REMOVAL OF SYNTHETIC METHYL ORANGE DYE AT NEUTRAL pH BY NR-*b*-PVP/Ag USING PHOTODEGRADATION TECHNIQUE

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By

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I hereby declare that all corrections and comments made by the supervisor(s) and examiner have been taken into consideration and rectified accordingly.

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ABSTRAK

Buangan air sisa dari industri tekstil perlu dirawat sebelum dilepaskan ke dalam alam sekitar kerana air kumbahan ini mengandungi kandungan toksik yang tinggi dan boleh membawa kepada pencemaran air yang serius. Model rawatan air sisa kos rendah yang mesra alam, telah dihasilkan untuk menyelesaikan masalah ini. Filem NR-b-PVP/Ag yang dihasilkan daripada campuran getah asli dengan polyvinylpyrrolidone (PVP) yang digabungkan dengan zarah perak dilapisi di atas permukaan kaca untuk menurunkan pewarna metil oren (MO) melalui cara fotodegradasi pada pH 7. Proses fotodegradasi dijalankan di bawah cahaya matahari selama 2 jam dan 2 mL sampel diambil untuk menganalisis kapasiti penyerapan pada panjang gelombang puncak untuk MO, 463 nm, melalui Spectrophotometer UV-Vis pada setiap 20 minit. Tesis ini menekankan kesan persediaan kaedah kaca, kesan kepekatan perak nitrat ($AgNO_3$) dan kesan kelajuan aliran larutan MO. Degradasi tertinggi untuk 5 liter larutan MO yang dicapai dalam kajian ini adalah 86.6% apabila teknik Gabungan Kaca, 0.3 kepekatan $AgNO_3$ dan 400 mL/min digunakan.

ABSTRACT

Effluent of wastewater from textile industries need to be treated before discharge into environment as this wastewater contains high toxicity which can lead to serious water pollution. Environmentally friendly, low cost dye wastewater treatment model have been produced in order to solve this issue. NR-b-PVP/Ag film prepared from blends of natural rubber latex with polyvinylpyrrolidone incorporated with silver particle was coated onto the surface of the glass to degrade methyl orange (MO) dye via photodegradation at neutral pH. The process of photodegradation was conducted under the sunlight for 2 hours and 2 mL of sample was taken to analyse the absorbance capacity at peak wavelength of MO, 463 nm, via UV-Vis Spectrophotometer for every 20 minutes. This thesis emphasizes the effect of method setup of the glass, effect of silver nitrate ($AgNO_3$) concentration and effect of flowrate of the MO solution. The highest degradation of 5 Liters of MO solution achieved in this study was 86.6% when Glass Combine method, 0.3 g/mol of $AgNO_3$ with 400 mL/min was applied.

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LIST OF ABBREVIATIONS

Ag	**S**ilver
AgNPs	**S**ilver **N**ano **P**articles
AO7	**A**cid **O**range **7**
CR	**C**ongo **R**ed
FTIR	**F**ourier **T**ransform **I**nfra-**R**ed
MB	**M**ethylene **B**lue
MO	**M**ethyl **O**range
NR	**N**atural **R**ubber
PA	**P**oly-**A**crylamide
PVA	**P**oly-**V**inyl-**A**lcohol
PVP	**P**oly-**V**inyl-**P**yrrolidone
RBBR	**R**emazol **B**rilliant **B**lue **R**
RO16	**R**eactive **O**range **16**
RR2	**R**eactive **R**ed **2**
UV	**U**ltra **V**iolet

NOMENCLATURES

$AgNO_3$	**S**ilver Nitrate
H_2O	Water
O_2	Oxygen
OH	Hydroxyl Oxide
SiO_2	Silica Dioxide
TiO_2	Titanium Dioxide
ZnO	Zinc Oxide

CHAPTER 1

INTRODUCTION

1.1 Background

Colour is the main attraction in fabric and due to this factor, the use of synthetic dyes for fabric dyeing has therefore become a massive industry today (Rita, 2012). Large amount of dyes not only being used in the textile industry but also contribute to cosmetic, paper, leather, pharmaceutical and nutrition industries (Khataee and Kasiri, 2010). Approximately about 10 000 tons of dyes are produced per year (Sauro and Jiri, 2013). The huge amount of dyes used in the industry has usually cause environmental problem in form of coloured wastewater discharge into water bodies (Zhao et al., 2011).

Textile industries utilize and consume large amount of water during processing of dyes and generate substantial amount of wastewater. About 10-15% of dyes are lost in the wastewater during the dyeing process. This coloured dye wastewater surely can cause severe pollution effect on aquatic life (Sathian et al., 2013).

Basically, dyes can be divided into three different categories which are cationic, anionic and also non-ionic dyes. These different dyes have different function and application. For cationic dyes are known as basic dyes while anionic dyes include direct, acidic and reactive dyes (Asgher, 2012). The main difference between cationic dyes and anionic dyes are their charges. The positively charge of cationic dyes are water soluble while anionic dyes carry negative charge in their molecule (Salleh et al., 2011).

The most common of anionic dyes are Methyl Orange (MO). This type of dye is usually for dying cotton, wood and silk and considered as hazardous chemical because it contains highly toxic due to large number of metal complex dye (Nasuha et al., 2011). Hence, in this study, MO was chosen as a model of anionic dye to investigate the degradation capacity by Natural Rubber blended with Polyvinylpyrrolidone incorporated with silver (NR-b-PVP/Ag) under different experimental conditions.

1.2 Problem Statement

The discharge effluent of dyes into water bodies can cause serious water pollution problems. Dyes are causing problem not only because of their colour, but also because of their harmful breakdown products which are toxic, carcinogenic and other aromatic compound that can affect the aquatic life (Zaharia and Suteu, 2012).

Other than that, the effluent contained with dyes is full of organic chemical. The examples of the chemicals are sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals which make the effluent highly toxic. Other harmful chemicals present in the water may be formaldehyde based dye fixing agents, hydro carbon based softeners and nonbio degradable dyeing chemicals (Sacco et al., 2012)

The presence of natural chemicals also increases the temperature of the effluent (Rita 2012). The colloidal matter present along with colors increases the turbidity and gives the water a bad appearance and foul smell. It prevents the penetration of sunlight necessary for the process of photosynthesis (Bhakya et al., 2015). Therefore, the treatment of effluent contained dyes is an important issue and effective treatment is needed.

Wastewater contained can be treated or removed in three different group of methods which are physical, chemical and biological. Physical and chemical methods include adsorption, chemical precipitation, flocculation, photolysis, chemical oxidation and reduction while biological method include anaerobic, aerobic and bioremediation technologies (Sathian et al., 2013).

However, there are numbers of methods are not suitable due to the cost is too expensive and cannot degrade the dyes fully. Therefore, many researches have been conducted too investigate the most suitable and effective treatment that can be used to remove dyes from wastewater (Bhakya et al., 2015).

1.3 Objectives

This study is conducted with the following objectives:

a) To determine the effectiveness of photodegradation physical model to degrade Methyl Orange dye

b) To obtain the optimum method of model setup, concentration of silver nitrate ($AgNo_3$) and suitable flowrate to remove Methyl Orange dyes at neutral pH

1.4 Scope of Study

This study focused on investigating the optimum adsorption conditions for the methyl orange dye removal at neutral pH. The method used for this study is photodegradation technique which apply a lower cost, renewable, biodegradable and easy to operate. The adsorbent and photocatalyst material which are natural rubber blended (NR) blended with polyvinylpyrrolidone (PVP) and silver (Ag) nanoparticles are the main focus in this study. In addition, this study also is concentrated onto finding the optimum condition for the adsorption and degradation of MO in terms of agitation time and the amount of silver nitrate ($AgNO_3$).

1.5 Benefits of Study for Civil Engineering

Dyes contains high toxicity thus the removal of dyes before discharge into water bodies is essential. The chemical and physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultrafiltration can be used for colour removal from textile effluents. However, these techniques are non-destructive, since they only transfer the non-biodegradable matter into sludge, giving rise to new type of pollution, which needs further treatment. Photodegradation method has emerged important destructive technology that can lead to total mineralization of most organic pollutant including organic dyes (Kansal, 2007).

Besides, degradation of dye at neutral pH also had never been conducted yet. Therefore, this study can be the starting point and pioneer to the removal of dye at neutral pH. Besides, this method does not require any additional chemical and can operate at near room temperature thus, the process of this method is not complex and easy to conduct (Rajesh et al., 2007). Therefore, by conducting this study, a new method for dye treatment which is more effective, green and sustainable can be developed.

CHAPTER 2

LITERATURE REVIEW

2.1 Classification of Dyes

Dyes can be classified based of fiber type. For example, there are dyes for nylon, dyes for cotton and dyes for polyester. Classify through type of fiber attachment mechanism is one of the way to categorised type of dyes. This is because fifferent types of dyes have different types of fiber attachment mechanism. Basic dyes are attached to fiber by ionic bond while reactive dyes are attached by covalent bond (Akbari et al., 2002). Dyes also can be classified by their method of application to the substrate. This category includes acid, basic, direct dyes, reactive dyes, vat dyes, disperse dyes and azoic dyes (Zhai et al., 2017). For example, all types of

The most favuor method among the researchers to classify dyes is through determination of their particle charge which are cationic (all basic dyes), anionic (direct, acid and reactive dyes) and lastly non-ionic (disperse dyes) (Mustafa et al., 2014). Basic dyes which are cationic charge are water soluble. This type of dye is usually being applied to acrylic fibers and also can be used for a purpose of colouration of paper. Acid dye on the other possess anionic charge, water insoluble and typically being applied wool, nylon and also leather. Non-ionic dye is known as disperse dyes as it is normally appeared in dispersion in water. This dye shows no charge due to the groups presented in the dye molecules (Rafatullah et al., 2010).

2.2 Methyl Orange Dye

Methyl Orange (MO) is a water soluble anionic type of dye. The molecular formula for this type of dye is $C_{14}H_{14}N_3NaO_3S$. MO dye belongs to the azo dyes. Azo dyes are characterized by presence of one or more azo groups substituted with aromatic amines. A substituent often found in azo dyes is the sulfonic acid group. Record stated that more than 50% azo dyes are used annually due to simple diazotization reaction mechanism for the production (Maulin et al., 2013).

Most of the MO dye are used in the textile, leather, plastic, paper, cosmetics and food industries. This type of azo dye is carcinogenic and water soluble. Therefore, the release of MO directly into the water will release toxic product into the body of the water (Mazumder and Rano, 2018).

Other than that, MO usually functions chemically as pH indicator in the titrations process. It is suitable to be used because of its clear and distinct colour change to yellow. As it changes colour at the pH of a acid, it is usually used in titrations for acids. MO does not have a full spectrum of colour change like universal indicator, but it has a sharper end point. It shows red colour in acidic medium and yellow colour in basic medium (Eumann and Schaeberle, 2016).

MO dye contains stable chain and shows low biodegradability. Therefore, it is difficult to remove MO from aqueous solutions by conventional water treatment method. Total removal of organic substance can be used to remove MO dyes in the water effectively (Fortunate et al., 2016).

2.3 Toxicity Effects of Dyes

Nowadays, the usage of dyes in the textile industry is increasing year by year. The increase usage of dyes has cause severe environmental pollution. The effluent contains dyes has affected aquatic life. This is because, some dyes contained toxic and carcinogenic (Ling-Ling et al., 2009).

Furthermore, wastewater containing dyes is very difficult to treat since the dyes are recalcitrant organic molecules, resistant to aerobic digestion and are stable to light. The presence of dyes even in very low concentration is highly visible and causes damage to the environment as they are toxic to aquatic life (Nasuha et al., 2011).

Dyes also come along with colloidal matter and oily scum which can increase the turbidity of water. As the result, it makes the water a bad appearance and gives unpleasant smell. The subsequent effect of this matter can prevent the penetration of sunlight thus process of photosynthesis which required sunlight could not occur. As a result, no process of oxygen transfer will occur in the water. This situation will affect the aquatic life as there is not enough dissolve oxygen in the water. At the end of the result, algae bloom could occur throughout the times. In addition, when this effluent is allowed to flow in the fields it clogs the pores of the soil resulting in loss of soil productivity. The texture of soil gets hardened and penetration of roots is prevented (Rita, 2012).

Furthermore, basic dyes have high intensity of colours and are greatly visible even in very little concentration. The complex dyes are generally chromium based which is carcinogenic. It also can cause severe damage to human beings such as dysfunction of kidney, reproductive system, liver, brain and central nervous system (Mustafa et al., 2014).

Azo dyes are toxic because of the presence of toxic amines in the effluent. Amines emitted from the azo dyes can be absorbed by the skin and accumulate in the body. These toxic amines also capable of producing allergy on skin contact and being toxic by inhalation. Reactive dyes are water soluble and 5-10% of the dyes go in the dye bath giving highly coloured effluent causing serious troubles in the environment. Reactive dyes that are chemically stable and having little biodegradability are likely to pass through conventional treatment like oxidation process. Therefore, removal of dyes from wastewater is really important to preserve the environment (Venkateswaran et al., 2015).

2.4 Dyes Waste Treatment Studies

Recently, there have been different kinds of ways for removal of dyes in wastewater. These methods are categorised into three groups which are physical, chemical and biological. Physical treatment involved physical approached such as, adsorption, membranes separation and magnetic separation. Chemical treatment involves, electrochemical process, photochemical and photocatalytic oxidation, flocculation and ultrafiltration. Biological treatment process which usually being used are, anaerobic method, aerobic method and combination of aerobic-anaerobic method (Elvis et al., 2015).

The best method for removal of dyes is the one that lead to fully degradation of dyes without the need of secondary or further treatment. If the method can lead to full degradation, it can save time and reduce the pollution to the environment. However, most of the treatment has not meet the full removal of dyes thus need further treatment. This difficult situation has urge the textile industrial to avoid the treatment of dye wastewater treatment before discharging it into water bodies. Therefore, need of treatment which can fully degrade the dyes is important to encourage the treatment of dyes wastewater to save the environment (Kansal,2006).

2.4.1 Photodegradation

Photocatalysis or known as photodegradation is one of the method that has potential to produce fully degradation. This method has many advantages such as lead to complete mineralization of pollutants, use of UV light or solar light, no additional chemical is needed and lastly, operation can be conducted at nearly room temperature (Rajesh et al., 2007). Oxidation process basically occurs in the photodegradation method. The photocatalyst used for this method is the main key for this method to successfully oxidized the organic compound to carbon dioxide, water and inorganic anions (Nyabaro et al., 2013).

The main advantages of photocatalytic degradation compare to conventional methods such as quick oxidation is this method can prevent the formation of polycyclic and other oxidation pollutants. Furthermore, unlike adsorption method, photodegradation method is reusable and contributes much less to toxic waste than adsorbents. Furthermore, photodegradation has the ability to use the solar energy to degrade dyes in sunlight conditions thus make this method relatively cheap (Elvis et al., 2015). In addition, the key advantage of the photodegradation method is its inherent destructive nature. This method also is simple as it does not involve with mass transfer and can be carried out under ambient conditions. With proper handling, this process can lead to complete mineralization of organic carbon without the need of further treatment. Moreover, the main parameter of this method is the semiconductors which is largely available and easy to get (Khataee and Kasiri, 2010).

For the recent years, various semiconductors nanostructures or metal oxide materials such as titanium dioxide (TiO_2), silver nano particles (Ag), zinc oxide (ZnO) and silica dioxide (SiO_2). The mechanism behind the process of the photodegradation is depend on the availability of the hydroxyl radical (OH). Generally, there are five essential key steps in the heterogenous photocatalysis on the surface of this semiconductors. The five key steps are, (1) photoexcitation (light absorption and charge carriers generation), (2) diffusion, (3) trapping, (4) recombination, and (5) oxidation (Foo and Hameed, 2010). When semiconductor is irradiated with ultraviolet (UV) light, electrons are promoted from the valence band to the conduction band, resulting in the generation of energized "holes" in the former. Free electrons react with the oxygen to form superoxide radical anions (O_2), while energized holes react with water (H_2O) or hydroxyl ion (OH) to form hydroxyl radicals (OH). OH radicals are very strong oxidative species and are able to oxidize almost all organic molecules. These organic intermediates are further oxidized by molecular oxygens and finally mineralized to carbon dioxide and water (Kaushik et al., 2015).

Each of these semiconductors has its own advantages and many studies have been conducted to examine each effectiveness. Titanium dioxide (TiO_2) is one of the most popular semiconductors being used for the photodegradation method. This metal oxide is the most chosen semiconductors is due to its low cost and high stability. Furthermore, this metal is widespread availability and noncorrosive property (Haoran et al., 2015). A study to investigate the capability of photodegradation using TiO_2 to degrade anionic dyes and cationic dyes was conducted by Elvis et al., (2015). In this project, the performance of TiO_2 was evaluated for the photocatalytic degradation under sunlight conditions. The experiments were done in a lightproof chamber with a 92,4% simulation of sunlight. Methylene blue

(MB), a cationic dye was easily degraded compared to MO (MO) and congo red (CR) which are anionic dyes. In addition, Jan and Pavel (2013) conducted an experiment on the capability of photodegradation method using TiO_2 in two different ways of immobilization to decolorize methylene blue (MB) and two other dyes which are remazol brilliant blue R (RBBR) and reactive orange 16 (RO16). The first immobilization was using the polyacrylamide (PA) and the second condition was entrapment in polyvinyl alcohol (PVA). Based on the result, the degradation of three dyes were much faster using the second condition which was entrapment in polyvinyl alcohol (PVA). The time taken to degrade 100% of MB, RBBR and RO16 in this condition was 20, 35 and 38 minutes respectively. In other way, the time taken for fully degradation of MB, RBBR and RO16 by using the polyacrylamide was 60, 75, and 90 minutes respectively.

Juang, Lin and Hsueh (2010) studied removal of binary dyes under UV light photodegradation by using silica dioxide (SiO_2). The photodegradation efficiency of single dye was tried initially. For single dye, the photodegradation rate is faster than binary dye. For binary dye, different ratio concentrations of both dyes were tried, which are, 1:1, 2:1 and 1:2 ratio of Acid Orange 7 (AO7) and Reactive Red 2 (RR2). Zainal, et al. (2005) studied the photodegradation efficiency by SiO_2 in mixture of dyes. Mixture of dyes is usually difficult to undergo photodegradation. Therefore, prolong of irradiation time may needed. Besides that, each of the dye have own characteristics in binary system. Thus, longer time for photodegradation is required. On top of that, authors mentioned when two dyes mixed together, the initial concentration is two times higher than the single dye. So, higher concentration may be another factor to make it difficult to undergo photodegradation.

Another commercial semiconductors and metal oxide that usually being used is zinc oxide (ZnO). The ZnO nanostructures are fascinating material with versatile properties and are used in several fields such as light emitting diodes, photodetectors, chemical and biosensors, energy harvesting devices including solar cells (Ahmad et al., 2014). ZnO usually being used because it has a wide band gap which makes it suitable for short wavelength optoelectronic applications. The high exciton binding energy in ZnO can endure efficient excitonic emission at room temperature. Furthermore, the structure of ZnO possess large specific surface area and provide good surface permeability thus, provides suitable environment for organic pollutants transport and enhances catalytic activity (Khan et al., 2014).

A study to investigate the effectiveness of photodegradation method by using ZnO nanoneedle under UV irradiation to degrade MO dye was conducted by Nirmalaya et al., (2014). In this study, the photocatalytic degradation of MO was performed in a conical flask using as-synthesized ZNNs under UV illumination for 140 mins. At the end of the result showed that a fast decomposition of MO dye was degrade with the rate of 95.4% within 140 minutes. The fast reaction was due to rapid formation of oxygenated radicals via capture of electrons and holes generated in ZNNs by UV irradiation.

2.4.2 Silver (Ag) Nanoparticles as Photocatalyst

Silver nanoparticles have the ability to act as photocatalyst. Silver nanoparticles have attracted researchers because of their distinctive optical, chemical, electronic, mechanical and magnetic properties. These special properties could be ascribed to their large surface area and relatively small sizes. As these nanoparticles having very high surface to volume ratio thus possess large fraction of highly active surface atoms which are exposed to hazardous material. The size, shape and morphology of these nanoparticles determine this fraction of surface atoms, hence improves the catalytic properties in comparison to bulk materials (Kaushik et al., 2015).

Silver also is highlighted to be considered a promising candidate for improving the photoreactivity due to the electron transfer from covalent bond. The electron transfer from photoreactivity of silver also can restrict the recombination of charge carried and enhance the oxidizing power of the catalyst in mineralizing various organic containments. This characteristic has make silver as preferable photocatalyst compare to other semiconductors and metal oxide (Khan et al., 2016). Silver nanoparticles exhibits varied properties like optical and magnetic, electrical conductivity, catalysis, antibacterial activities, DNA sequencing and Raman scattering. Diverse methods are developed for silver nanoparticles synthesis including chemical, thermal, decomposition and biological. Each method comes along with advantages and disadvantages (Gracias et al., 2002).

Selvam and Sivakumar (2015) have investigated the effectiveness of silver nanoparticles synthesized from Hypnea musciformis to degrade MO dye. In this study, red alga Hypnea musciformis has been used to synthesized 50 ml of silver nitrate ($AgNO_3$) solution into silver nanoparticles. These silver nanoparticles were used to degrade MO dye using photodegradation method. The optical properties of the obtained silver nanoparticles were characterized by applying UV-visible absorption and room temperature photoluminescence. The X-ray diffraction results revealed that the synthesized silver nanoparticles were in the cubic phase. The existence of the functional group was identified using Fourier transform infrared spectroscopy. Photocatalytic degradation of MO was measured spectrophotometrically by using silver as nanocatalyst under visible light illumination. The final results revealed that biosynthesized silver nanoparticles using Hypnea musciformis was found to be impressive in degrading 98% of MO dye within 5 hours.

In addition, a study on the photocatalytic activity of biogenic silver nanoparticles synthesized using potato (Solanum tuberosum) infusion has been conducted by Kaushik et al., (2015). In this study, the synthesizes of silver nanoparticles using potato (Solanum tuberosum) infusion was conducted at the room temperature to degrade MO dye. After addition of potato infusion to silver nitrate ($AgNO_3$) solution, the colour of the mixture change indicating formation of silver nanoparticles. Time dependent UV-Vis spectra were obtained to study the rate of nanoparticle formation with time. Purity and crystallinity of the biogenic silver nanoparticles were examined by X-ray diffraction (XRD). Fourier transform infra-red spectroscopy (FTIR) was employed to detect functional bio-molecules that contribute to the reduction of silver nanoparticles. Sunlight was used as the source of the energy. At the end of the results showed that effective photocatalytic property of these biogenic silver nanoparticles by taking 3 hours of time to fully degrade 50 ml of MO.

Furthermore, Kumari et al., (2016) has investigated the effectiveness of silver nanoparticles biosynthesized using Cordia dichotoma leaf to act as photocatalyst in the process of photodegradation of methylene blue (MB) and congo red (CR) dyes. In this study, the synthesized process was characterized using UV-vis spectroscopy to determine the formation of silver nanoparticles. The synthesizes of silver nanoparticles was observed after 40 minutes as the solution turned from light yellow to brown in colour. The photocatalytic activity of silver nanoparticles was determined using degradation of MB and CR under sunlight for a particular period of time. At the end of the result showed that after 6 hours exposed under the sun, both MB and CR were fully degrading and decolourize.

2.4.3 Adsorption of Dyes by Polyvinylpyrrolidone (PVP)

Adsorption is one of the method for dye wastewater treatment. This method is simple but need a further process to fully degrade the dyes. The combination processes of adsorption and photodegradation can help to improve the degradation of dyes. As such, number of studies have employed polymers such as polyether-sulfone, chitosan, polyacrylonitrile and natural rubber have the ability to adsorb the organic material. These polymers also are important for the immobilization of the photocatalysts as this process allows the photocatalysts to be collected and re-used (Bakar et al., 2017).

Polyvinylpyrrolidone (PVP), commonly called polyvidone is a water-soluble polymer made from the monomer N-vinylpyrrolidone. Dry PVP is a light flaky hygroscopic powder and readily absorbs up to 40% of water by its weight. In solution, it has excellent wetting properties and readily forms films which makes it goo as a coating or an additive to coatings (Mahadevappa et al., 2014). PVP is used in as a binder and complexation agent in agro applications such as crop protection, seed treatment and coating (Joly and Manas, 2013).

Sema et al., (2003) has investigated the adsorption capacity of crosslinked polyvinylpyrrolidone (CPVP) for some textile dyes which are Indigosol Blau IBC, Iyozol Turkish G and Remazol Brilliant Orange 3R. In this study, adsorption of these textiles onto

CPVP was studied by batch adsorption technique at 25ºC. The adsorption isotherms obtained ere L-type (Langmuir type) according to the Giles classification system. Adsorption studies indicated that monolayer coverage of the CPVP by the dyes studied increased in the order: Indigosol Blau IBC > Iyozol Turkish G > Remazol Brilliant Orange 3R. The results showed that the removal and adsorption capacity of the dyes by CPVP ranged from 21% to 81%. In addition, Ukuser at al., (2012) also investigated the capability of crosslinked polyvinylpyrrolidone nanocomposites and their adsorption kinetics on cationic dye methylene blue (MB). In this study, nanocomposites of CPVP was chosen to analyze the adsorption properties. For this purpose, nanofiller sodium montmorillonite with two types of cation exchange capacity values of 92.6 and 145 meq/100 g ere used and modified into organoclay. Monomer, initiator and crosslinker with organoclay in the specificied reaction conditions were mixed together and purified to prepare CPVP. The synthesized samples were structurally identified by performing FTIR, DSC and TGA. The results revealed that the adsorption capacity of MB was increasing with the increasing of temperature, Increasing of MB concentration and decreased with the increasing amount of adsorbent.

PVP was also used as for the synthesized of metal particles such as silvernanoparticles (AgNPs). Jolly and Manas, (2014) has compared the efficient adsorption of congo red dye from aqueous solution using green synthesized silver nanoparticles and gold particles coated with activated carbon. In this study the silver nanoparticles supported by PVP were synthesized by using microwave irradiation method. The effect of various process parameters has been investigated by following the adsorption technique. Equilibrium adsorption data of congo red wre carried out at room temperature. The adsorption data were analyzed by using isotherm studies. The characteristic parameters for isotherm and related correlation coefficients were determined form graphs of their linear equations. Kinetic studies showed that the adsorption of congo red followed pseudo-first-order. The adsorption of congo red dyes by silver nanoparticles supported by PVP and gold particles coated with activated carbon were 88% and 82 % respectively.

Besides PVP, other polymers such as chitosan has been used as an adsorbent of dyes. A study on the effectiveness and the ability of chitosan (natural biosorbent material) for the adsorption of MO had been conducted by Zhai eta al., (2017). Chitosan is the second most abundant polysaccharide in nature after cellulose and it is the only basic polysaccharide in nature. The advantages of using chitosan for the adsorption of dyes compares to other adsorbents are because, it is non-toxic, bio-compatible, biodegradable and low cost. Chitosan is a type of natural polyaminosaccharide which has one primary amino and two free hydroxyl groups. In this study, chitosan microspheres with high mechanical strength were synthesized by microfluidic technology combining chemical crosslinking abd used as an adsorbent for MO. Experimental results revealed that adsorption capacity by the chitosan reached to 207 mg/g and mechanical strength was suitable to resist force. In addition, the adsorption isotherm was well fitted with Langmuir model and the adsorption kinetic was best described by the pseudo-second-order kinetic model.

2.4.4 Other Treatment Method

As mention before, there are several ways that can be used for the removal of dyes in wastewater systems. Examples of popular treatments are electrochemical, coagulation and flocculation, biodegradation, precipitation, reverse osmosis and air stripping.

The electrochemical treatment of wastewater was studied by Balakrishan et al., (2011). From this study, it discovered that almost 92% of COD and 95% of dye can be removed with the help of biological treatment as an advanced treatment. The best bacterium for reduction of colour and COD was Pseudomonas putida. Electrochemical processes generally have lower temperature requirement than other equivalent non-electrochemical treatments and there is no need for additional chemicals.

A review on coagulation and flocculation method as economical dye treatment process was conducted by Verma et al., (2011). Based on the review, pre-hydrolysed coagulants such as Polyaluminium chloride (PACl), Polyaluminium ferric chloride (PAFCl), Polyferrous sulphate (PFS) and Polyferric chloride (PFCl) have been found to be more effective and suggested for decolourisation of the textile wastewater. Moreover, due to some novel properties of natural coagulants such as non-toxic, biodegradability, environment friendly and ability to encapsulate, these may also be considered as the promising coagulants as well as coagulant aids for textile wastewater treatment specially at first stage.

A study conducted by Maris et al., (2015) on anaerobic biofilm process which categorised in biological treatment to treat and removal dye in wastewater system. In this study, anaerobic was chosen because of efficient in color removal, has lower nutrients requirements than the conventional activated sludge process, which is desirable since textile wastewater is characterized by a low content of nitrogen and phosphorous. From this study, this method has potential to remove and degrade organic compound and remove toxicity from textile effluents. However, it needs additional process which is advanced oxidation.

2.5 Summary

This chapter has presented a study on the classification of dyes and its hazard to the environment. Other than that, this chapter also highlight about the photodegradation technique, the capability of silver particle as photocatalyst, adsorption of dyes by PVP and other methods of dye removal from wastewater effluent from other researchers. Next chapter will be discussed on the method and procedure of experimental work, characterization techniques and the materials to be used in the experiment.

CHAPTER 3

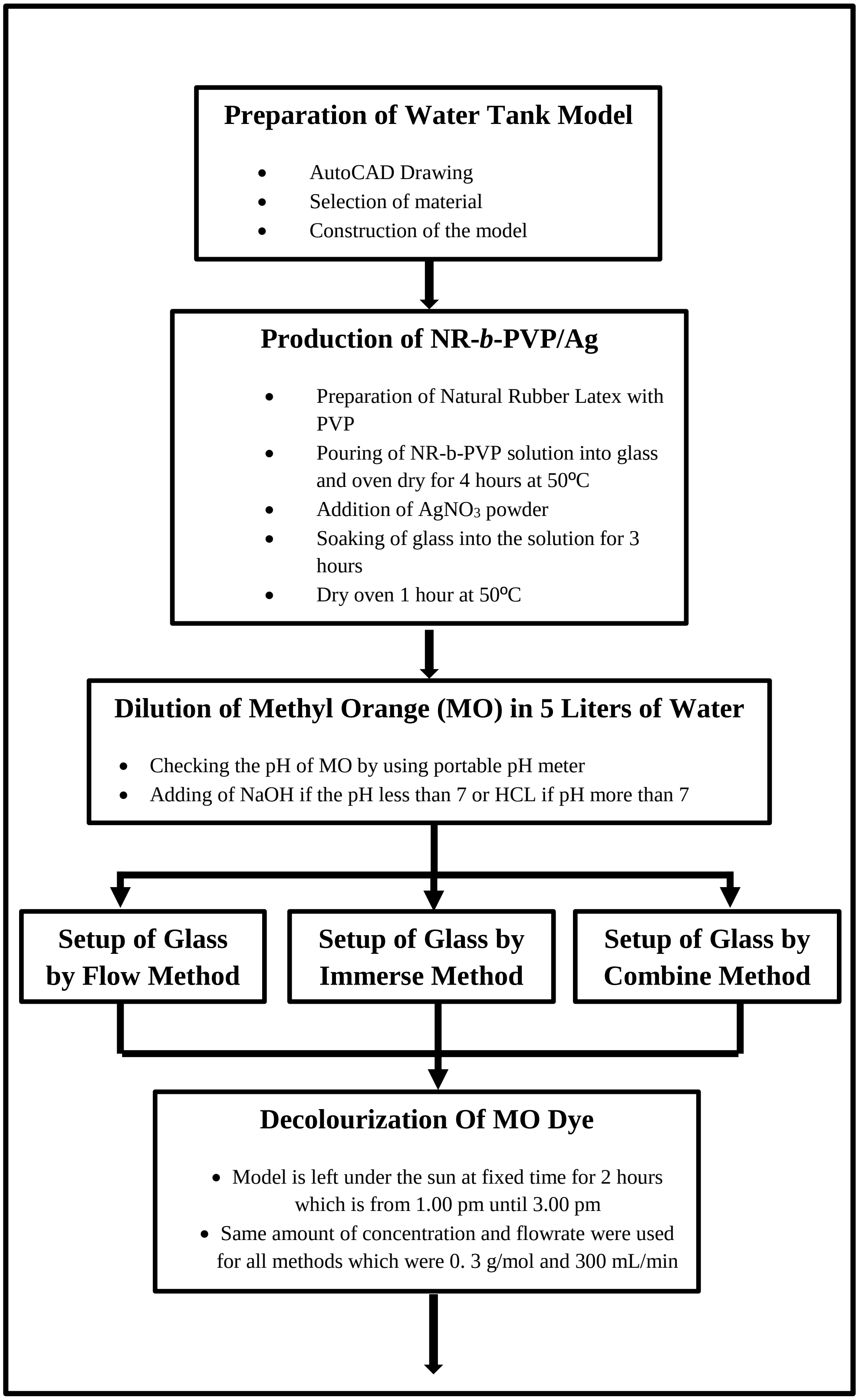
METHODOLOGY

3.1 Overview

This chapter describes the method on how to achieve the objectives stated in Chapter 1. The initial work for this experiment is to make sure the materials to be used have been prepared and the experimental procedure of all laboratory analyses were conducted in this study for the photodegradation of MO dye by NR-b-PVP incorporated with Ag in water treatment tank will be discussed further. The flow chart of this study is shown in Figure 3.1.

3.2 Experimental Works

This study was conducted at two separated locations. The first place was in the laboratory of School of Chemical Science (PPSK) USM Main Campus, Gelugor, Penang and the second place were in the Hydraulic and Environment Laboratory of School of Civil Engineering (PPKA) USM Engineering Campus, Nibong Tebal, Penang, Malaysia. The early sample of NR-b-PVP/Ag was prepared in PPSK while the analysing of the reactions and tests were conducted in PPKA.


Preparation of Water Tank Model
AutoCAD Drawing
Selection of material
Construction of the model
Production of NR-*b*-PVP/Ag
Preparation of Natural Rubber Latex with PVP
Pouring of NR-b-PVP solution into glass and oven dry for 4 hours at 50ºC
Addition of $AgNO_3$ powder
Soaking of glass into the solution for 3 hours
Dry oven 1 hour at 50ºC
Dilution of Methyl Orange (MO) in 5 Liters of Water
Checking the pH of MO by using portable pH meter
Adding of NaOH if the pH less than 7 or HCL if pH more than 7
Setup of Glass by Flow Method
Setup of Glass by Immerse Method
Setup of Glass by Combine Method
Decolourization Of MO Dye
Model is left under the sun at fixed time for 2 hours which is from 1.00 pm until 3.00 pm
Same amount of concentration and flowrate were used for all methods which were 0. 3 g/mol and 300 mL/min

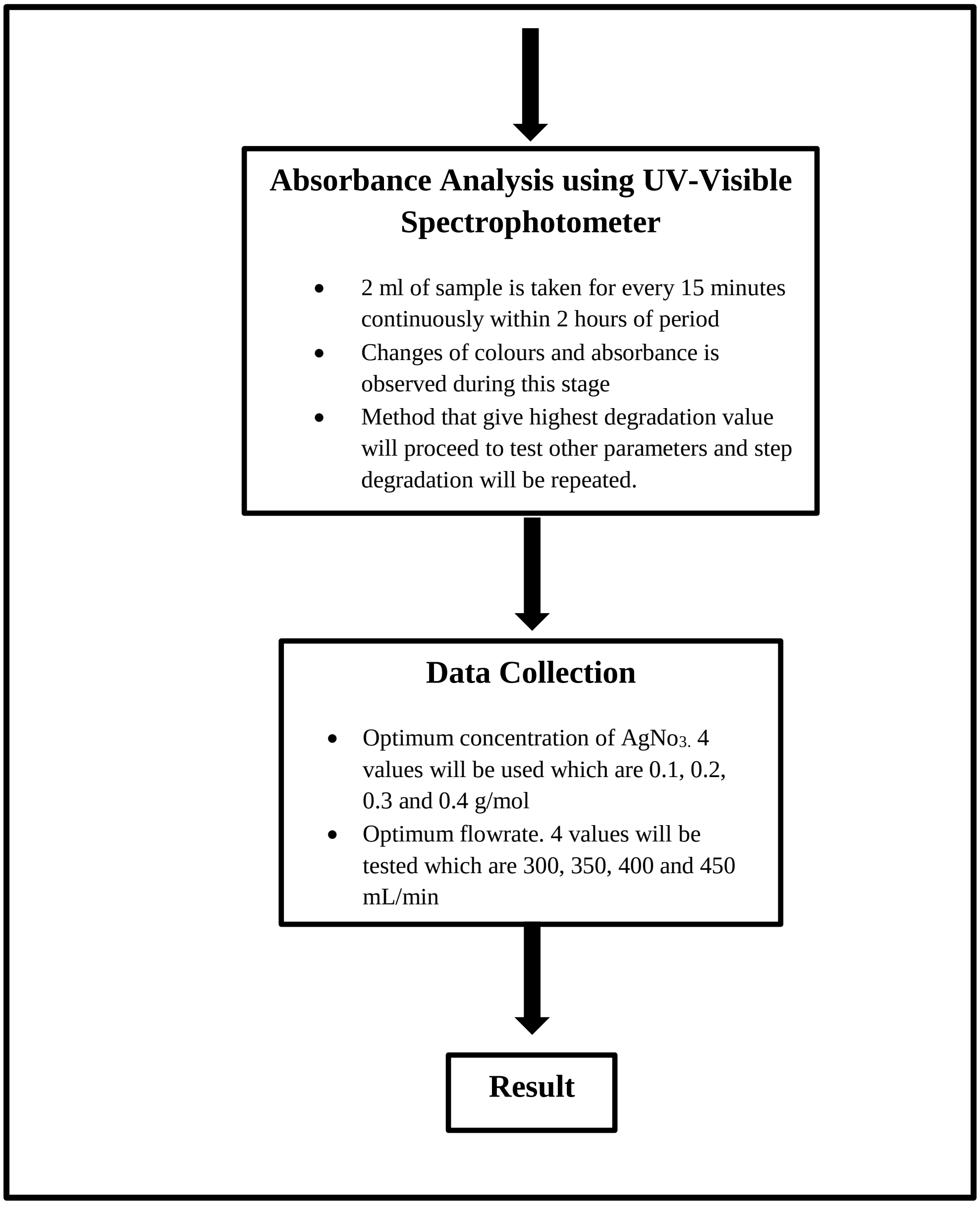


Figure 3.1: Flow Chart of Study

3.3 Materials

The main materials used in this study were methyl orange (MO), natural rubber (NR) latex, polyvinylpyrrolidone (PVP) and $AgNO_3$. The NR latex as shown in Figure 3.2 was supplied by the Rubber Research Institute of Kuala Lumpur. On other hand, both of MO and $AgNO_3$ as shown in Figure 3.4 and 3.3 (a), were purchased from R&M Chemical. In addition, PVP for the synthesized of silver metal and adsorption of dye as shown in Figure 3.3 (b) was obtained from Sigma-Aldrich.

Figure 3.2: Natural Rubber Latex (NR)