K) is the absolute temperature, R is the Universal gas constant (8.314 J/mol K)	(Al-Ghouti & Da'ana, 2020; Ayawei et al., 2017)

2.6 Kinetic Analysis

Adsorption kinetic should be understood to recognise adsorption efficiency and methods for improvement of a specialized usage. Pseudo-first-order and pseudo-second-order kinetic models are studied to analyse adsorption mechanism of dyes on the adsorbent (PET/MWCNTs nanofibers) through experimenting different conditions.

For **pseudo-first-order** kinetic model, the equation is shown as (Moussout et al., 2018):

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

Integration and expression of the equation in linear form is shown as:

$$ln(q_e - q_t) = lnq_e - k_1 t$$

For **pseudo-second-order** kinetic model, the equation is shown as:

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

Integration and expression of the equation in linear form is shown as:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e}$$

where q_t (mg/g) and q_e (mg/g) are the adsorbate concentration in the solid phase at time t and at equilibrium, k_1 is adsorption rate constants of first order kinetic model in min^{-1} and k_2 is adsorption rate constant in second order kinetic model in g/mg min.

2.7 Carbon Nanotubes (CNTs)

The composition of CNTs comprised of graphical sheets or graphene which they are rotated into shape of cylinder. Generally, their length is more than 20 μm and their radius is less than 100 nm. They possess a π-conjugative structure with a highly hydrophobic surface and exhibit a special sidewall curvature which allows adsorption of organic chemicals (Vinod Kumar Gupta et al., 2013). There are other special properties of CNTs including large specific area, rich hollows and layered structure which lead to variety of applications in wastewater treatment especially removal of organic contaminants such as dyes (Shan et al., 2017). Mechanisms including π- π interactions between bulk π systems on CNT surfaces, organic molecules with C-C double bonds, hydrogen bonds (due of the functional groups on CNT surfaces), and electrostatic interactions (due to charged CNT surface) allows more types of chemical substances to be adsorbed on surface of CNTs (Mishra et al., 2010). Thus, understand the properties of CNTs is important.

There are two types of CNTs including SWCNTs and MWCNTs. Single layer carbon atoms or graphene will form SWCNTs whereas multilateral graphene sheet that rolled into dozens of concentric tubes will form MWCNTs. Figure 3 shows the structure of SWCNTs and MWCNTs. By comparing these two types of CNTs, it is noticeable that MWCNTs have better performance due to its structural configuration. MWCNTs have large number of structural defects which allows attachment of different types of active sites for adsorption usage (Jun et al., 2018). Oxidized MWCNTs have been studied to show effective removal of methylene red (Mehrorang Ghaedi & Kokhdan, 2012b) and methylene blue (Vinod K. Gupta et al., 2006). Table 4 shows the list of dyes adsorbed using SWCNTs and MWCNTs without any treatment and functionalization.

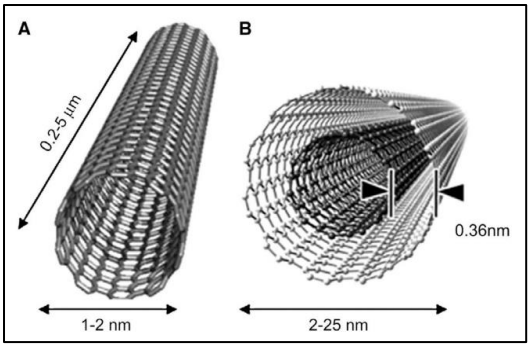

Figure 2.3: Structure of SWCNTs (A) and MWCNTs (B) (Fiyadh et al., 2019)

Table 2.4: List of dyes adsorbed using SWCNTs and MWCNTs

Type of CNTs	Name of dye adsorbed	Adsorption effect (mg/g)	Reference
SWCNTs	Reactive Blue 29 (RB 29)	496	(Nadafi et al., 2011)
	Reactive Red 120 (RR 120)	426.49	(Zare et al., 2015)
MWCNTs	Alizarin red S (ARS)	161.29	(M. Ghaedi, Hassanzadeh, et al., 2011)
	Morin	26.25	(M. Ghaedi, Hassanzadeh, et al., 2011)
	Eriochrome cyanine R (ECR)	73.18	(V. K. Gupta et al., 2014)
	Arsenazo (III)	-	(M. Ghaedi, Shokrollahi, et al., 2011)
	Reactive red M-2BE (RRM)	335.7	(Machado et al., 2011)
	Methylene blue (MB)	77.83	(Rodríguez et al., 2010)
	MO	-	(Yao et al., 2011)

2.8 Polyethylene terephthalate (PET)

PET is the most common thermoplastic polymer resin with repeating units of ethylene terephthalate having chemical formula of $C_{10}H_8O_4$. PET can be functionalized with other materials in synthesizing a better and effective component. As PET does not contain any chemically active groups, it is resistant against moisture and dyes. Hence, specific functional groups can be introduced to PET by using grafting method with different vinyl monomers including acrylic acid, methacrylic acid and acrylamide. These vinyl monomers could be grafted onto PET fibers through chemical or radiation initiation (Abdouss et al., 2013).

PET acts as a supportor carrier material for other materials to fabricate or immobilized on it. This will provide it to have more effective and greater adsorption capacity. A study was carried out that PET was used as a fibrous carrier where immobilization of chitosan particles was done on this chemically activated PET fiber. Adsorption of anionic phthalocyanine dyes with different molecular sizes, nature and number of anionic groups could be done by this adsorbent. The surface of PET fiber was activated by weak alkaline hydrolysis in increasing the particle immobilization. This process resulted in increment of adsorption rate and dye binding capacity about 300 to 1050 mg/g (Lipatova et al., 2018).

Moreover, PET is suitable to be used as precursor in preparing low cost and effective carbon-based material adsorbents including CNTs, graphene and activated carbon due to its high content of carbon and low (considerably negligible) amount of impurities present. According to research done by El Essawy (2017), it was discovered that graphene prepared by PET waste acquired high surface area and micropore volume, thus considering PET to be a possible adsorbent in removing dye. This adsorbent could adsorb both acid red 25 (AB 25) and methylene blue. There

is lower adsorption of AB 25 due to existence of negative charges in sulfonic group which caused repulsion between graphene and dye molecules.

Studies and research had proved that PET is an economic and effective material to be used in dye removal. PET can be used as adsorbent, support, carrier or raw material to synthesis new form of adsorbents, thus proving PET to be a beneficial component. PET can be recyclable from its waste which provide a sustainable method in adsorbing dyes from the wastewater. Thus, it is important to understand the properties of PET in assisting dye adsorption.

2.9 Electrospinning

Electrospinning is the process of spinning fibers with the assist of electrostatic forces. This method has some advantages including high efficiency, low cost and high reproducibility (Shi et al., 2015). It is capable to produce fibers with diameters of range from scale of nanometer to micrometer. These nanofibers have higher surface area and smaller pores which has used in several applications such as tissue scaffolds, nanocatalysis, filtration, protective clothing and optical electronics (Subbiah et al., 2005). Figure 5 shows the schematic setup for the electrospinning method in laboratory-scale.

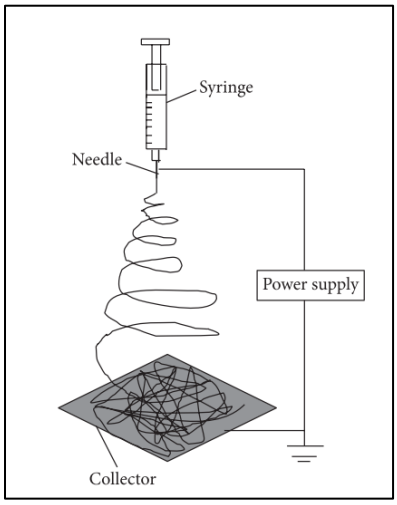

Figure 2.4: Schematic setup for the electrospinning method in laboratory-scale (Shi et al., 2015)

Three major components needed in the electrospinning setup are a syringe with metallic needle, a grounded conductive collector and high voltage power supply. The polymer solution inside the syringe should be applied by high voltage supply so that free charges can be induced into the solution. Initially, pendant droplet will form when high voltage is used. Deformation of pendant droplet into conical droplet (Taylor cone) occurs when the electrostatic repulsion begins to overcome the surface tension of the fluid. A fine, charged jet of polymer solution will be ejected out of the syringe once the electrostatic forces overcame the surface tension of fluid. During the ejection process, the dry fiber is formed due to evaporation of solvent and it is being collected at the collector (Subbiah et al., 2005).

In adsorption aspect, there is electrostatic interaction between the carbon nanomaterials attached on the electrospun latyer with the dye molecules. For oxidized electrospun carbon nanofibers (O-ECNFs), methylene blue dye was adsorbed onto the electrospun layer due to electrostatic forces on the negatively charged surface and π - π stacking interactions (Thamer et al., 2019).

CHAPTER 3

METHODOLOGY

3.1 Flow of experimental work

This chapter is about the overall flow of the experimental work. Figure 3.1 showed the flow diagram of the experimental work including synthesis of PET/MWCNTs electrospun nanofibers, batch experimental studies, study of adsorption isotherm and adsorption kinetics.

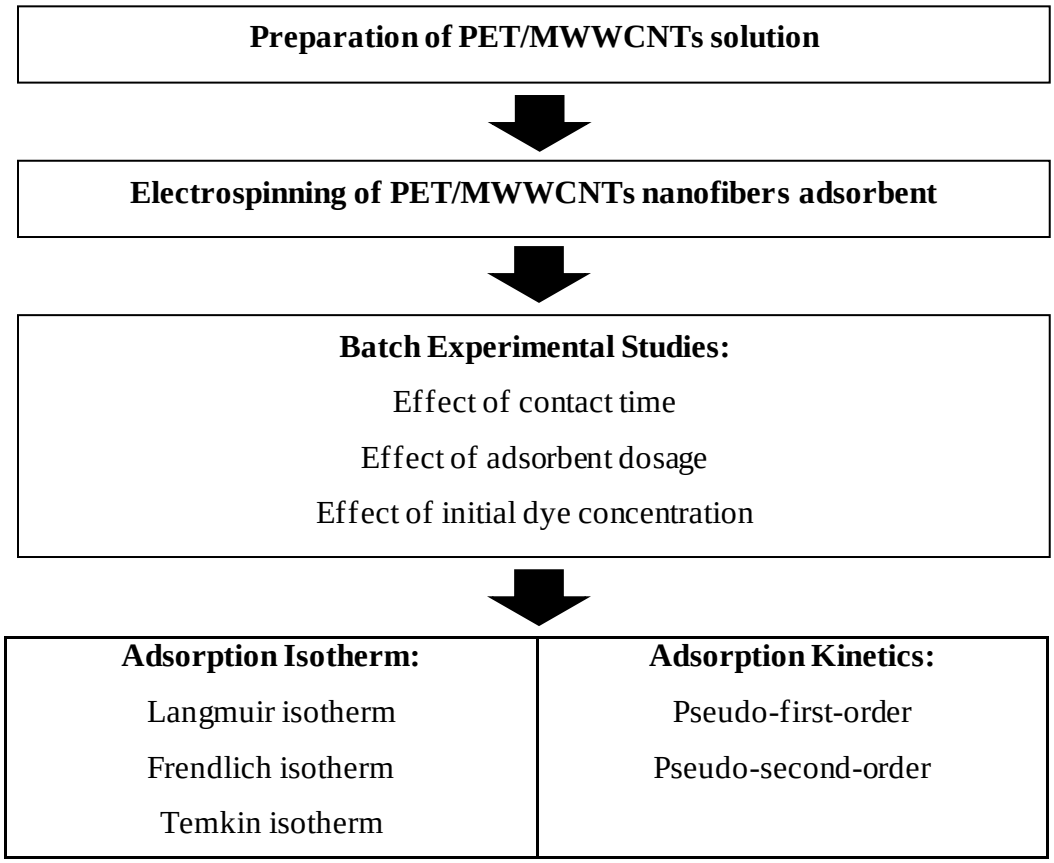

Figure 3.1: Flow diagram of experiment work

3.2 Materials

Table 3.1 shows the list of materials and chemicals used in this study.

Table 3.1: List of materials and chemicals in study

Material	Specifications	Supplier	Purposes
PET	Waste plastic water bottles. Cut into small pieces by using scissors.	Obtained from plastic bottle waste (Spritzer)	Acts as a polymer solution.
PES support	Large piece with interspaces.	-	Acts as PES adsorbent and support for attachment of PET-MWCNTs fibers
MWCNT	Purity > 95%	Prepared from chemical vapour deposition method	Act as filler.
Hexafluoro-2-propanol (HFIP)	Molecular weight: 168.05 Density (20 ℃): 1.596	Revlogi Materials	Solvent for PET
MB	Methylene blue (C.I.52015), StainPur® Molecular weight: 355.89	System Chemicals	Adsorbate

Distilled water	Laboratory produced distilled water	Produced in lab	Non-solvent agent
Syringe with needle	10 ml syringe equipped with 21-gauge needle	Available in lab	To eject PET/MWCNTs for electrospinning

3.3 Equipment

Some equipment used in this study for preparation and collecting data for adsorption experiment. The list of equipment was stated in Table 3.2.

Table 3.2: List of equipment used in this project

Equipment	Model	Purposes
Magnetic stirrer	IKA® C-MAG HS 157	To stir PET/MWCNTs solution
Electronic balance	Standard electronic analytical balance	To measure the weight of PET, HFIP and MWCNT
Double-beam UV-visible spectrophotometer	Shimadzu UV-1800, Japan	To measure adsorbance of dye solution
Sonicator	Branson 3800 Ultrasonic	To disperse MWCNTs into PET solution
Electrospinning Machine	N/A	To synthesis PET/MWCNTs electrospun nanofibers

3.4 Preparation of PET/MWCNTs solution

PET polymer used as a matrix polymer to disperse MWCNTs in this study. Phase inversion is applied in fabrication of 0.1 wt% PET/MWCNT solution. PET pellets was obtained by cutting in pieces from recycled Spritzer water bottle. 4.995 g of PET pellets was added into a stirrer beaker filled with 44.955 of HFIP solution. 0.05g of purified MWCNTs powder is added later into the stirrer beaker. The PET/MWCNTs solution contained in a stirrer beaker was covered and stirred overnight at room temperature for 24 hours by using magnetic stirrer with 500 rpm as shown inFigure 3.2. Then, the MWCNTs fillers were dispersed into the PET solution by using ultrasonicator. The amplitude was set at 50% and cycle of 0.5 for the sonicator. The PET/MWCNTs solution was being ultrasonicated for 10 minutes as shown in Figure 3.3.

Figure 3.2: Stirring PET/MWCNTs solution by magnetic stirrer with 500 rpm

Figure 3.3: Ultrasonication of MWCNTs fillers into the PET solution

3.5 Electrospinning of PET-MWCNTs nanofiber adsorbent

Electrospinning method is applied to produce PET-MWCNTs nanofibers. PES support was covered around the collector drum for attachment of PET-MWCNTs nanofibers. After sonification, the PET-MWCNTs solution was inserted into a syringe. It is important to ensure no air bubbles present in the solution. The applied voltage was set at 20 kV and the electrospinning distance was fixed at 19 cm. 0.6 mL/h was set as flow rate of solution and 5 mL was set as volume. The first water droplet was pushed out of the syringe using the pusher plug. Next, the collector drum speed was adjusted to 300 rpm and start the turning of the drum. One clip from the power supply was attached to the tip of the needle of syringe and another clip was attached to the collector drum. Then, the syringe pump was started for the electrospinning process. After 5 hours, the PET and PET-MWCNTs nanofibers were electrospun on the PES supports attached on the collector