SYNTHESIS OF POLYVINYL ALCOHOL/ MULTIWALLED CARBON NANOTUBES COMPOSITES FOR MALACHITE GREEN ADSORPTION

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2022

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by

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Project report 3 submitted in partial fulfilment of the requirement for the degree of

Bachelor of Chemical Engineering

2022

ACKNOWLEDGEMENT

Firstly, I would like to extend my most sincere gratitude to Associate Professor Dr. Tan Soon Huat, who served as my supervisor, for his invaluable advice, kind assistance and supportive encouragement throughout this project. His enlightened suggestions motivated me in the research.

Besides, I want to express my appreciation to my coursemates, especially Muhammad Azrie Bin Razam and Karthigesan A/L Velautham, for their kindness and helping hands in guiding me during my work. We worked together and shared their valued knowledge while lending precious time to guide me. Next, I would like to express my gratitude to the staff and technicians for their assistance and direction with the equipment.

Not to mention thanking my family members for their encouragement and support throughout the process. They always give me motivation when times get rough. I would especially like to thank my sister for her love, patience and unwavering support.

All in all, the project completion could not have been accomplished without the support of everyone who had helped me either directly or indirectly during the process. Thank you for allowing me time away from you to your work. My heartfelt thanks.

Chong Yian Sing

July 2022

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LIST OF SYMBOLS

Symbol	Description	Unit
B	Constant related to the heat of adsorption	J/mol
B_t	Temkin constant	-
C_e	Equilibrium concentration of dye in solution	mg/L
C_o	Initial concentration of dye in solution	mg/L
C_t	Concentration of dye in solution at time instant	mg/L
k_1	Pseudo-first order kinetic rate constant	1/min
k_2	Pseudo-second order kinetic rate constant	g/mg min
k_f	Freundlich constant corresponds to adsorption capacity	$mg/g(L/mg)^{1/n}$
k_l	Langmuir constant	L/mg
k_t	Equilibrium binding constant	L/mg
M	Mass of absorbent	mg
n	Freundlich constant corresponds to adsorption intensity	-
q_{calc}	Calculated adsorption capacity at equilibrium	mg/g
q_e	Adsorption capacity at equilibrium	mg/g
q_{exp}	Experimental adsorption capacity at equilibrium	mg/g
q_m	Theoretical maximum adsorption capacity	mg/g
q_t	Adsorption capacity at time instant	mg/g
R	Universal gas constant	J/mol K
R^2	Correlation coefficient	-
R_L	Separation factor	-
t	Contact time	min
T	Absolute temperature	K

V	Volume of adsorbate solution	L

LIST OF ABBREVIATIONS

ADS	Adsorbance
AC	Activated carbon
CNTs	Carbon nanotubes
MG	Malachite green
MWCNTs	Multiwalled carbon nanotubes
PANI	Polyaniline
PFO	Pseudo-first order
PSO	Pseudo-second order
PVA	Polyvinyl alcohol
PVA/MWCNTs	Polyvinyl alcohol/ Multiwalled carbon nanotubes
SEM	Scanning electron microscopy
SWCNTs	Single-walled carbon nanotubes
UV-Vis	Ultraviolet-visible
vdW	Van der Waals

SINTESIS POLIVINIL ALKOHOL/ NANOTIUB KARBON BERBILANG KOMPOSIT UNTUK PENJERAPAN HIJAU MALACHITE

ABSTRAK

Pewarna sintetik diaplikasikan secara meluas dalam industry, biasanya industry tekstil, menyebabkan peningkatan pencemaran air. Salah satu pewarna sintetik yang sering digunakan ialah hijau malachite (MG). Matlamat projek ini adalah untuk mensintesis polivinil alcohol/ nanotub karbon berbilang (PVA/MWCNTs) nanokomposit dengan polivinil alcohol sebagai sokongan bagi penyingkiran pewarna MG daripada larutan akueus. Cara sintesis untuk penyediaan manik PVA tulen dan PVA/MWCNTs ialah penyongsangan fasa. Bagi keseimbangan kelompok, kesan beberapa parameter termasuk kepekatan pewarna awal, masa hubungan dan dos adsorben diselidiki. Masa hubungan optimum ialah 2880 minit. Keputusan diperoleh mencadangkan kecekapan penyingkiran menaik dengan pemanjangan masa optimum dan peningkatan dos adsorben, serta penurunan kepekatan pewarna awal. Pada kepekatan pewarna awal 5 mg/L dengan dos adsorben 2500 mg, kecekapan penyingkiran diperoleh adalah 100 %, sangat tinggi jika berbanding dengan PVA tulen dengan 42.26 %. Kapasiti penyerapan adsorben meningkat dengan penaikan kepekatan pewarna awal kerana kewujudan daya penggerak iaitu kecerunan kepekatan yang semakin menaik. Dari segi isoterm penjerapan, isoterm Langmuir dan kinetic pseudo-tertib-kedua ialah model yang paling sesuai menurut data kajian. Penjerapan lapisan tunggal dengan penjerapan kimia sebagai langkah penuntu kadar dicadangkan untuk menghuraikan penjerapan pewarna MG. Maksimum kapasiti penjerapan pewarna MG asas penjerapan lapisan tunggal adalah 2.28 mg/g bagi PVA/MWCNTs komposit manakala 0.02 mg/g bagi PVA adsorben. Oleh itu, keputusan kajian ini menunjukkan PVA/MWCNTs nanokomposit ialah satu potensi adsorben yang menjanjikan untuk rawatan pewarna MG dalam air sisa.

SYNTHESIS OF POLYVINYL ALCOHOL/ MULTIWALLED CARBON NANOTUBES COMPOSITES FOR MALACHITE GREEN ADSORPTION

ABSTRACT

Synthesic dyes are widely applied in the industries, typically textile industries, resulting the growth of water pollution. One of the common dyes used is malachite green (MG). This project aimed to generate polyvinyl alcohol/ multiwalled carbon nanotubes (PVA/MWCNTs) nanocomposites using polyvinyl alcohol (PVA) as the support for the MG adsorption from aqueous solution. Phase inversion was the synthesis technique employed to prepare the pure PVA beads as well as PVA/MWCNTs beads. The effects of several parameters, such as the initial dye concentration, adsorbent dosage, and contact time, were studied. The optimum contact time was 2880 minutes. The findings revealed that there are several ways to increase the removal efficiency, firstly, by lowering the starting dye concentration and secondly, by increasing contact time and lastly, by increasing the adsorbent dosage. At an initial dye concentration of 5 mg/L and PVA/MWCNTs adsorbent dosage of 2500 mg, the removal efficiency obtained was 100 % which is significantly higher as compared to pure PVA adsorbent, which was only 42.26 %. The adsorbent's adsorption capacity decreased as the initial dye concentration decreased, resulting from the higher driving force of the concentration gradient. The Langmuir isotherm model and the pseudo-second order kinetic model provided the best fits for the experiment data in terms of adsorption isotherm and kinetics. The uptake of MG dye was referred to as monolayer adsorption, with chemisorption as the rate-determining step. The monolayer maximum adsorption capacity of MG dye attained was 2.28 mg/g for PVA/MWCNTs composites and 0.02 mg/g for PVA adsorbents. In light of these findings, PVA/MWCNT nanocomposites are a promising potential adsorbent for the treatment of MG dyes in wastewater.

CHAPTER 1

INTRODUCTION

1.1 Research Background

In the domains of modern technology, synthetic dyes are frequently utilised. Typically, they are used in the textile, leather, paper, food processing, pharmaceutical, electroplating, paper and pulp mills, and dye-making sectors (Shirmardi et al., 2013; Karimifard and Alavi Moghaddam, 2018). Annually, over 7×10^5 tonnes of synthetic dyes are produced per year with more than 1,00,000 kinds (Yagub et al., 2014; Raval et al., 2017). Among the 10,000 tonnes of dye consumed in the textile industry around the world per year, nearly 100 tonnes of dyes are discharged into wastewater streams (Yagub et al., 2014). Dye-contaminated wastewater is hazardous that leads to environmental pollution and health hazards. This is because dyes, although in low concentrations only, prevent aquatic life from photosynthesis. Meanwhile, they are poisonous, carcinogenic, mutagenetic, and xenobiotic in nature (Modak et al., 2016). The most significant potential human health hazard in the long term is the dyes' genotoxicity (Lellis et al., 2019). Moreover, most dyes are very stable and challenging to be removed as they have aromatic molecular structures. Due to their devastating effects on aquatic and human life, synthetic dyes are recognised as one of the most significant types of environmental contaminants (Karimifard and Alavi Moghaddam, 2018).

The 17 Sustainable Development Goals (SDGs) are developed to promote a sustainable future for worldwide beings. One of the SDGs: GOAL 6, is water and sanitation, aimed to ensure the sustainability of clean water and sanitation. Another SDG is GOAL 14, life below water, which proposed to conserve and sustainably manage marine resources. In this study, these two goals are engaged to attain sustainable development. Many treatments are available to be used for the removal of dye to address water pollution. Basically, there are three types of methods, typically chemical, biological, and physical methods. One of the techniques that are frequently used to remove the colour from wastewater is adsorption. The adsorption technique is straightforward, simple to use, unaffected by harmful compounds, and economical. Polymer nanocomposites are considered new materials, emerging as a promising option in the adsorption study (Maghfirah et al., 2018). In the membrane technique, polyvinyl alcohol (PVA) polymer is widely applied due to its hydrophilicity and chemical resistivity (Jose et al., 2015). It is a non-toxic, water-soluble polymer consisting of many reactive hydroxyl groups (Maghfirah et al., 2018). This project examines the use of a PVA/MWCNT nanocomposite as an adsorbent for the malachite green (MG) dye adsorption. The impacts of operational parameters, such as initial dye concentration, adsorbent dosage, and contact time between adsorbent and adsorbate, are investigated, and the ideal operating factors are identified. Besides, the process's adsorption isotherms and kinetics are evaluated.

1.2 Problem Statement

Annually, tonnes of dyes are being discharged into industrial wastewater worldwide. The dyes in effluent cause hazards to humans as well as to the environment. This is due to its toxicity and non-biodegradable nature. Thus, dye removal treatment is vital to be taken action to ensure environmental sustainability for future generations (Jordão et al., 2018). The dye removal is able to be accomplished using a variety of techniques. The adsorption technique is one of the most well-liked and successful methods for dye removal. Due to its excellent removal effectiveness, activated carbon is one of the most commonly utilised adsorbents. Anyhow, research has shown that carbon nanotubes feature a greater adsorption efficiency than activated carbon, backed by their vast specific surface area as well as their unique hollow structure with strong mechanical strength and outstanding thermal and electrical conductivity (Long and Yang, 2001; Shirmardi et al., 2013). In this regard, multiwalled carbon nanotubes

(MWCNTs) are a good choice for dye removal. However, the powder form of MWCNTs has possessed difficulties for it to be recovered, regenerated, and reused. To overcome this problem, the polymer nanocomposite, which commonly exists in film form, may ease the recovery process of the adsorbent. MWCNTs incorporated into polymers are suspended to form a film that can be easily removed from the wastewater. This research proposed incorporating MWCNTs with polyvinyl alcohol (PVA) polymer to enhance the sustainability of adsorbent and the adsorption efficiency of malachite green (MG). Many parameters can affect the adsorption performance, including initial dye concentration, adsorbent dosage, and contact time. Therefore, these operating parameters are evaluated.

1.3 Objectives

The objectives of this research are:

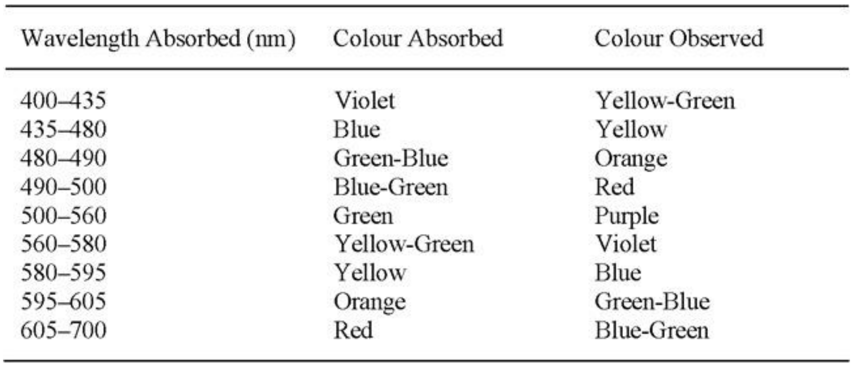
1. To synthesise the PVA beads and PVA/MWCNTs nanocomposite beads as adsorbents for dye adsorption.
2. To explore the effect of initial dye concentration, adsorbent dosage, and contact time on the malachite green adsorption.
3. To identify the adsorption performance of the PVA and PVA/MWCNT adsorbents through adsorption isotherm and kinetics studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Classification of Dyes

Basically, dyes are complex organic molecules that are attached to surfaces and add colour (Yagub et al., 2014). However, unlike most organic compounds, dyes possess colour due to their chromophore and the conjugated system, as well as the exhibition of electrons resonance. Besides, dyes can adsorb light in the visible spectrum (Abrahart, 1977). Figure 2.1 shows the light adsorption wavelengths concerning the colour absorbed and colour viewed, respectively.



Wavelength Absorbed (nm)	Colour Absorbed	Colour Observed
400–435	Violet	Yellow-Green
435–480	Blue	Yellow
480–490	Green-Blue	Orange
490–500	Blue-Green	Red
500–560	Green	Purple
560–580	Yellow-Green	Violet
580–595	Yellow	Blue
595–605	Orange	Green-Blue
605–700	Red	Blue-Green

Figure 2.1 Wavelength of light adsorption versus colour in organic dyes (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 2010)

Dye types fall under a broad classification. Based on the origin of the dye sources, dyes are most frequently categorised. In this view, there are two different sorts of dyes: natural dyes and synthetic dyes. Natural sources, such as plants, animals, and minerals, are used to create natural dyes. Most of them are negatively charged. Conversely, the colour spectrum of synthetic dyes is broader than that of natural dyes since they are made from organic or inorganic substances. In addition to source-based classification, dyes can also be grouped based on their application method to the substrate, their chemical properties, or the electronic origins of colour (Raval et al., 2017). Figure 2.2 visualises the broad classification of dyes.

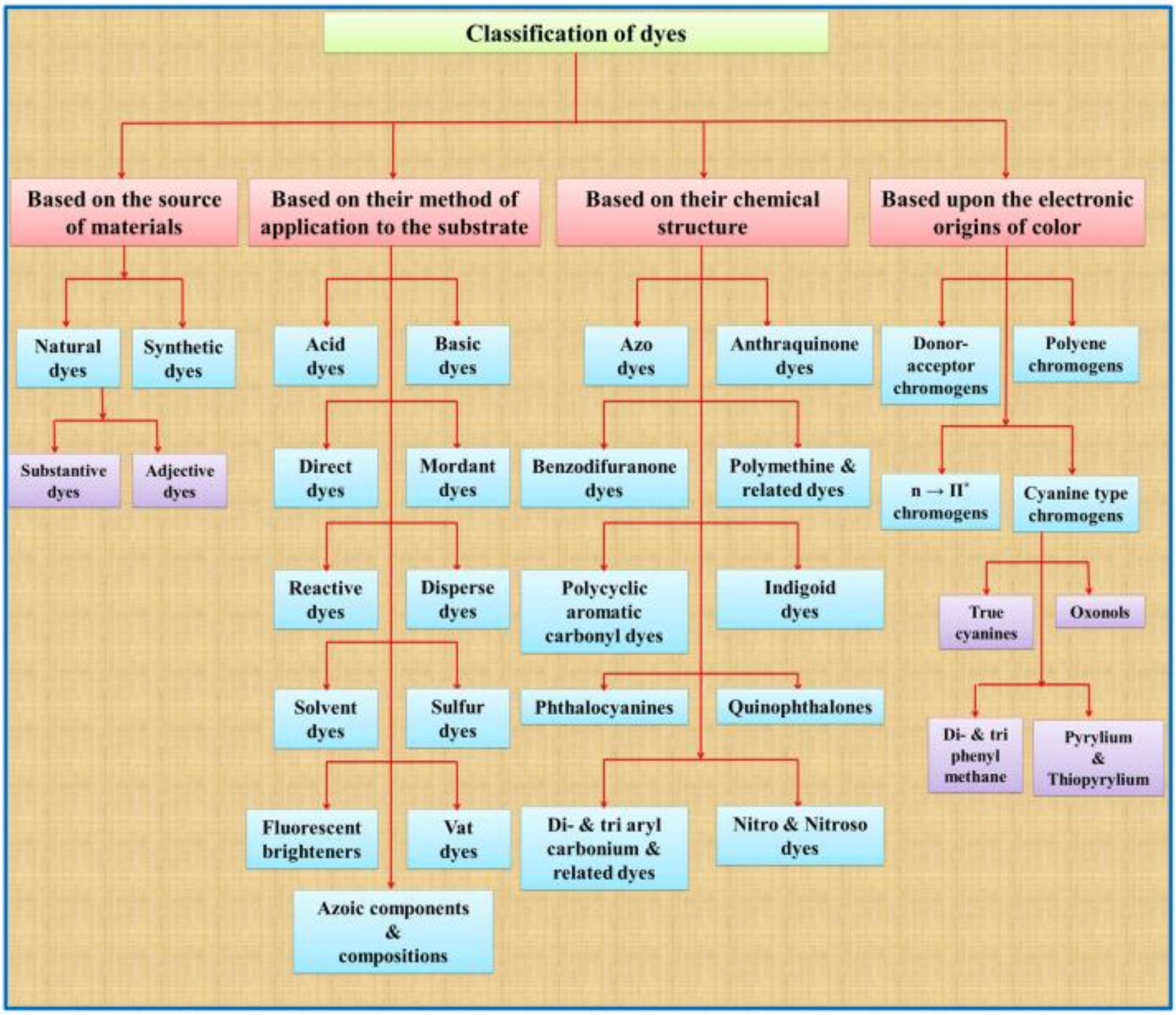


Figure 2.2 Broad classification of dyes (Raval et al., 2017)

2.2 Malachite Green

A green crystalline powder known as malachite green (MG) is a cationic dye that is water soluble. It falls into the triphenylmethane group. Particularly, MG is a monochloride salt of MG cation with chemical formula of $C_{23}H_{25}ClN_2$ while its IUPAC name is [4-[[4-(Dimethylamino)phenyl]-phenylmethylidene]cyclohexa-2,5-dien-1-ylidene]-dimethylazinum; chloride. Other names for MG include diamond green B, aniline green, Victoria green B and basic green 4 (Raval et al., 2017). It has one amide group that possess a positive charge even in highly acidic conditions. Figure 2.3 depicts the 2-dimensional chemical structure of MG dye (Rajabi et al., 2016).

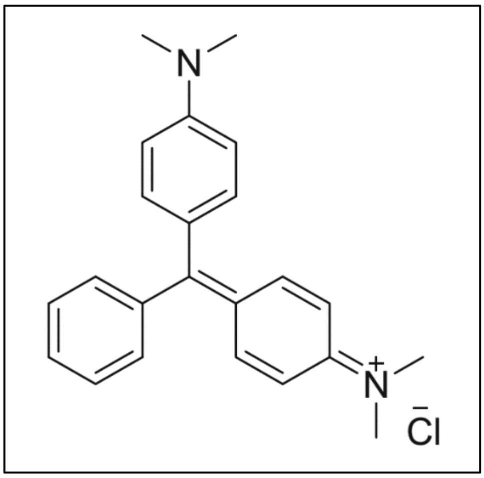


Figure 2.3 2D chemical structure of malachite green (Raval et al., 2017)

The dyeing of cotton, silk, wool, leather, and jute products as well as aquaculture and animal husbandry, make extensive use of MG (Shirmardi et al., 2013; Raval et al., 2016b). However, due to its mutagenic and carcinogenic properties, the US Food and Drug Administration has not authorised it (Raval et al., 2016b). Its toxicity can lead to severe consequences on the brain, liver, kidney, reproductive system, and nervous system. Besides causing health hazards, MG can also reduce photosynthesis and obstruct the growth of aquatic life since it colours large areas of water bodies even with a deficient concentration, thus blocking the light penetration. In addition, MG is non-biodegradable in nature. Therefore, necessary treatment should be implemented for MG removal from the industrial effluent (Raval et al., 2016b).

2.3 Dye Removal Method

There are three different types of dye removal methods, including chemical method, biological method, and physical method. For the chemical treatments, chemicals are utilised in dye removal. For instance, oxidative process, ozonation, photochemical, coagulation-flocculation, electrochemical destruction, Fenton's reagent, sodium hydrochloride, etc. Next, the biological method is biodegradable as a living organism are used, and at the same time, it is economically attractive. Decolorization by white-rot fungus or mixed bacteria, anaerobic textile-dye bioremediation systems, as well as adsorption by living or dead microbial biomass are examples of appropriate approaches. Moving on to physical method, some examples include ion exchange, radiation, electrokinetic coagulation, membrane filtration, adsorption by activated carbon, etc. (Yagub et al., 2014). Table 2.1 indicates the examples of dye removal methods concerning chemical, biological and physical methods, respectively.

Table 2.1 Various dye removal techniques (Yagub et al., 2014; Katheresan et al., 2018)

Method	**Example**	**Description**
Chemical	Oxidative process	Multiple oxidation processes are carried out simultaneously for dye removal. Simple but expensive and inflexible.
	Ultraviolet irradiation	UV light decomposed dyes. No sludge formation but expensive and energy depleted.
	Electrochemical destruction	Insoluble anodes or electro-coagulation is used to consume dye. No chemical consumption and sludge build-up, but expensive.
Biological	Enzyme degradation	Enzyme extracted to degrade dye. Non-toxic, cheap, reusable and highly efficient,

		but the enzyme production amount is unreliable.
	Algae degradation	Sludge prepared to degrade complex dye. Easily accessible and cheap, but the system is unstable.
	Fungal cultures	Fungus consume dye for self-growth. Flexible but lengthy growth phase and unstable.
Physical	Adsorption	Adsorbents adsorbed dye with high adsorption capacity and efficiency, but the adsorbents may be expensive.
	Ion exchange	Similar ions are swapped with the existing ion in dye. Reversible and can be recovered, but only effective to little types of dye.
	Membrane filtration	Dye is separated by membrane from solution by passing through them. Reusable, but expensive and membrane fouling occurred easily.

2.4 Adsorption Method

The adsorption is the best choice among all the methods. It is simple, with high efficiency and economically manageable (Raval et al., 2016). Chemisorption and physisorption are the two different categories of adsorption techniques. Strong chemical linkages are formed between the adsorbate and the adsorbent surface during chemisorption, also known as chemical adsorption. The process is slow and irreversible. On the other hand, physisorption or physical adsorption is illustrated by weak Van der Waals (vdW) forces of attraction that existed between the adsorbate and adsorbent. In this regard, the primary physical forces that contribute to the adsorption are the vdW forces, polarity, dipole-dipole interactions, hydrogen bonds, etc. The fact that this method's adsorption process is reversible is one of its benefits. As a result, the adsorbents can be recycled or renewed. The adsorption process can be affected by several factors; hence the effects of these factors should be considered (Yagub et al., 2014).

2.4.1 Adsorbent

There are many adsorbents used for malachite green (MG) dye removal. Five classifications of the respective adsorbents include activated carbon (AC) adsorbents, non-conventional low-cost adsorbents, nanomaterial adsorbents, composite and nanocomposite adsorbents as well as miscellaneous adsorbents (Raval et al., 2017).

In this regard, activated carbon is well known due to its effectiveness. This is backed by its high degree of surface reactivity, micro-porous structure as well as the great surface area for adsorption. There are four types of AC, namely granular (GAC), fibrous (FCF), cloth (ACC), and powder (PAC). In this regard, commercial AC and AC prepared with sources from agricultural waste materials are the most frequently utilised AC in dye adsorption. However, the high production costs of AC have made it more expensive than other adsorbents (Raval et al., 2016a). An example of commercial AC is mesoporous carbon, in which the MG removal is greater than 99% (Anbia and Ghaffari, 2011). On the other hand, the AC obtained from biomass and other waste materials is a potentially cheap alternative to the more commonly utilised commercial AC (Bello et al., 2012). In any case, the US Environmental Protection Agency lists AC adsorbent as one of the best possible control methods (Raval et al., 2017).

Next, non-traditional low-cost adsorbents can be made from materials including biosorbents, industrial by-products, solid agricultural waste, and solid industrial by-products or waste. This type of adsorbents is relatively cheaper in cost and abundant. Looking into the agricultural solid wastes, the lignocellulosic stalk consisting of cellulose, hemi-cellulose, silica ash and lignin is studied. Rice stalk, categorised under lignocellulosic stalk, was thermochemically modified with citric acid to introduce free carboxyl groups. The MG removal efficiency is 94.34%. (Gong et al., 2006). Apart from that, bagasse fly ash (BFA), a by-product of industry obtained from the sugar mills' particulate separation machinery, is another valuable adsorbent. It has strands inside each fibre, a fibrous structure, and huge pores. The maximum MG adsorption capacity is 170.33 mg/g (Mall et al., 2005). Further, Persian Kaolin, an inexpensive white inorganic powder, is another natural substance utilised as MG adsorbent. It contains particles of flaky shaped quartz and kaolinite. Its maximum MG adsorption capacity is 52.91 mg/g (Tehrani-Bagha et al., 2011). Looking into the biosorbents, one of the cases is chitin grafted poly (acrylic acid) (chi—g-PAA), a toxic organic compound. This grafted copolymer consists of carboxylic groups that can be readily hydrolysed to sodium salt with the aid of a dilute sodium hydroxide aqueous solution. The monolayer adsorption capacity for MG dyes is 285.70 mg/g (Huang et al., 2012).

Besides, there are many types of nanomaterial, including nanoparticles, nanotubes, nanowires, nanofibers, nanorods and fullerenes (Saravanan et al., 2014). Among these nanomaterials, carbon nanotubes are the most well-known adsorbents due to their effective adsorption characteristics. There are two types of carbon nanotubes, typically single-walled carbon nanotubes (SWCNTs) and MWCNTs. Concentric graphene cylinders that are 1 to 2 nm in diameter make up SWCNTs, whereas MWCNTs are a combination of several cylinders thus considered a mesoscale graphite system (Odom et al., 1998). For the adsorption of MG dyes, functionalised MWCNTs which had undergone acid treatment is utilised. It possesses an exceptional hollow structure, a sizable surface area, high mechanical strength, and a carboxylic functional group. The maximum adsorption capacity of MG is 142.85 mg/g (Shirmardi et al., 2013).

On the other hand, concerning composites and nanocomposites can be classified as polymer-based and non-polymer-based. The polymer-based nanocomposites have complex interfacial areas between their matrices. The addition of polymer supports remarkably enhanced the nanomaterials' mechanical, barrier, thermal properties, and recyclability (Sen, 2020). For instance, MWCNT-filled polyaniline (PANI) composites are studied for MG's adsorption. Since MG is a cationic dye, deprotonated PANI emeraldine base (EB) is more suitable for the amine and imine nitrogen in its structure can form electrostatic interactions with the cationic group in MG. The MWCNTs are entangled and develop a rigid porous framework. The maximum adsorption capacity attained is 11.73 mg/g (Zeng et al., 2013). As for the non-polymer-based nanocomposites, the metal nanocomposite is one of the types. The gold nanoparticles loaded on activated carbon (Au-NP-AC) are efficacious for the MG adsorption, with the maximum adsorption capacity attained of 142.85 mg/g. The active adsorption sites on AC include reactive hydroxyl and carboxyl groups, forming electrostatic interaction and hydrogen bonding with the MG dyes compounds (Roosta et al., 2014).

Last but not least, the miscellaneous adsorbents. For instance, polyethylene terephthalate (PET) by chemical activation with sodium hydroxide (PETNa8) is one of the miscellaneous adsorbents. The total surface area of the adsorbent is 410 m^2/g, where the 41% and 59% have existed in meso plus macropores and micropores, respectively. The maximum adsorption capacity achieved is 169.49 mg/g (Akmil-Başar et al., 2005).

In this project, the adsorbent investigated is polymer nanocomposites, typically PVA/MWCNTs composites. As mentioned before, the unique structure of MWCNTs provides unique chemical and physical properties, which is beneficial for the adsorption of dyes. All the individual carbon nanotubes (CNTs) have evenly distribution of hydrophobic sites provided for organic molecules on their exterior surface. In this perspective, the π- π interactions between the bulk π system on the CNTs surfaces, carbon-carbon double bonds or benzene rings on the organic compounds, hydrogen bonds caused by the functional groups on CNTs surfaces, electrostatic interactions due to the surfaces' charges are also suggested to be the mechanisms that can explain the CNTs and organic molecules interactions (Mishra et al., 2010). The MWCNTs have been widely studied and utilised for the adsorption of synthetic dyes. For instance, methylene blue (Rodríguez et al., 2010),

Meanwhile, the PVA is a synthetic semi-crystalline polymer with molecular weight ranging from 20000 to 400000 Da (Gaaz et al., 2015). It is potentially efficacious support for dye removal backed by its high adsorption capacity, large surface area, excellent selectivity, high durability and reusability (Mok et al., 2020). Besides, it is also degradable and biocompatible (Yang et al., 2016). Furthermore, there is a presence of free hydroxyl and acetate groups on PVA, which aids in the adsorption of dyes (Areal et al., 2018).

2.4.2 Parameters Affecting Adsorption Efficiency

The efficiency of malachite green removal can be affected by several factors, including initial dye concentration, adsorbent dosage, and contact time. Shirmardi et al. (2013) proposed utilising functionalised-MWCNT for MG dye adsorption. The dye removal efficiency is always higher with the longer contact time on the MG. In this perspective, the efficiency of adsorption reduced gradually since the occupancy of the vacant adsorption sites on the adsorbent surface decreased gradually. The repulsive forces between the adsorbent and dye grew as the occupation of the remaining unoccupied active sites decreased over time. Initial dye concentration is another important parameter affecting adsorption efficiency. As the initial dye concentration of MG decreases, the adsorption capability decreases as well. This is explained by the higher driving force produced by the growing concentration differential between the MG dye adsorbed on the adsorbent surface and the MG dye in solution. This finding is supported by Mall et al. (2005). On the other hand, it is evident that the higher the adsorbent dosage, the higher the adsorption efficiency. This is backed by the rise in the specific surface area and active site availability of adsorbents. However, Senthilkumaar et al. (2006) findings showed an opposite trend in which the quantity of adsorbed MG reduced with increased adsorbent dosage.

2.4.3 Adsorption Isotherm

When adsorption reaches an equilibrium condition, the adsorbate molecules are distributed between the phases of solid and liquid according to an isotherm known as the adsorption isotherm. The typical adsorption isotherms to explain experimental data are Langmuir, Freundlich and Temkin. The performance and efficiency of dye adsorption can be enhanced by correctly analysing the adsorption isotherm. Among the three adsorption isotherms mentioned, the Langmuir adsorption isotherm is acknowledged to be the most extensively employed isotherm for solute adsorption from liquid solution. In this regard, all the adsorbents' active sites on the surface contain the same adsorbate affinity since no further adsorption occurs at one site once a dye compound has occupied that site (Shirmardi et al., 2013). As a result, this isotherm is an empirical model that assumes monolayer adsorption. Even on adjacent sites between the adsorbates, the lateral interaction and steric hindrance are absent (Al-Ghouti and Da'ana, 2020). Next, the Freundlich isotherm is associated with heterogeneous adsorbent surfaces, where the surface of the adsorbents contains a variety of functional groups. Heterogeneity may result from a variety of interactions between the adsorbate and adsorbent (Shirmardi et al., 2013). This isotherm applies to monolayer and also multilayer adsorption. Moreover, it is suitable to describe the non-ideal and reversible adsorption process (Adamson and Gast, 1997). Next, the Temkin adsorption isotherm postulates that the increase in coverage will decrease the heat adsorption of molecules (Shirmardi et al., 2013). Table 2.2 shows the equations in linear form and parameters for the Langmuir, Freundlich and Temkin adsorption isotherms, respectively.

Table 2.2 Adsorption isotherm models description (Shirmardi et al., 2013)

Isotherm	**Equation**	**Parameter**
Langmuir	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k_l q_m C_e}$	C_e = equilibrium concentration of dye in solution (mg/L) q_e = quantity of dye adsorbed per unit mass of adsorbent (mg/g) k_l = Langmuir constant (L/mg) q_m = theoretical saturation capacity of monolayer (mg/g)
Freundlich	$\ln(q_e) = \ln(k_f) + \frac{1}{n}\ln(C_e)$	q_e = quantity of dye adsorbed per unit mass of adsorbent (mg/g) k_f = Freundlich constant correspond to adsorption capacity of adsorbent (mg/g(L/mg)$^{1/n}$) n = Freundlich constant corresponds to adsorption intensity of adsorbent C_e = equilibrium concentration of dye in solution (mg/L)
Temkin	$q_e = B\ln(k_t) + B\ln(C_e)$	q_e = quantity of dye adsorbed per unit mass of adsorbent (mg/g)

	$B = \frac{RT}{B_t}$ is a constant (J/mol) where R is the universal gas constant (8.31 J/mol·K), and T is the absolute temperature (K) k_t = equilibrium binding constant (L/mg) corresponds to the maximum binding energy C_e = equilibrium concentration of dye in solution (mg/L) B_t and k_t are obtained from the intercept and slope of the plots of q_e against $\ln(C_e)$

2.4.4 Adsorption Kinetics

A quantification technique to characterise adsorption rate is called adsorption kinetics (Shah et al., 2021). Typically, it assesses the adsorption uptake concerning contact duration while maintaining a constant concentration and pressure. To evaluate the adsorption dynamics, there are two frequently employed kinetic models, namely pseudo-first order (PFO) and pseudo-second order (PSO).

PFO kinetic model proposed by Lagergren assumed that the adsorbate uptake rate is directly proportional to the concentration difference. The rate expression is shown as in Equation (2.1) (Lagergren, 1898).

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

Integration of the differential equation with respect to time forms in Equation (2.2).

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \qquad (2.2)$$

Therefore, Equation (2.3), the linearised equation is formed as shown.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2.3}$$

where,

q_t = amount of adsorbate adsorbed at time instant t (mg/g)

q_e = amount of adsorbate adsorbed at equilibrium (mg/g)

k_1 = rate constant of PFO kinetics (min^{-1})

t = contact time (min).

PSO kinetic model or Ho's model considered the rate-determining step or rate-limiting step to be the chemical reaction between the adsorbent and adsorbate. As a result, this model is frequently used to describe chemisorption. The model can be used to forecast the behaviour of the entire adsorption process depending on adsorption capacity. Equation (2.4) below is the rate equation (Ho and McKay, 1999).

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2.4}$$

Integration of the differential equation with respect to time forms Equation (2.5).

$$1_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{2.5}$$

Therefore, Equation (2.6), the linearised expression is formed as shown.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2.6}$$

where,

q_t = amount of adsorbate adsorbed at time instant t (mg/g)

q_e = amount of adsorbate adsorbed at equilibrium (mg/g)

k_2 = rate constant of PSO kinetics (g/mg min)

t = contact time (min).

CHAPTER 3

MATERIALS AND METHODS

3.1 Research Procedure

The research is conducted in accordance with the flowchart as shown in the Figure 3.1.

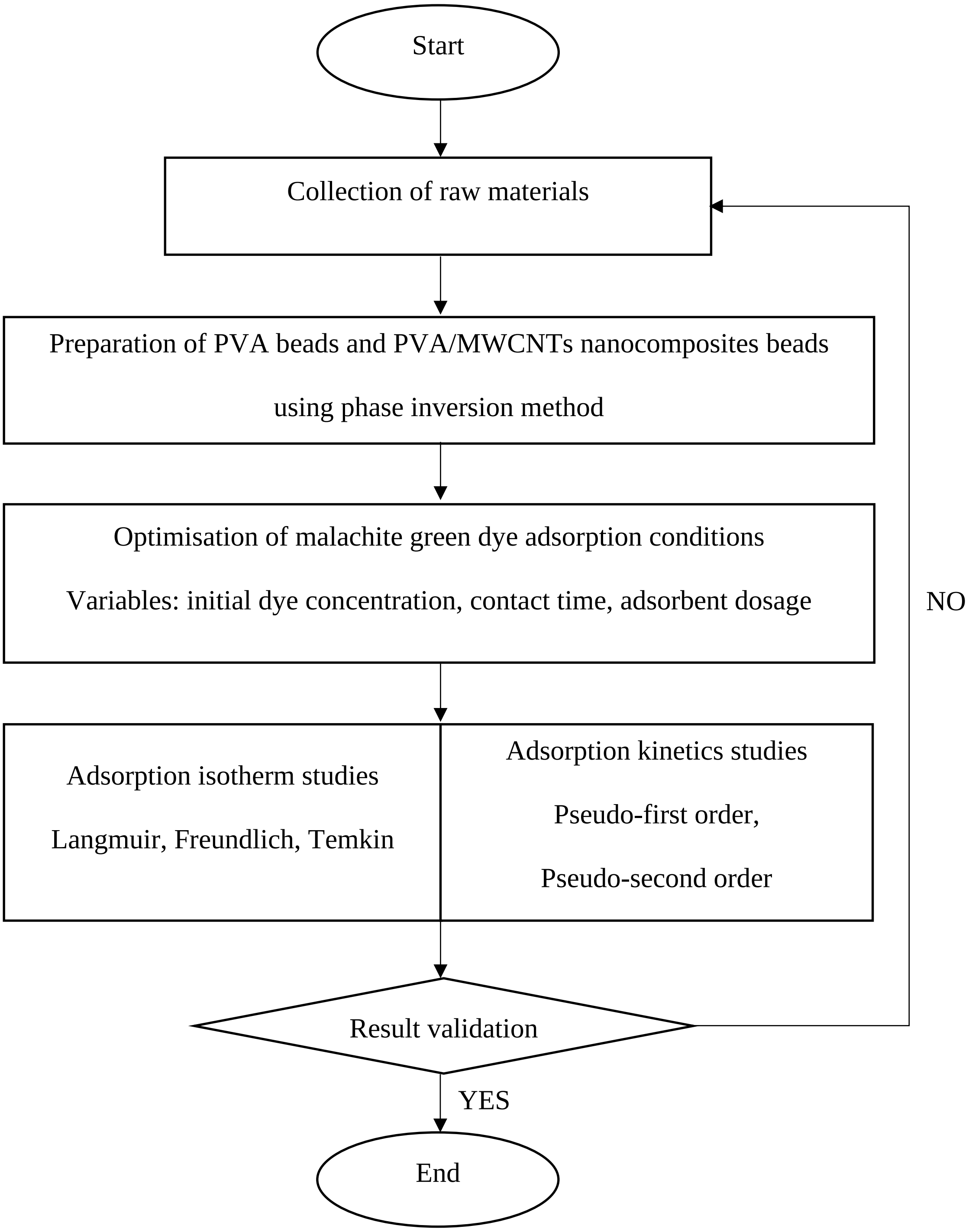


Figure 3.1 Schematic diagram of the whole experimental procedures

3.2 Material

The MG dyes were supplied by Sigma-Aldrich (M) Sdn. Bhd., Malaysia. They were used as received without further purification. The MG chemical formula, maximum adsorption wavelength λ_{max} and molecular weight are $C_{23}H_{26}N_2O\cdot HCl$, 618 nm and382.93 g/mol. A preweighed amount of dyes were dissolved in deionised water to a specific concentration to create stock dye solutions. The adsorbents used were PVA and PVA/MWCNTs composites. The PVA powder is of molecular weight of 85000 to 124000. It is 87% to 89% hydrolysed. Meanwhile, the MWCNTs powder was prepared in the lab via the chemical vapour deposition method. The purity of MWCNTs is more than 95%. Besides, acetone is used as the non-solvent for PVA, which leads to beads formation. Throughout the study, deionised water prepared in the lab was used. Table 3.1, Table 3.2, Table 3.3, Table 3.4 and Table 3.5 show the properties of MG, PVA, MWCNT, acetone and deionised water, respectively.

Table 3.1 Properties of malachite green (Sigma-Aldrich, 2018)

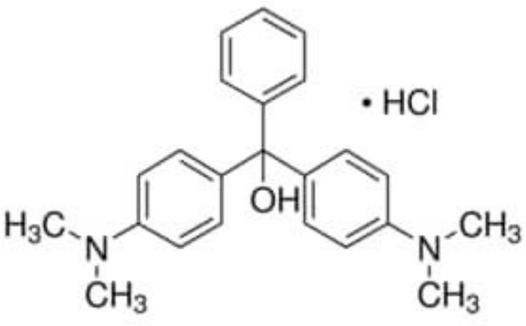
Property	Description	Supplier
Chemical name	4-[(4-Dimethylaminophenyl(-phenyl-methyl)-N,N-dimethyl-aniline	Sigma-Aldrich (M) Sdn. Bhd. 
Common name	Malachite green hydrochloride	
Generic name	Basic green 4	
CAS number	123333-61-9	
Colour index number	42000	
Ionisation	Basic	
Maximum wavelength	618 nm	
Empirical formula	$C_{23}H_{26}N_2O\cdot HCl$	
Molecular weight	382.93 g/mol	
Chemical structure		

Table 3.2 Properties of PVA (Thermo Scientific, 2022)

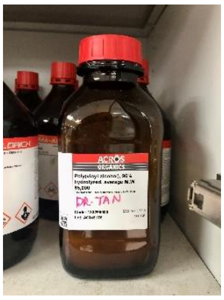
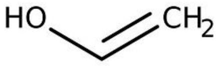
Property	Description	Supplier
Chemical name	Ethenol	Acros Organics
Common name	Polyvinyl alcohol, 96% hydrolysed	
CAS number	9002-89-5	
Maximum wavelength	618 nm	
Empirical formula	C_2H_4O	
Molecular weight	95000	
Chemical structure		

Table 3.3 Properties of MWCNTs

Property	Description	Supplier
Chemical name	Multiwalled carbon nanotube	Prepared in lab through chemical vapour deposition Method 
Linear formula	C	
Purity	>95%	

Table 3.4 Properties of acetone (Modern-Lab Chemicals, 2022)

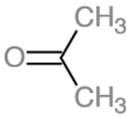
Property	Description	Supplier
Chemical name	Propanone or dimethyl ketone	Modern-Lab Chemicals Sdn. Bhd.
Common name	Acetone	
Grade	Analytical reagents (AR)	
CAS number	67-64-1	
Empirical formula	C_3H_6O	
Molecular weight	58.08	
Assay	>99.8%	
Chemical structure		

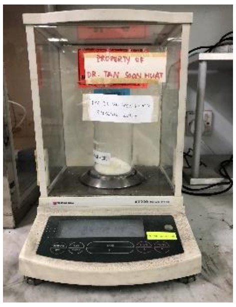
Table 3.5 Properties of deionised water

Property	Description	Supplier
Chemical name	DI water	Prepared in lab
Common name	Deionised water	
Empirical formula	H_2O	

3.3 Equipment

Several equipment was used in this study for the materials' preparation and data collection. Table 3.6 shows the respective list of equipment.

Table 3.6 List of equipment

Equipment	Model	Purpose
Electronic balance	Shimadzu AY220 	To measure weight of PVA, MWCNT and dye
Magnetic stirrer	IKA® C-MAG HS 7 	To prepare PVA solution
Bath sonicator	Branson 3800 Ultrasonic 	To disperse MWCNTs into PVA solution
Tip sonicator	Hielscher UP200S Ultrasonic 	To disperse MWCNTs into PVA solution
Double-beam UV-visible spectrometer	Shimadzu UV-1800, Japan 	To measure adsorbance of dye solution

3.4 Preparation of PVA Beads and PVA/MWCNTs Nanocomposite Beads

The round-bottom flask containing the PVA and water mixture was immersed in an oil bath, and the suspension was stirred with the assistance of a mechanical stirrer at a temperature of 80 ℃ for 4 h to form a homogeneous 8 wt% PVA solution, as demonstrated in Figure 3.2. Later, the solution was then stirred overnight. To prepare pure PVA beads, the PVA solution was added dropwise into a precipitation bath containing acetone solution as the non-solvent reagent, as shown in Figure 3.5. On the other hand, for PVA/MWCNT nanocomposite, 1 wt% of MWCNTs was added to the PVA solution and ultrasonicated via the Ultrasonic Bath Sonicator for 30 minutes as visualised in Figure 3.3. Then followed by the tip sonication at a cycle of 0.5 and amplitude of 60% for another 30 minutes, as pictured in Figure 3.4. Thus, a homogeneously dispersed PVA/MWCNT suspension is attained. After that, a similar procedure as the preparation of pure PVA beads was carried out to produce the PVA/MWCNT nanocomposite beads. Finally, the pure PVA beads and PVA/MWCNT nanocomposite beads were left to be dried at room temperature.

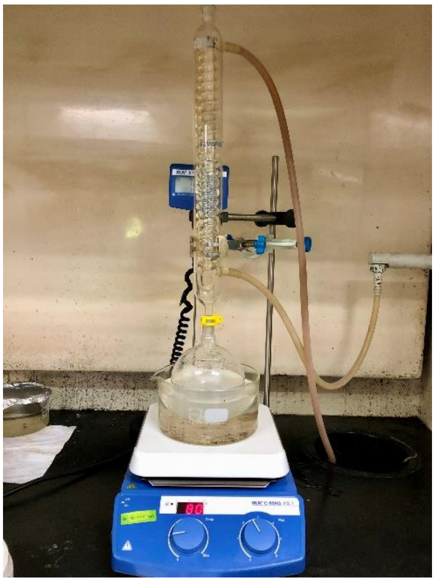


Figure 3.2 Preparation of PVA solution using magnetic stirrer

Figure 3.3 Dispersion of MWCNT in PVA solution using ultrasonic bath sonicator

Figure 3.4 Further dispersion of MWCNT in PVA solution using tip sonicator

Figure 3.5 Formation of beads with the addition of acetone as non-solvent of PVA