PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE BY USING WO_3/g-C_3N_4 CATALYST UNDER VISIBLE LIGHT

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by

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LIST OF SYMBOLS

SYMBOL	DESCRIPTION	UNIT
C_t	MB concentration at time t	mg/L
C_o	Initial MB concentration	mg/L
CB	Conduction band	-
dC/dt	Derivative of concentration	-
k_{sch}	Scherrer’s constant and equal to 0.9	-
k_{ads}	Adsorption rate constant	mg/L.min
k_{app}	Pseudo-first-order rate constant	min^{-1}
k_d	Desorption rate constant	mg/L.min
K	Adsorption equilibrium rate constant	L/min
R^2	Coefficient of relation	-
r	Reaction rate	mg/L.min
t	Time	-
VB	Valence band	-
mol%	Mol in percent	-
k_{app}	Pseudo-first-order rate constant	min^{-1}

GREEK SYMBOL

λ	Wavelength	nm
θ	Surface coverage	-
α	Alpha	-

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
MB	Methylene blue
SEM	Scanning Electron Microscope
UV-vis	UV-visible spectrophotometer
XRD	X-Ray diffraction

DEGRADASI FOTOMANGKIN TERHADAP METILENA BIRU DENGAN MENGGUNAKAN PEMANGKIN WO_3/g-C_3N_4 DI BAWAH CAHAYA YANG KELIHATAN

ABSTRAK

WO_3/g-C_3N_4 pemangkin ditambah dengan pelbagai beban WO_3 (0.5 - 1.5 mol%) telah berjaya disediakan dengan kaedah pengisitepuan. Sampel yang disediakan dicirikan oleh Pembelayan Sinar X (XRD), pengimbasan mikroskop elektron (SEM), serakan sinar X(EDX), ciri-ciri permukaan dan UV pemantulan spectrum. Dalam kajian ini, hasil XRD menunjukkan bahawa penambahan pemuatan WO_3 dalam penyediaan pemangkin tidak memberikan sebarang puncak yang berbeza berbanding dengan g-C_3N_4 tulen. Ujian fotomangkin membuktikan bahawa pemangkin 1.5 mol% WO_3/g-C_3N_4 memberikan kecekapan penyingkiran tertinggi. Prestasi fotomangkin yang disediakan telah dinilai dengan memantau kemerosotan metilena biru di bawah cahaya yang kelihatan. Tiga pemboleh ubah proses dikaji; kesan berat pemangkin, kesan kepekatan awal metilena biru dan kesan oksigen terlarut. Keadaan optimum diperolehi seperti berikut: berat pemangkin 2.0 g/L, kepekatan awal metilena biru 10 mg/L dan oksigen terlarut 10 cm^3/min. Kinetik untuk degradasi metilena biru juga telah dikaji. Keputusan menunjukkan bahawa kinetik reaksi untuk kajian ini mengikuti kinetik urutan pertama-pseudo dengan k_{app} adalah 0.0057 min^{-1}. Pemangkin menunjukkan ciri-ciri pengulangan kerana ia mempunyai kemerosotan lebih daripada 84% selepas 3 ulangan kitaran.

PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE BY USING WO_3/g-C_3N_4 CATALYST UNDER VISIBLE LIGHT

ABSTRACT

WO_3/g-C_3N_4 catalyst coupled with various WO_3 loadings (0.5 – 1.5 mol%) were successfully prepared by impregnation method. The prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray (EDX), surface characteristics and UV-vis reflectance spectra. In this study, XRD result showed that the addition of WO_3 loading in catalyst preparation did not give any significant peak of WO_3 due to the less amount of WO_3 than g-C_3N_4. Photocatalytic test revealed that 1.5 mol% WO_3/g-C_3N_4 catalyst gave the highest degradation efficiency. The performance of prepared photocatalyst was evaluated by monitoring the degradation of methylene blue under visible light. Three process variables were studied; effect of catalyst loading, effect of initial methylene blue concentration and effect of dissolved oxygen. The optimum conditions obtained as followed: catalyst loading of 2.0 g/L, initial concentration of methylene blue 10 mg/L and dissolved oxygen of 10 cm^3/min. Kinetic for degradation of methylene blue also has been studied. Result showed that the reaction kinetic for this study followed pseudo-first order kinetic with k_{app} was 0.0057 min^{-1}. The catalyst shows repeatability characteristics as it possess higher than 84 % degradation efficiency after 3 cycles.

CHAPTER 1

INTRODUCTION

In recent years, many problems related to water contamination, especially the toxic and coloured dyestuff has been paid close attention in industry (Chowdhury and Balasubramanian, 2014). Water contamination can come from industries that may excrete different waste that have different chemical, physical and biological properties. Industries such as textiles, paint, ink, plastics and cosmetics uses many kinds of artificial composite dye and discharge large amounts of highly coloured wastewater. (Kant, 2012) stated that fabric or textiles industry contributed largest source of water pollution come from dye waste. (Şen and Demirer, 2003) also stated that textile industry consumes a lot of water in its manufacturing processes used mainly in the dyeing and finishing operations of the plants. By considering the volume generated as well as the effluent composition, textile industry can be classified as the most polluting of all the industrial sector. These wastes must be treated prior to discharge in order to comply with the environmental protection laws for the receiving waters. Major pollutants in textile wastewaters are high suspended solids, oxygen consuming matter, heat, colour, acidity and other soluble substances. Even at very low concentration (10-50 mg/L) water-soluble dyes may intensively affect the aquatic organisms and interfere with the transmission of sun beams into streams and, therefore, reduce photosynthetic activity (Çiçek et al., 2007).

Many types and colours of dyes that are sold worldwide makes the procedure to purify it a lot more complex and complicated. Throughout the years, many sorts of purification studies have been carried out which includes both physical and chemical processes such as active carbon sorption, flocculation, electro-coagulation and redox treatment. Each of these mentioned technique possess one common disadvantage which is they produce another side product which also can act as a pollutant.

Biological treatment processes are frequently used to treat textile effluents. These processes are generally efficient for biochemical oxygen demand (BOD) and suspended solids removal (TSS) but they are largely ineffective for removing colour from the waste (Aziz et al., 2007). After biological treatment, treated wastewater effluents still contains significant amount of coloured compounds, microorganisms, recalcitrant organic compounds and suspended solids. One of the challenges to purify a dye is the process of colour removal. To counter this drawbacks, purification method using photocatalysis is introduced.

1.1 ADVANCED OXIDATION PROCESS

Photocatalysis can be applied as it is an attractive yet very challenging process to convert solar energy into chemical energy. The photocatalysis can be used in cleaning polluted water and water splitting to produce hydrogen and consequently store energy as a fuel (Karimi et al., 2010) . A photocatalyst is defined as a substance which is activated by adsorbing a photon and is capable of accelerating a reaction without being consumed. This process is known as advanced oxidation process (AOP) and is suitable for the oxidation of a wide range of organic compounds. AOPs include photocatalysis system like the combination of semiconductor and light, and semiconductor and oxidants (Kansal et al., 2009). Among AOPs, heterogeneous photocatalysis have been proven to be of interest due to its efficiency in degrading recalcitrant organic compounds. Compare to other treatment technologies, photocatalysis can be called as a ‘green method’ for the complete decomposition of organic pollutants in water and air (Goharshadi et al., 2013).

1.2 SEMICONDUCTOR COUPLING

Recently, photocatalysis technique based on semiconductor photocatalyst have been used extensively. Photocatalysis is a process where light and catalyst are concurrently used to support or speed up a chemical reaction. It also can be defined as catalysis driven acceleration of a light induced reaction. Metal semiconductors such as WO_3, TiO_2 and ZnO have been widely utilize as an effective heterogeneous photocatalyst because of a favourable combination of electronic structure, light absorption properties, charge transport characteristics and excited-state lifetimes (Kumar and Rao, 2017). Semiconductors also act as sensitizers for light induced redox processes due to their electronic structure, which is characterized by a filled valence band (VB) and an empty conduction band (CB) which is called the band gap (Hoffmann et al., 1995). There are several advantages using heterogeneous photocatalyst which are complete mineralization, no waste disposal problem, low cost and necessity of mild temperature and pressure condition only.

Instead of using metal semiconductors such as WO_3, TiO_2 and ZnO, g-C_3N_4 can be used as heterogeneous photocatalyst because of interesting properties such as good visible light absorption, graphene-like structure and its band potentials are suitable for water splitting under visible light irradiation. In order to improve stability, visible light utilisation, charge separation and transfer and efficiency of oxidation species, coupling g-C_3N_4 with other semiconductor to form semiconductor/semiconductor heterojunction is the most promising strategies towards synthesising more efficient photocatalysts.

1.3 PROBLEM STATEMENT

Recently, researchers have put extensive efforts to prepare semiconductors for the photocatalytic reaction with acceptable band gap such as metal-containing oxide, sulphide and oxynitride(D. F. Ollis, 1991, Osterloh, 2008). For the design of semiconductor photocatalyst, n-type semiconductors, such as TiO_2, ZnO, Fe_2O_3, and WO_3, have been broadly explored for their use in photocatalytic degradation and photoelectrochemical applications (Karimi-Nazarabad and Goharshadi, 2017).

In recent years, a novel stable metal-free photocatalyst which is polymeric graphitic-like carbon nitride (g-C_3N_4) has attracted interest for its applications in water splitting and photocatalytic decomposition of organic pollutants under visible light. g-C_3N_4 is environmental amicable, inexpensive and it has a band gap of 2.7 eV which can absorb light until 460 nm (Xinchen Wang and Yidong Hou, 2009). g-C_3N_4 exhibits a unique stability, including the heat endurance and chemical resistance. Despite of the advantages, the photocatalytic efficiency of single g-C_3N_4 is limited due to the high recombination of photoexcited electron-hole pairs and very poor response to visible light thus hindered its application in photocatalysis. In order to improve photocatalytic activity of g-C_3N_4 under visible light, several strategies have been implement-such as doping and coupling of g-C_3N_4 with other semiconductor materials (Liying Huang, 2013, Wang et al., 2011, Ge and Han, 2012). Among these methods, semiconductor coupling is one of the effective strategies for separation of photoinduced electron–hole pairs and improvement of photocatalytic activity (Liao et al., 2012).

Tungsten oxide, WO_3 is n-type semiconductor with a small bandgap of 2.6 eV which implies that it has potential applications under visible light in the environment field (Gratzel, 2001). It has unique thermal, optical, physicochemical and electrical properties (Yang et al., 2014). However, there is limitation of WO_3 under visible light due to the drawback that WO_3 has a conduction band edge lying in a position unfavourable for single-electron reduction of O_2, leading a poor photocatalyst for organic degradation under O_2 conditions (Bai et al., 2014). When WO_3 is combined with g-C_3N_4, a g-C_3N_4/WO_3 heterojunction photocatalyst may be formed between WO_3 and g-C_3N_4 and this composite may be a promising candidate for efficient photocatalytic activity under visible light.

1.4 RESEARCH OBJECTIVES

The aim of this research is to develop a photocatalyst with high photocatalytic activity to degrade methylene blue (MB) under visible light irradiation. The specific objectives of this research are:

i) To prepare g-C_3N_4 /WO_3 catalyst via facile impregnation method

ii) To characterize physical and chemical properties g-C_3N_4/WO_3 catalyst

iii) To evaluate the effect of process parameter on the photocatalytic degradation of methylene blue (MB) under visible light.

iv) To determine the kinetic process of photodegradation under optimum condition

CHAPTER 2

LITERATURE REVIEW

This chapter gives overview and background information regarding degradation of methylene blue by using heterogeneous photocatalyst that been used throughout this research.

2.1 ORGANIC DYES

Colorants or can be called dyes are characterized by their ability to absorb or emit light in the visible range of 400 nm to 700 nm. Table 2.1 shows the relationship between wavelength of visible and colour absorbed/observed.

Table 2.1 : Relationships between wavelength of visible and colour absorbed/observed (Gürses et al., 2016)

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

Dyes possess colour because they have at least one chromophore (colour-bearing group), have a conjugated system for example they have alternating double and single bonds and they exhibit resonance of electron which is a stabilizing force in organic compounds. Dyes also contain group known as auxochromes or can be called as colour helpers which can shift the colour of colorants and usually used to influence dye solubility. Example of auxochromes are carboxylic acid, sulfonic acid, amino and hydroxyl groups.

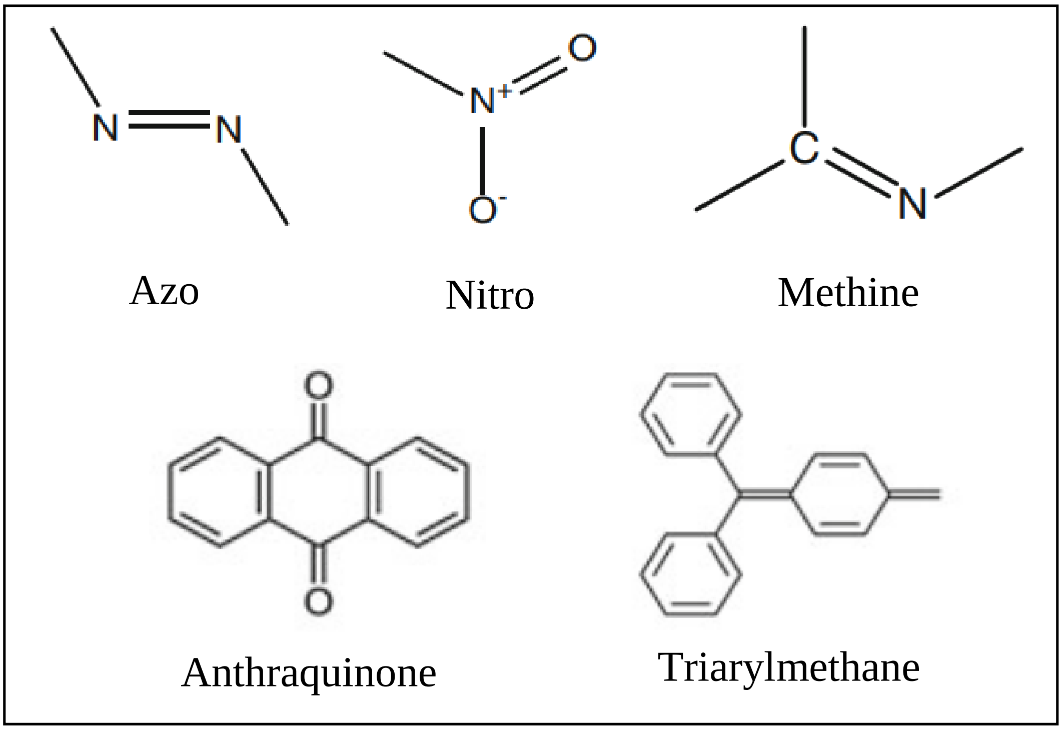
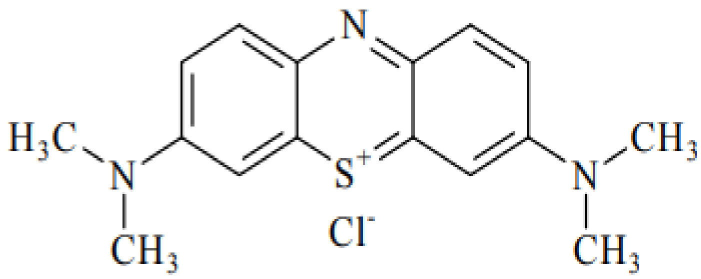


Figure 2.1: Examples of chromophoric groups present in organic dyes (Gürses et al., 2016)

2.1.1 Methylene blue (MB)

Methylene blue (MB) is a basic aniline dye with the molecular formula $C_{16}H_{18}N_3SCl$. MB is slightly odor, stable in air and it is dark green powder that yields a blue solution in water or alcohol. This compound decomposes at 100 to 110 °C. Table 2.2 shows the physical and chemical properties of methylene blue.

Table 2.2: Physical and chemical properties of methylene blue (PubChem, 2013)

Structural formula	
Molecular formula	$C_{16}H_{18}N_3SCl$
Molecular weight	319.851 g/mol
Description	Dark green crystal or crystal-line powder with bronze lustre and able forms double salts
Density	1.0 g/mL at 20°C
Melting point	100-110 °C (decomposition)
Solubility	43.6 g/L in water at 25 °C, soluble in ethanol, slightly soluble in pyridine and insoluble in ethyl ether
Stability	Sensitive to light and stable in air

Methylene blue can be bleached easily and their decomposition is difficult. From Table 2.2, it can be seen that MB is composed of sulphur, nitrogen, carbon, hydrogen, oxygen and chlorine. When MB is dissolved in water to form solution, the main body with positive charge and chloric ion will be produced (Tang et al., 2005).

2.1.2 Methylene blue in surroundings

Methylene blue is example of discharge dye in the environment and may cause major concern due to their adverse effects to many forms of life. MB commonly used substance for colouring paper, temporary hair colorant, dying cotton, wood and silk it is not considered to be toxic dye but it can cause harmful effects to human and animals. MB can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. MB also can give rise to short periods of rapid or difficult breathing on inhalation. Otherwise, ingestion through the mouth produces a burning sensation and may cause nausea, vomiting and mental confusion (Rafatullah et al., 2010).

In environments, methylene blue may inhibit light penetration into water, reduces photosynthetic activity and depletes dissolved oxygen in water as well as producing trihalomethanes during chlorination. This effect may cause serious problem and difficulties to the aquatic organisms (Ahmad et al., 2009). In addition, the availability of colouring substance in water even at low concentration may limit light diffusion and as a result photosynthesis processes of the polluted ecosystem are inhibited (Hajjaji et al., 2006).

2.2 TECHNOLOGIES FOR DYE REMOVAL

Among the pollutants present in water, dyes represent one of the most problematic groups of the pollutant in environment. There are over 100,000 commercially available dyes exist and more than 7×10^5 tonnes per year are generated in the world annually. Due to increase amount of release and their serious potential hazard to aquatic life, it is necessary to eliminate dyes from waste water system before they are discharged into the environment. Wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light. According to Robinson et al. (2001), colour removal technologies can be divided into three main categories which are biological, chemical and physical treatment. Table 2.3 shows different process with different technologies for dye removal.

Biological methods proved to be the most economical compared to physical and chemical treatment. This treatment used different type of microorganisms such as bacteria, yeasts, algae and fungi to accumulate and degrade different pollutants by using biodegradation methods (McMullan et al., 2001). However, biological treatment encounter some drawbacks which are the toxicity of the chemical used, sensitivity toward diurnal variation and also required large land area (Bhattacharyya and Sarma, 2003). Biological treatment unable obtaining satisfactory colour elimination compare to current conventional biodegradation method because some dye degraded but some are not due to their complex chemical structure and synthetic organic origin (Robinson et al., 2001).

Chemical methods consist of several processes such as coagulation or flocculation combined with floatation and filtration, electro-kinetic coagulation, conventional methods (ozone), irradiation and electrochemical processes. This type of method is efficient for waste water treatment contaminated with different pollutants but this method not much used. It is due to high cost because of high electrical demand and large consumption of the chemical reagents and it will create large amount of concentrated sludge that will creates a disposal problem (Kharub, 2011).

For degradation of dye, physical method also can be used such as membrane-filtration processes which includes reverse osmosis, electrodialysis and nano-filtration. However, membrane filtration has some drawback which are the they have limited life time, membrane fouling that will decrease the efficiency and high cost due to periodic replacement. In physical method, they are adsorption which is an equilibrium separation process and it is very effective for water decontamination purposes (Dąbrowski, 2001). Decolourisation of dye occurred in two mechanisms which is adsorption and ion exchange. These two mechanisms is influenced by physio-chemical factors such as dye/sorbent interaction, sorbent surface area, particle size, temperature, pH and contact time (Kumar et al., 1998).

Table 2.3: Different processes with different technologies for dye removal (Kharub, 2011)

Process	Technology	Advantages	Disadvantages
Conventional treatment processes	Coagulation Flocculation	Simple and economically feasible.	High sludge production, handling and disposal problems
	Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, need of optimal environment , maintenance and nutrition requirements
	Adsorption (activated carbon)	Produce a high quality treated effluent	The regeneration step is expensive and non-destructive process.
Established recovery processes	Membrane separations	Removes all dye types, produce a high-quality treated effluent	Expensive and not suitable for treating large volumes
	Ion-exchange	No loss of sorbent on regeneration	Not effective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost, chemicals required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals	Technical constraints
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on micro-organisms	Slow process, performance depends on some external factors (pH and salts)

2.3 ADVANCED OXIDATION PROCESS

Advanced oxidation processes (AOP) is known as the recent developments of chemical treatment of waste water which improve the oxidative degradation of the organic compounds dissolved or dispersed in aqueous media. AOP can be characterised by a common chemical feature which is the capability of exploiting the high reactivity of hydroxyl radicals (∙OH) in driving oxidation processes (Andreozzi et al., 1999). ∙OH possess higher oxidation potential compare to other oxidants and they are extraordinarily reactive species which they attack most part of organic molecules with rate constants usually in the order of f 10^6–10^9 M^{-1} s^{-1} (Hoigné and Bader, 1983). AOP is versatile because they offer different possible ways for ∙OH production thus allowing better suitability with the specific treatment requirements. The degradation of organic compounds by the ∙OH proceeds can either through hydrogen abstraction, electrophilic attack or electron transfer. Table 2.4 shows different type of possibilities offered by advanced oxidation process

Table 2.4: Different type of possibilities offered by advanced oxidation processes (Andreozzi et al., 1999)

Advance oxidation processes	**Possibilities offered**
Fenton Method	H_2O_2/Fe^{2+}
Fenton-like	H_2O_2/Fe^{3+}
Photo assisted Fenton	$H_2O_2/Fe^{2+}(Fe^{3+})/UV$
Photocatalysis	$TiO_2/hv/O_2$
Ozone water system	O_3/H_2O_2

2.3.1 Heterogeneous photocatalysis

Heterogeneous photocatalysis can be defined as the acceleration of photoreaction in the presence of a catalyst. Photocatalysis has been suggested in environmental protection due to its ability to oxidise the organic and inorganic substrates. Two or more phases such as gas phase, pure organic liquid phases or aqueous solutions are used in photocatalytic reaction. In photocatalysis, light source together with semiconductor material is used to let the photoreaction occur (Al-rasheed, 2018). The overall process of heterogeneous photocatalysis shown in the Figure 2.2.

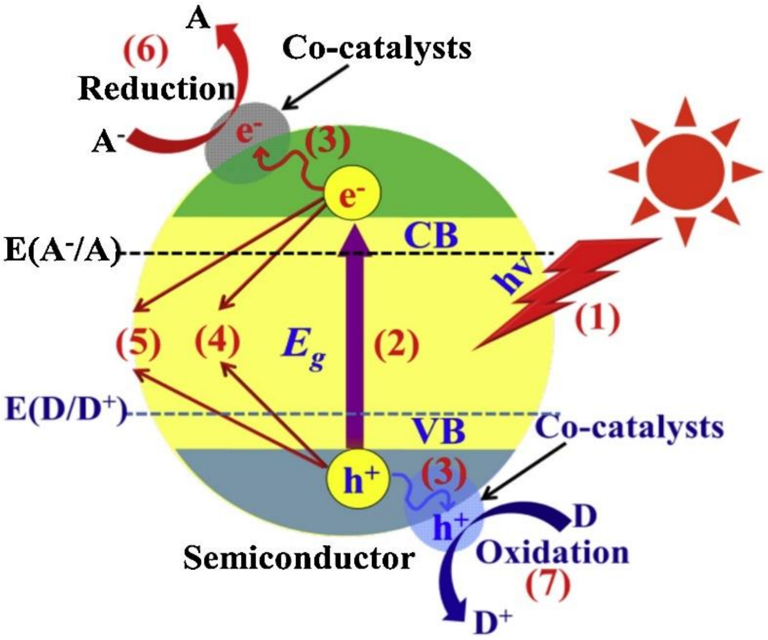


Figure 2.2: The fundamental mechanism of heterogeneous photocatalysis(Wen et al., 2017)

According to Figure 2.2, the heterogeneous photocatalysis involve seven key stage which is:

1. Light harvesting
2. Charge excitation of a semiconductor
3. Charge separation and transfer
4. Bulk charge recombination
5. Surface charge recombination
6. Surface reduction reactions
7. Surface oxidation reactions where reactants adsorbed on the semiconductor.

Photocatalysis is differed from the conventional catalysis in terms of the mode of activation of the catalyst in which the thermal activation is replaced by a photonic activation. Light irradiation is important to excite electron in VB of the semiconductor to its CB with energy higher than or equal to its band gap energy.

2.4 SEMICONDUCTOR CATALYST

Generally, semiconductor is a material that is characterized by non-overlapping bands. In solid semiconductor such as g-C_3N_4, electrons occupy these bands according to their energy. The occupied bands are called valence bands (VB) and the next band above, or the conduction band (CB) is totally empty. Between these two bands, there are region called band gap. The size of this band gap is referred to classify materials as semiconductors or insulators because acts as barrier for electronic mobility. Semiconductor photocatalyst absorbs energy equal or above its band gap energy and the size of band gap which is the energy gap determines its optical properties and colour (Mamba and Mishra, 2016). Table 2.5 shows list of semiconductor and their band gaps.

Table 2.5: List of semiconductor and their band gaps (Sobczyński and Dobosz, 2001)

Semiconductor	Band gap (eV)	Semiconductor	Band gap (eV)
Fe_2O_3	2.3	CdSe	1.7
CdS	2.5	g-C_3N_4	2.7
WO_3	2.8	Cu_2O	2.2
TiO_2 (rutile)	3.0	TiO_2 (anatase)	3.2
ZnO	3.2	ZnS	3.6

Upon light irradiation, electrons will be promoted from VB to the CB. This will result in vacancy in VB causing a hole of positive charge. Positive holes move when an electron enters them, leaving its own position vacant as a fresh positive hole. This vacant positive hole will become the site of oxidation and reduction to occur on the surface of the photocatalyst. Positive holes react with the donors of electron such as water, anions -OH and organic products, adsorbed on the surface of the semiconductor forming the hydroxyl radicals. Meanwhile electrons react with the electron acceptors such as dissolved oxygen to form superoxide radicals, preventing the recombination of charges (Bekkouche et al., 2004).

2.4.1 g-C_3N_4 photocatalyst

g-C_3N_4 is a 2-D π-conjugated polymeric, metal-free n-type semiconductor and semiconductor with 2.7 eV band gap. It possess promising properties such as unique electric, optical, structural and physiochemical properties which make g-C_3N_4 multifunctional nanoplatforms for electronic, catalytic and energy applications (Xu et al., 2015). The g-C_3N_4 based nanostructures is ideal for solving the energy and environmental issues such as photocatalytic water reduction and oxidation, degradation of pollutants and carbon dioxide reduction. Thermal gravimetric analysis (TGA) and thermal gravimetric (TG) on g-C_3N_4 also indicate that the as-prepared g-C_3N_4 is non-volatile up to as high as 600°C, and will be almost completely decomposed until the temperature rises to 700 °C (Rong et al., 2015).

There are several allotropes of C_3N_4 such as α-C_3N_4, β-C_3N_4, pseudocubic C_3N_4, cubic C_3N_4 and g-C_3N_4. Among all of this allotropes, g-C_3N_4 is considered as the most stable form of C_3N_4 under room conditions (Semencha and Blinov, 2010). g-C_3N_4 have a moderate band gap and an optical wavelength of 460 nm which will make it active under visible light. Water-splitting with enough endothermic driving forces which is much larger than 1.23 eV and light absorption in the visible range can be achieve because the band gap of 2.7 eV accidentally lies in between 2 eV and 3.1 eV (Li et al., 2015). In addition, g-C_3N_4 has a suitable CB position for various reduction reactions and it has more negative CB than those of conventional inorganic semiconductor. g-C_3N_4 possess a large thermodynamic driving force to reduce various kinds of small molecules, like H_2O, CO_2 and O_2 and this kind of properties make g-C_3N_4 favorable for wide applications such as photocatalytic water splitting, CO_2 reduction, pollutant degradation, organic synthesis and disinfection.

Apart from suitable band gap and position, metal-free g-C_3N_4 material also possesses a stacked 2D layered structure, in which the single-layer nitrogen heteroatom-substituted graphite nanosheets, formed through sp^2 hybridization of C and N atoms, are bound by van der Waals forces (Gong et al., 2015). Below are the advantages of using g-C_3N_4 semiconductor,

1. Strong reduction ability
2. Active in visible light
3. Suitable band gap
4. Can easily be fabricated from readily available precursors
5. 2D layered structures
6. Non-toxicity
7. High chemical and thermal stability

In preparation of g-C_3N_4, thermal condensation of nitrogen-rich precursors such as urea, cyanamide, dicyanamide, melamine, thiourea and triazoles has been most suitable method due to the simplicity and use of cheap, readily available precursors (Kumar et al., 2014). Apart from advantages, g-C_3N_4 encounter several challenges which are low efficiency of visible light utilisation, high recombination rate of the photo generated charge carriers that will result in poor formation of radical species, low electrical conductivity and smaller specific surface area. The band gap of g-C_3N_4 is still considered large for visible light harvesting and this will make large portion of visible light spectrum unexploited (Su et al., 2014). Hence, some modification of g-C_3N_4 needed to be done in order to enhance the photocatalytic activity.

2.4.2 WO_3 photocatalyst

WO_3 is a photocatalyst that absorb light at wavelength up to 480 nm and has a band gap which is 2.5 eV to 3.0 eV depending on stoichiometry, crystalline structure and defects. It is known for their unique characteristics such as photocatalytic activity, gas sensing effects, electrochromic coatings and microelectronic applications (Ashkarran et al., 2008). WO_3 has several crystalline modifications which are triclinic, monoclinic, orthorhombic, tetragonal, hexagonal and cubic. However, the only reported as a photocatalysts are triclinical, monoclinic, orthorhombic and tetragonal phases (Qamar et al., 2009).

The advantages of using WO_3 photocatalyst are it shows high oxidation power of valence band holes, nontoxicity and it also have resistance toward physical and chemical harsh environments such as solar irradiation and exposure to water. This photocatalyst also exhibits enhanced photoabsorption in visible light irradiation because of its smaller band gap (Morales et al., 2008). WO_3 is low in cost, harmless and stable in both acidic and oxidative conditions.

However, (Zhang et al., 2016) has reported that the photocatalytic activity of pure WO_3 semiconductor without any modification or optimization is relatively low. This phenomenon can be attributed to the rapid recombination of photogenerated charges and relatively positive conduction band edge of $WO_{3.}$

According to (Bi and Xu, 2011), photocatalytic activity of WO_3 under visible light is limited due to WO_3 has a conduction band edge lying in a position unfavorable for single-electron reduction of O_2, leading to poor photocatalyst for organic degradation under O_2 conditions.

2.5 SEMICONDUCTOR COUPLING

In order to overcome limitation face by WO_3 and g-C_3N_4 photocatalyst, several modification such as size controlling, noble metal deposition and coupling with other have been tried. Among these strategies, semiconductor coupling is one of the effective strategies for separation of photoinduced electron–hole pairs and improvement of photocatalytic activity. In semiconductor coupling, the band alignment of two semiconductors with well-matched band structure is generally employed to promote the separation of charge at the interfaces of two semiconductors, subsequently reducing charge recombination. The construction of intimate heterojunction between two appropriate semiconductors is an effective strategy to enhance the photocatalytic performance. Recently, g-C_3N_4-WO_3 composites with enhanced photocatalytic activity have been reported in (Liying Huang, 2013, Zang et al., 2013).

In (Liying Huang, 2013), it is reported WO_3/g-C_3N_4 were synthesized via a facile calcination process and the role of heterojunction in photocatalytic activity is evaluated by mechanically blended WO_3 and g-C_3N_4 sample with 9.7% WO_3 content. According to this report, the highest degradation percentage of methylene blue within 2 h by using 9.7% WO_3 content is 97%. This show that the efficient synthesis method for WO_3/g-C_3N_4 composites and could be a new method to design new photocatalyst with high performance for environmental applications.

Studies by (Chen et al., 2014b) reported that WO_3/g-C_3N_4 is prepared with ball milling and heat treatment methods. Heterojunction photocatalyst may be formed between WO_3 and g-C_3N_4. It is reported, transfer of the photoexcited carriers of WO_3 and g-C_3N_4 will happen because of the position differences of VB and CB. Z-scheme photocatalyst may be formed because of the short distance between VB of g-C_3N_4 and

CB of WO_3. Hence, the photogenerated electrons on the CB of g-C_3N_4 exhibit strong reduction ability to reduce the molecular oxygen to yield $\bullet O_2^-$, and the photogenerated holes on the VB of WO_3 show excellent oxidation ability to oxidize H_2O or OH^- to generate abundant active •OH radicals.

(Chen et al., 2015) also reported that WO_3/g-C_3N_4 being synthesized by via ball milling and heat treatment.. It is reported that photocatalytic activity of WO_3/g-C_3N_4 is much higher than single g-C_3N_4 under visible light irradiation. The increased in photocatalytic activity may be result of fast combination between the photoexcited holes of g-C_3N_4 and photoexcited electron of WO_3.

CHAPTER 3

MATERIALS AND METHODS

In this chapter, the experimental procedures for preparation of $WO_3/g\text{-}C_3N_4$ catalyst, characterization of $WO_3/g\text{-}C_3N_4$ catalyst, process parameter studies and kinetic studies will be described. This chapter also include the materials, chemicals and equipment used throughout the experiment. The overall experimental activities carried out in this study can be seen in Figure 3.1.

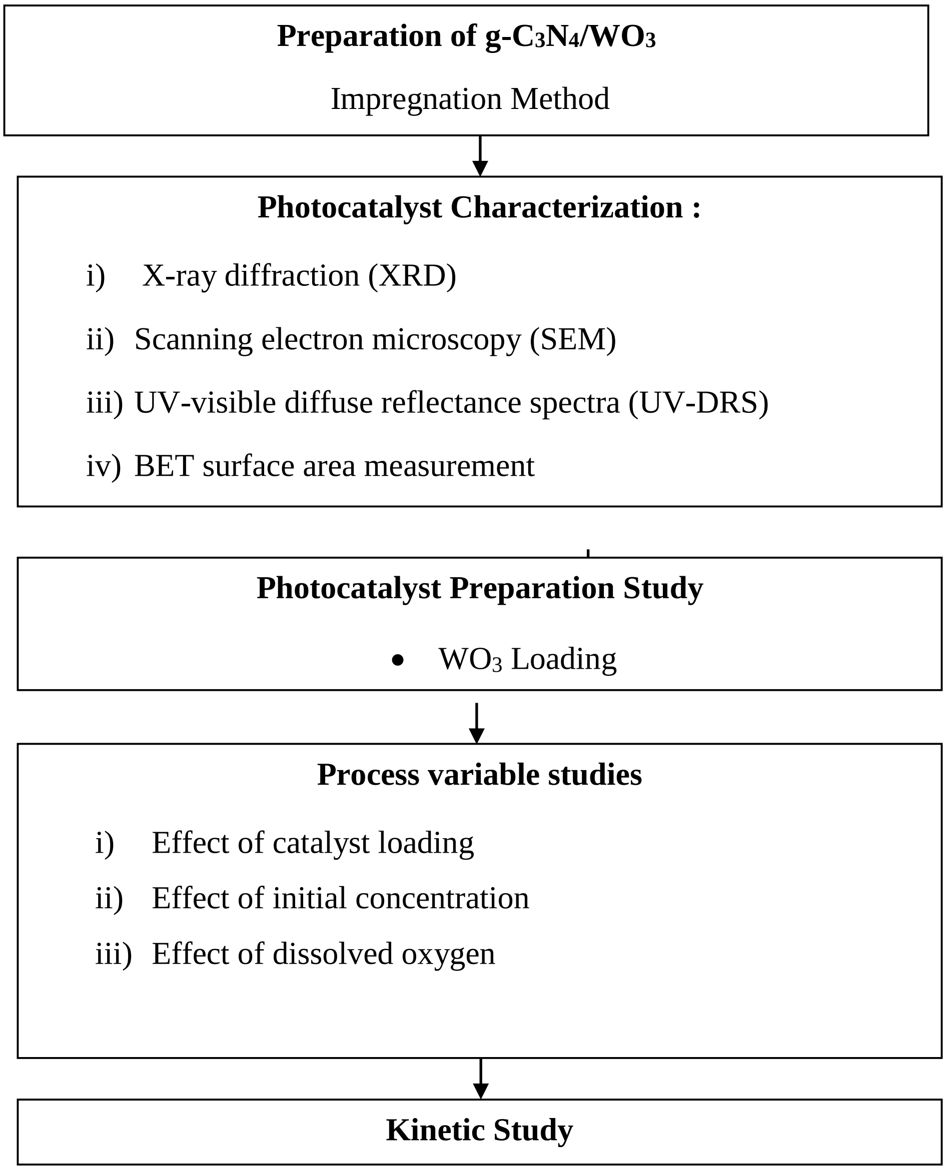


Fig. 3.1: Flow chart of method study in this research

3.1 MATERIALS AND CHEMICALS

In this experiment, urea was used to prepare g-C_3N_4 and sodium tungsten dihydrate was used as the precursor for WO_3. The WO_3/g-C_3N_4 was prepared through facile impregnation method.

Methylene blue was used as the model pollutant in this study. The stock solution of 1000 ppm was prepared by dissolving 0.25 g of methylene blue (MB) solid in 250 ml of deionized water obtained from ELGA Purelab Option Q with resistivity 18.2 Ω. Table 3.1 shows below were list of chemicals and reagents used in this study.

Table 3.1: Type of chemicals and reagents

Chemical/Reagent	Purity	Supplier	Purpose
Urea	99.5 %	Merck	Catalyst synthesis
Sodium Tungsten Dihydrate	99 %	Sigma-Aldrich	Catalyst synthesis
Deionized water	18.2 Ω	ELGA Purelab Option Q	Solution
Methylene blue (MB)		Merck	Organic dye/Model pollutant

3.2 EQUIPMENT

3.2.1 Photocatalytic batch reactor

In this study, photocatalytic degradation of methylene blue was conducted in photocatalytic batch reactor as shown in Figure 3.2. The photocatalytic batch reactor consists of several parts which are:

a) Magnetic stirrer to provide uniform mixing throughout experiment.

b) A 250 ml beaker filled with 10 mg/L of MB solution. This photocatalytic reactor consists of UV-vis lamp placed at the top of reactor. The reactor placed in black painted box to avoid any stray light entering the reactor

c) An UV-vis lamp (80W; λ=200-800nm) was used as the light source throughout experiment and located at the centre of reactor.

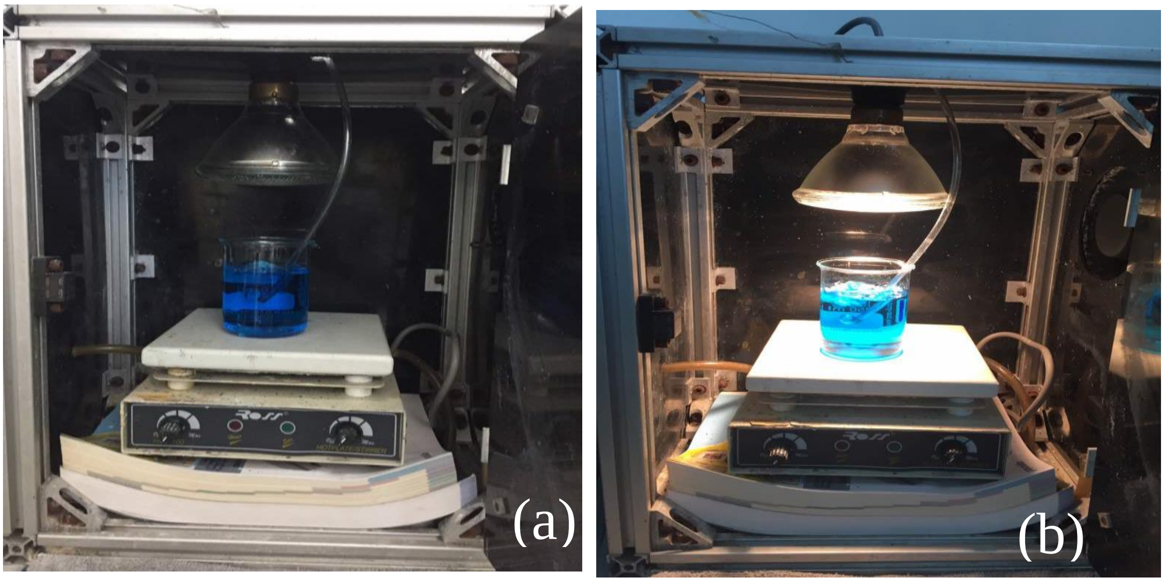


Figure 3.2: Experimental set up for photocatalytic degradation (a) dark (b)light