PHOTODEGRADATION OF AZO DYE USING TITANIUM DIOXIDE AS PHOTOCATALYST UNDER SOLAR LIGHT IRRADIATION

by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Ag	Silver
AO7	Acid Orange 7
AOPs	Advanced Oxidation Processes
Au	Gold
B	Boron
BB28	Basic Yellow 28
BB41	Basic Blue 41
BET	Brunauer-Emmett-Teller
C	Carbon
CB	Conduction Band
Ce	Cerium
C_2H_5OH	Ethanol
CH_3COOH	Acetic Acid
C.I	Colour Index
Cl	Chlorine
Co	Cobalt
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
CSD	Chemical Solvent Decomposition
Cu	Copper
Cu_2O	Copper Oxide
CVD	Chemical Vapour Decomposition
F	Fluorine
Fe	Iron
$FeCl_3.6H_2O$	Iron Chloride Hexa-hydrate
Fe_2O_3	Iron (III) Oxide
Fe_3O_4	Iron (IV) Oxide
FT-IR	Fourier Transform Infrared Spectroscopy
FWHM	Full Width at Half Maximum
H_2	Hydrogen
HCl	Hydrochloric Acid
H_2O	Water
H_2O_2	Hydrogen Peroxide

I	Iodine
$K_2Cr_2O_7$	Potassium Di-chromate
Mn	Manganese
MO	Methyl Orange
Mo	Molybdenum
N	Nitrogen
NaOH	Sodium Hydroxide
Nb	Niobium
NC	New Coccine
NH_3	Ammonia
Ni	Nickel
$NiCl_2.6H_2O$	Nickel Chloride Hexa-hydrate
O_2	Oxygen
O_3	Ozone
OG	Orange G
P	Phosphorous
Pt	Platinum
RB4	Reactive Black 4
RB5	Reactive Black 5
RG19	Reactive Green 19
RR2	Reactive Red 2
S	Sulfur
SEM	Scanning Electron Microscope
SILAR	Successive Ionic Layer Adsorption Reaction
SiO_2	Silicon Dioxide
TiO_2	Titanium Dioxide
$Ti(OC_3H_7)_4$	Titanium Isopropoxide
TiOH	Titanium Hydroxide
TiO_2/ZnO	Titanium Dioxide/Zinc Oxide
UV	Ultraviolet
UV/H_2O_2	Ultraviolet/Hydrogen Peroxide
UV-Vis	Ultraviolet-visible
V	Vanadium
VB	Valance Band

VOCs	Volatile Organic Compounds
WO_3	Tungsten Oxide
XRD	X-Ray Diffraction
Zn	Zinc
ZnO	Zinc Oxide
$Zn(OH)_2$	Zinc Hydroxide
$ZnSO_4.7H_2O$	Zinc Sulfate Hepta-hydrate

LIST OF SYMBOLS

%	Percentage
β	Full Width at Half Maximum of Diffraction Line observed in Radians
θ	Diffraction Angle
λ	X-Ray Wavelength
λ_{max}	Maximum Absorption Peak
µm	Micrometer
Å	Ampere
Abs	Absorbance
˚C	Degree Celcius
C_0	Initial Dye Concentration
COD_0	Initial Chemical Oxygen Demand
C_t	Dye Concentration at Time Intervals
cm^{-1}	Per Centimeter
cm^3/g	Centimeter Cube per Gram
D	Average Crystalline Size
e^-	Electron
Ebg	Band-gap Energy
eV	Electron Volts
g	Gram
g/L	Gram per Liter
g/mol	Gram per Mole
g/mL	Gram per Milliliter
h	Hour
h^{-1}	Per Hour
h^+	Hole
$HO_2^{\bullet}$	Hydroperoxyl Radical
hv	Ultraviolet Light ($\lambda < 390$ nm)
L	Liter
M	Molarity
m	Meter
m^2/g	Meter Square per Gram
mg/g	Milligram per Gram
min	Minutes
min^{-1}	Per Minutes
mL	Milliliter

mL/L	Milliliter per Liter
mg/L	Milligram per Liter
nm	Nanometer
N=N	Nitrogen Double Bond
-N=N-	Azo Bond
NO_3^-	Nitrate Ion
$O_2^{\bullet -}$	Superoxide Ion
$O_2^{\bullet}$	Superoxide Radical
OH^-	Hydroxyl Ion
$OH^{\bullet}$	Hydroxyl Radical
pH	Logarithmic Scale used to Specify the Acidity or Basicity of an Aqueous Solution
q_t	Adsorption Capacity of Azo Dye at Time Intervals
SO_4^{2-}	Sulfate Ion
t	Time
TiO^-	Titanium Ion
V	Volume
vs	Versus

Fotodegradasi of Pewarna Azo dengan menggunakan Titanium Dioksida sebagai Fotopemangkin bawah Radiasi Cahaya Matahari

ABSTRAK

Pewarna sintetik yang digunakan secara meluas dalam industri tekstil kertas dan dilepaskan ke persekitaran telah menyebabkan pencemaran alam sekitar yang serius disebabkan oleh sifat toksik dan ketahanan warna. Bahagian pertama kajian ini adalah berdasarkan kepada fotodegradasi tiga pewarna azo tunggal (pewarna diazo RG19, mono azo , AO7 dan mono azo; MO) dan dua pewarna azo binari (campuran MO dan RG19; AO7 dan RG19) menggunakan TiO_2 komersial dengan tindak balas sinaran cahaya matahari selama 6 jam masa tindakbalas. Beberapa parameter operasi seperti kesan penyinaran cahaya matahari, kepekatan azo pewarna awal (10, 30, 50 mg/L), kepekatan TiO_2 (600, 1200, 2000, 3000, 4000 mg/L), pH (1, 3, 6.8, 9, 11) dan pengudaraan (menggunakan pam udara) dikaji dalam larutan berair tunggal dan binari azo pewarna. Untuk sistem pewarna tunggal, kecekapan kelunturan bagi RG19, AO7 dan MO adalah 22 %, 12 % dan 8 % masing masing di bawah keadaan gelap selepas 6 jam tindakbalas mengikut susunan berat molekul RG19 > AO7 > MO (1418.92 g/mol > 350.32 g/mol > 327.33 g/mol). Selain itu, fotodegradasi bagi RG19 adalah 100 % selepas 2 jam tindakbalas, AO7 adalah 100 % dan MO adalah 60 % selepas 6 jam tindak balas di bawah sinaran cahaya matahari. Dalam sistem binari, kecekapan kelunturan RG19 dan AO7 adalah 18 % dan 4 % masing masing di bawah keadaan gelap, sementara 98 % dan 90 % di bawah sinaran cahaya matahari selepas 6 jam masa tindakbalas untuk campuran AO7 dan RG19. Selain itu, kecekapan kelunturan RG19 dan MO adalah 16 % dan 2% di bawah keadaan gelap dan 92 % dan 56 % masing masing di bawah sinaran cahaya matahari selepas 6 jam masa tindakbalas untuk campuran MO dan RG19. Bahagian kedua kajian ini memberi tumpuan kepada penyediaan TiO_2 yang disintesis, logam (zink, kromium, nikel dan besi) yang ditambah TiO_2 dan bukan-logam (nitrogen) ditambah TiO_2 melalui kaedah sol gel berserta kaedah refluks. Selepas itu, fotopemangkin yang disintesis telah dianalisis dalam pengimbasan mikroskop elektron (SEM), pembelauan sinar X (XRD), transformasi fourier spektroskopi inframerah (FT-IR) dan analisis penyerapan nitrogen masing-masing. Selain itu, prestasi fotopemangkin yang disintesis telah dikaji dengan fotodegradasi pewarna azo dalam dua parameter operasi seperti kesan penyinaran cahaya matahari dan pewarna azo yang berbeza. Di antara prestasi fotokatalis yang disintesis, fotodegradasi pewarna azo yang terpantas adalah dengan menggunakan TiO_2 yang dihidupkan Zn. Selaian itu, perbandingan antara fotodegradasi pewarna azo yang berbeza menggunakan TiO_2 komersil dan TiO_2 disintesis dengan penambahan Zn di bawah sinaran cahaya matahari telah dikaji. Secara keseluruhan, semua sampel air dianalisis dengan UV-Vis spektrofotometer. Kajian kinetik mengenai degradasi fotopemangkinan pewarna azo dinilai oleh model Langmuir-Hinshelwood. Analisis permintaan oksigen kimia (COD) telah dikaji untuk menilai mineralisasi pewarna azo di bawah sinar cahaya matahari. Fotodegradasi dan mineralisasi pewarna azo

menggunakan TiO_2 komersial dan fotopemangkin yang disintesis di bawah sinaran cahaya matahari dibandingkan. Mineralisasi pewarna azo lebih lambat daripada fotodegradasi pewarna azo dalam kajian ini.

Photodegradation of Azo Dye using Titanium Dioxide as Photocatalyst under Solar Light Irradiation

ABSTRACT

Synthetic dyes that are widely used in the textile and paper industries and being discharged into the environment have caused serious environmental pollution due to their toxicity and recalcitrant nature. The first part of this study was based on the photodegradation of three single azo dyes (diazo dye RG19, mono azo dye; AO7 and mono azo dye; MO) and two binary azo dyes (MO and RG19 mixture; AO7 and RG19 mixture) using commercial TiO_2 under solar light irradiation for 6 h reaction time. Some operating parameters such as the effect of solar light irradiation, initial azo dye concentrations (10, 30, 50 mg/L), TiO_2 loading (600, 1200, 2000, 3000, 4000 mg/L), pH (1, 3, 6.8, 9, 11) and aeration (using air pump) were studied in the single and binary azo dye aqueous solutions. In the single dye system, the decolourization efficiency of RG19, AO7 and MO was 22 %, 12 % and 8 %, respectively, under dark condition after 6 h reaction time following the sequence of molecular weight of RG19 > AO7 > MO (1418.92 g/mol > 350.32 g/mol > 327.33 g/mol). Besides, the photodegradation of RG19 was 100 % after 2 h reaction time, AO7 was 100 % and MO was 60 % after 6 h reaction time under solar light irradiation. In the binary system, the decolourization efficiency of RG19 and AO7 was 18 % and 4%, respectively, under dark condition, while the photodegradation efficiency was 98 % and 90 % under solar light irradiation after 6 h reaction time for AO7 and RG19 mixture. Besides, the decolourization efficiency of RG19 and MO was 16 % and 2 % under dark condition and that was 92 % and 56 % under solar light irradiation after 6 h reaction time for MO and RG19 mixture, respectively. The second part of this study was focused on the preparation of synthesized TiO_2, metal (zinc, chromium, nickel and iron) doped TiO_2 and non-metal (nitrogen) doped TiO_2 by sol-gel assisted reflux method. After that, the synthesized photocatalysts were characterized by using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and nitrogen sorption analysis, respectively. Besides, the performances of synthesized photocatalysts on photodegradation of azo dyes were studied in two operating parameters such as the effect of solar light irradiation and different azo dyes. Among the performance of synthesized photocatalysts, the fastest photodegradation of azo dyes was investigated by using Zn-doped TiO_2. Therefore, the performance of commercial TiO_2 and synthesized Zn-doped TiO_2 was compared for photodegradation of azo dyes under solar light irradiation. Overall, all water samples were analysed by using UV-Vis spectrophotometer. The kinetics study of photodegradation of azo dye was evaluated by using Langmuir-Hinshelwood model. Chemical oxygen demands (COD) analysis was used to evaluate the mineralization of azo dye under solar light irradiation. Finally, the photodegradation and mineralization of azo dye using commercial TiO_2 and synthesized photocatalysts were compared under solar light irradiation. The mineralization of azo dye was slower than the photodegradation of azo dye in this study.

CHAPTER 1 : INTRODUCTION

1.1 Research Background

Colour is the most apparent indicators of wastewater pollution. The releasing of higher coloured dye effluents may be harmful to the receiving wastewater bodies (Petrou, Chatzisymeon, & Mantzavinos, 2013). The textile wastewater is the most polluting wastewater among various industrial sectors because the considerable amount of wastewater is produced in effluents of textile dyeing process and finishing industries. Moreover, the high colour intensity and chemical oxygen demand (COD) were supported the environmental contamination levels become higher in these industries (Bizani, Fytianos, Poulios, & Tsiridis, 2006; Shu, Chang, & Fan, 2004). It was found that textile dyes and other industrial dyestuffs involved one of the largest groups of organic compounds because the worldwide annual production was over 7×10^5 tons and approximately about 1–20% of the overall dyes worldwide production was released by the textile industry. The formation of textile wastewaters in the environment is generated non aesthetic pollution and eutrophication, which may support to the harmful by-products through oxidation hydrolysis, or other chemical reactions, happened in the wastewater fields. Therefore, dyes contained the toxic effects and decreased the light penetration in contaminated waters (Dehghani, Karimi, & Rajaei, 2016; Akpan & Hameed, 2009). When industries used the large quantity of water, it was released the large volume of wastewater in dyeing process. The releasing wastewater were colourful and various types of dye was contained in it (Divya, Bansal, & Jana, 2013).

When investigating the wastewater, it was found that many dyes was simultaneously existed in the effluent water of various industries, such as textile, leather, paper, rubber, plastics, printing, cosmetics, pharmaceuticals and food industries, etc. Moreover, dyes are abundant class of coloured organic compounds which support to increase the environmental pollution (Regti, El Kassimi, Laamari, & El Haddad, 2017; García, Trevin, Lahitte, & Oturan, 2014; Wang, 2000). Dyes can be identified by acidic (anionic), basic (cationic), direct, disperse, mordant, reactive, solvent and vat dyes depend on the colour index (C.I.), convention and condition of the substrate application. Due to the chemical structure, dyes can be further analyzed as azoic, anthraquinonic, heteropolyaromatic, aryl methane, xanthene, indigo, acridine, nitro, nitroso, cyanine and stilbene in each of the above types. Azo dyes presented as 50% of commercial dyes' market and the photodegradation of azo dyes have been investigated extensively compared with all the above dye utilities (Vinu, Akki, & Madras, 2010). Azo dyes are especially concerned with the textile dyes because it was most widely used in textile industry (Hashemian, 2011). Azo dyes conduct with benzidine and its derivatives, dimethylbenzidine and dimethoxybenzidine which produces the potential carcinogenic products by reduction under anaerobic condition (Xu, Ng, Zhang, Bai, & Sun, 2011a). The toxicity, persistency, mutagenicity, non-biodegradation and potentially carcinogenic of these azo dyes displayed to enhance the several ecological and environmental problems (Yang, Yang, Shao, Niu, & Wang, 2011; Stylidi, Kondarides, & Verykios, 2003). Therefore, the effective method of azo dyes wastewater treatment is more important than other colourless organic substances (Liu, Hu, & Liu, 2017).

Chemical method of wastewater treatment can be accomplished colour and

organics removal. In this method, organic materials can be oxidized by oxidizing agents such as ozone or chlorine, H_2O_2 and UV light or combination of such oxidants, that represented to Advance Oxidation Processes (AOPs) (Fahmi, Zulzikrami, Abidin, & Rahmat, 2011; Stylidi, Kondarides, & Verykios, 2003). AOPs are very promising and more powerful technique which may be treated to remove the dye contaminated from wastewaters (Rauf, Meetani, & Hisaindee, 2011). These processes are based on the production and oxidative action of reactive species such as hydroxyl and oxygen radicals (Daneshvar, Salari, & Khataee, 2003). The function of AOPs is to reduce the strong colour of the effluents and their toxicological effects (Guivarch, Trevin, Lahitte, & Oturan, 2003). Among AOPs, photocatalytic degradation process represented a very interesting of study due to its continuous developing wastewater treatment (Song, Xu, He, Ying, Chen, Xiao, & Yan, 2008). Furthermore, this process supported to degrade of air, water and wastewater pollutants especially inflexible organic substances (Mahmoodi, Arami, & Limaee, 2006).

The meaning of solar photocatalysis technique is the semiconductor photocatalyst degrading harmful dyes by its higher treatment efficiency under solar energy (Gajbhiye, 2012). In solar photocatalysis process, the semiconductor particle suspension is to catalyse the oxidative or reductive reaction of substrates in water solution which process is especially used for the transformation of toxic substances into less harmful products (Naýo, Colón, Trillas, Peral, Domènech, Testa, & Litter, 1998). Many researchers were used TiO_2 photocatalyst more than other semiconductor materials due to its unique optical property and chemical stability (Shi, Lai, Yao, & Wang, 2012). Moreover, TiO_2 is non-toxic semiconductor that was confirmed by American Food and Drug Administration (FDA) and it was used in various consumer

goods such as human foods, drugs, cosmetics and food contact materials, respectively (Chawengkijwanich & Hayata, 2008). The advantages of TiO_2 are high catalytic activity, low cost, good mechanical and chemical stability, and non-toxicity to human beings and environment in wastewater treatment (Liao & Que, 2010)

TiO_2 can be produced easily and low cost. In this study, the synthesized TiO_2 nanoparticle was prepared by the sol–gel assisted reflux method. This method is one of the most widely used in TiO_2 nanoparticles preparation due to many advantages, such as high homogeneity, low processing temperature, stability and versatility of processing (Behnajady, Eskandarloo, Modirshahla, & Shokri, 2011). The doping TiO_2 materials are prepared by metal and non-metal elements or compounds with the semiconductor substrate to develop the photocatalytic activity of wastewater treatment. Among non-metal doped elements or compounds for TiO_2, nitrogen was recognized more than other non-metal elements because it was supported the most effective non-metal catalyst under visible light irradiation (Chen et al., 2007). Many researchers mentioned that zinc ions, chromium ions, nickel ions and iron ions used as metal doped for TiO_2 is especially to improve the separation of electron-hole pairs on the surface of the TiO_2 (Nguyen, Hwang, & Ryu, 2012; Begum, Ahmed, & Gunashekar, 2008; Tong, Zhang, Tian, Chen, & He, 2008; Venezia, Palmisano, Martin, Martin, 1994). In this study, chosen Zn, Cr, Ni and Fe as metal doped TiO_2 and elected N as non-metal doped TiO_2 to modify the photocatalytic activity of TiO_2.

1.2 Problem Statement

Textile industries discharge to the large quantity of colouring wastewater which is harmful to the ecosystem. Not only extraordinary colourful but also high COD is found in textile wastewater (Min, Ho, Ong, & Wong, 2015). Basically, the textile industries emitted some significant negative side-effects to the environment. It is important to manage the textile wastewater pollution in environment and human health because it have considerably provided to the business of Malaysia. Moreover, the batik industries should maintain the releasing of wastewater more than other industries in Malaysia. However, it was the small scale industries but it does bring the colourful textile wastewater into environment (Goh, Chan, & Ong, 2016). In textile wastewater, it was involved many types of dyes, detergents, insecticides, pesticides, grease and oils, sulfide compounds, solvents, heavy metals, inorganic salts, and fibres (Ong, Eiichi, Makoto, & Tadashi, 2008). The concentration of dye wastewater is normally lower than the concentration of other chemical in wastewater. But, it can cause the toxic effect in wastewater disposal due to their strong colour effect although at very low dye concentrations (Moghaddam, Moghaddam, & Arami, 2010).

Among the various dye molecules, the azo dyes are highly related to the textile wastewater, due to extensively used in the textile industry. The highly toxic and potentially carcinogenic effects can be formed in the azo dyes and dye determined products are distinguished to contain such as aromatic amines and amino-azo compounds (Zuorro, Fidaleo, & Lavecchia, 2013). The one popular thing is that soluble azo dyes may cause cancer in human beings (Wawrzyniak, Morawski, & Tryba, 2006). Besides azo dyes are a class of colourful organic compounds which have been

widespread used in many industries, such as textile, leather, plastics, paper, food and cosmetics, etc. (Uçar, Güvenç, & Mehmetoglu, 2011). Azo dye was characterized by azo bond (–N=N–) which may cause various ecological and environmental problems. Moreover, it is unsuitable to release into the water due to its rich in colour, toxicity, non-biodegradation and potentially carcinogenic, respectively (Yang et al., 2011).

Within various types of azo dyes, the reactive dye was characterized by one or more azo bonds with the organization of one or more aromatic systems. Among reactive dyes, Reactive Green 19 (RG19) is widely used in the textile industry due to the colourful, good in wash and light fastness properties (Zuorro et al., 2013). In mono azo dyes, Acid Orange 7 (AO7) was interested to use not only for the single aqueous solution but also for the binary azo dye aqueous solution in many researches due to its high photo, thermal stability, carcinogenic and mutagenic, and affects the aquatic life seriously (Divya et al., 2013; Juang, Lin, & Hsueh, 2010). As reported by Kansal, Singh, & Sud (2007) Methyl Orange (MO) was one of the mono azo dye likely used in many industries such as textile, foodstuff, pulp and paper, and leather. The emission of MO and their products into the environment may cause toxicity problems. Therefore, RG19, AO7 and MO were elected to conduct the experiments in this study.

The effective method of wastewater treatment is necessary for removing the colour from textile effluents. Advanced Oxidation Processes (AOPs) are concerned with newer, more powerful and very promising techniques which has been degraded and mineralized of organic pollutants in wastewater effluents (Bansal, Dhir, Prakash, & Sud, 2011). Several years ago, semiconductor photocatalysis can perform as an environmentally friendly technology, which has attracted significant application to

remove harmful organic pollutants in wastewater (Tian, Wang, Dong, Bao, Yang, & Zhang, 2014). Among advanced oxidation processes, TiO_2 photocatalysis is more popular than other water treatment technologies due to its advantages such as containing the lack of mass transfer limitations, operation at ambient conditions and the potential use of solar radiation (i.e. a cheap, abundant and clean source of energy) (Petrou et al., 2013). TiO_2 photocatalysis under solar light irradiation become more interested than other process because it was followed with green chemistry concept in advance innovative technologies. The photocatalysts supports the solar energy can be transformed into chemical energy and consequently it can be applied the degradation of dyes in wastewater treatment (Khanna & Shetty, 2014).

TiO_2 has been used more than other semiconductor materials due to its high photocatalytic efficiency, low cost, and high stability (Wang, Shen, & Zhu, 2012). Moreover, TiO_2 is competent catalyst for photocatalytic degradation of pollutants because it can transfer electron faster to molecular oxygen (Sze, Mariana, Chiang, & Gordon, 2006). Moreover, TiO_2 has a higher oxidation quality which can convert organic compounds into harmless compounds such as CO_2 and H_2O (Damodar, Swaminathan, & You, 2009). In this study, it is to investigate the photodegradation of azo dyes in binary system. Even though, some researchers already studied about binary system in azo dyes (binary azo dyes mixture) but still not used RG19 and AO7 binary solution and RG19 and MO binary solution in their research. Therefore, it was chosen the photocatalytic activities of azo dyes in these two binary solutions have been investigated in this research. Furthermore, many researchers synthesized TiO_2 by sol-gel method and reflux method. Sol-gel method is very helpful and eco-friendly method.

In this study, it was prepared TiO_2, N-doped TiO_2, Zn-doped TiO_2, Cr-doped TiO_2, Ni-doped TiO_2 and Fe-doped TiO_2 by sol-gel assisted reflux method.

1.3 Research Objectives

This study was based on the photodegradation of azo dye, using TiO_2 under solar light irradiation. The objectives of this study are as follows:

1. To study the decolorization efficiency of single azo dyes (RG19, AO7, MO) and binary azo dyes (MO and RG19 mixture, AO7 and RG19 mixture) using commercial TiO_2 as photocatalyst in some operating parameters such as solar light, initial dye concentrations, TiO_2 loading, pH and aeration, respectively
2. To synthesize and characterize the TiO_2, N-doped TiO_2, Zn-doped TiO_2, Cr-doped TiO_2, Ni-doped TiO_2 and Fe-doped TiO_2 by sol-gel assisted reflux method and evaluate their performances on photodegradation of azo dyes
3. To compare the photodegradation and mineralization of azo dyes using commercial TiO_2 and synthesized photocatalysts under solar light irradiation

1.4 Scope of Study

The first step of this study was aimed for the photodegradation of single azo dyes and binary azo dyes using commercial TiO_2 as photocatalyst under solar light irradiation within 6 h reaction times. The experimental was conducted in a simple batch study. The water samples are analysed in UV-Vis spectrophotometer (UV-2800, Japan) which can be evaluated the decolorization efficiency of azo dye and the function of

absorbance peak during experimental time intervals. Some operating parameters such as solar light, initial dye concentrations, TiO_2 loading, pH and aeration was studied in this step. The experiments were conducted under sunlight and dark condition for the decolorization efficiency of azo dye in solar light parameter. Again, the experiments were investigated by using 10 mg/L, 30 mg/L and 50 mg/L of azo dyes under solar light irradiation for the photodegradation of initial dye concentration parameter. In TiO_2 loading parameter, the different amount of TiO_2 such as 0.3 g, 0.6 g, 1 g, 1.5 g and 2 g were studied for photodegradation of azo dye under solar light irradiation. In pH parameters, the different pH value of azo dyes such as pH 1, pH 3, pH 6.8, pH 9 and pH 11 were used for photodegradation of azo dye under solar light irradiation. The experiments were evaluated in aeration and without aeration for photodegradation of azo dye in aeration parameter.

The second step of this study was focused on the preparation of TiO_2, metal-doped TiO_2 and non-metal doped TiO_2 by sol-gel assisted reflux method. The synthesized photocatalysts was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and Nitrogen Sorption analysis, respectively. After that, the function of synthesized photocatalysts, which was evaluated with the photocatalytic activities of azo dye under dark and solar light conditions. Furthermore, the comparison between the photodegradation of different azo dyes using commercial TiO_2 and synthesized Zn-doped TiO_2 was investigated under solar light irradiation in 6 h reaction times.

The final step of this study was pointed to investigate the chemical oxygen demand (COD) analysis of azo dye using commercial TiO_2 and synthesized

photocatalysts under solar light irradiation because COD was supported to confirm the mineralization of azo dye. Besides, the comparison between the photodegradation and mineralization of azo dye was studied.

1.5 Thesis Structure

This thesis is arranged into five chapters.

Chapter 1 introduced about the thesis such as the research background, problem statement, research objectives and scope of the thesis, respectively. The research background discussed about the major facts of the thesis.

Chapter 2 is desired to introduce the backgrounds of the azo dye, TiO_2 photocatalyst and effective treatment methods. The general of the azo dye and different treatment methods of azo dye are demonstrated by details. The benefits and mechanism of TiO_2 photocatalyst are discussed in this chapter which can be decolorized the harmful azo dyes under solar light irradiation.

Chapter 3 is showed that the materials and the photocatalytic experimental procedures of azo dye. The synthesis procedure of photocatalyst materials is also discussed. Moreover, the characterization parameters and the analytical procedure are described in this chapter.

Chapter 4 is provided that the decolorization efficiencies of azo dye using commercial TiO_2 and synthesized photocatalysts under dark and solar light irradiation.

Moreover, the effect of solar light irradiation, azo dye concentrations, TiO_2 loading, pH changes and aeration are reported by details. The kinetics studies and mineralization of azo dye are described. It was discussed about the colour removal efficiency was concerned with the particle size, crystallite size and surface area of synthesized materials in this chapter.

Chapter 5 is concluded that the important findings and novel observations from this study. This research effort to complete a low cost of experimental methods by removing colour from harmful dyes and also synthesized photocatalyst materials. Moreover, the description about the future direction and recommendation of this study for future research work by shortly.

CHAPTER 2 : LITERATURE REVIEW

2.1 Textile Wastewater

Wastewater is exceeded colouring water with a significant amount of auxiliary chemicals which released from textile and dye industries. The textile industries release wastewater directly into the water source, and which has been occurred serious environmental pollution, and toxicity to aquatic environment (Ay, Catalkaya, & Kargi, 2009). Moreover, textile industries released large amounts of colourful wastewater that can harm the ecosystem (Daneshvar et al., 2003). And then, there are large amount of azo dyes containing in textile wastewater, which was pervading to their non-biodegradability, toxicity and carcinogenic nature constitute a major threat to the ecosystem (S. Kaur & Singh, 2007). The wastewaters released from textile industries promoted to disruption of the environment, eutrophication, the production of hazardous and toxic by-products through chemical reactions like oxidation, hydrolysis, and an adverse effect aesthetically, an acceptor water quality drop, and the effect on light penetration, which can be provided the formation of dangerous by-products through the chemical reactions with wastewater (Dehghani et al., 2016).

The textile dyes and other industrial dyestuffs contained one of the largest group of organic compounds (Konstantinou & Albanis, 2004). Many carcinogenic effects are found in azo dyes and their related products. Among the azo dyes, the commercial dyes are used the most widely. When these dyes are released directly into the environment, it will cause several ecological problems in the nature. Moreover, the

stronger colour of textile wastewaters have higher chemical oxygen demand (COD) (Behnajady et al., 2008).

2.1.1 Characteristic of Harmful Dye

The large amount of the intense colour and toxicity wastewater are involving dyestuffs in dye production and textile manufacturing processes, which can be advanced into aquatic systems (Khataee et al., 2009). This study was focused on dyeing textile because dyeing industries use approximately 10000 dyes and pigments that can be produced 7 x 10^5 ton per year (Daneshvar, Aber, & Hosseinzadeh, 2008). In manufacturing or processing, dyes advance an important source of contamination, considering that approximately 15 % of the synthetic textile dyes are lost in waste streams and also perform about 50 % of the worldwide production (Petrou et al., 2013). Due to the dyeing process, 1-20 % of the total worldwide dyes production is disappearing and also remitting in the textile effluents. Those releasing coloured wastewater is a significant source of non-aesthetic pollution, and eutrophication in the environment and can cause dangerous by-products through oxidation, hydrolysis, or other chemical reactions occurred in the wastewater phase (Konstantinou & Albanis, 2004).

Dyes are represented an increasing environmental danger, which is an abundant class of coloured organic compounds. In dye production and textile manufacturing processes, a large amount of wastewater, including dyestuffs with concentrated colour and toxicity can be introduced into aquatic systems. The conventional biological treatment methods are limited for decolourization and degradation because of the large

degree of aromatics contain in these molecules and the stability of modern dyes (Wang, 2000). Dyes are released from the textile industry, photocatalytic industry, coating industry, and photochemical application, respectively. Coloured wastewater treatment from textile or other industries is a serious issue because many researchers interested about this research for several years ago (Sohrabi & Ghavami, 2008). Dye pollutants are an important source of environmental pollution which released from the textile industry. These effluents are certainly toxic, non-biodegradable and resistant to destruction by physical-chemical treatment methods (Daneshvar et al., 2003). Moreover, textile and other industrial dyes contain one of the largest groups of organic compounds, which perform an increasing environmental danger (R.-S. Juang, Lin, & Hsueh, 2010).

2.1.2 Azo Dye

Azo dyes are the class of coloured organic compounds which can be easily collected from textile, papers and cosmetics industries (Wawrzyniak et al., 2006). Moreover, azo dyes can be classified by mono azo, diazo, tri azo classes that was found in many types such as acid, basic, direct, disperse, azoic, and pigments, respectively (Konstantinou & Albanis, 2004). Azo dyes are characterized by the existence of one or more azo bonds (–N=N–) which are an abundant class of synthetic, coloured, organic compounds (Maria Stylidi et al., 2003). The azo group is attributed to benzene or naphthalene groups and it was involved different substituents such as chloro (–Cl), methyl ($–CH_3$), nitro ($–NO_2$), amino ($–NH_2$), hydroxyl (–OH), and carboxyl (–COOH), respectively. The different substituents are supported to obtain the different types of azo dyes (R.G. Saratale, Saratale, Chang, & Govindwar, 2011). Besides, various industries

such as textile, paper, leather, ceramic released more than 50 % of azo dyes and it is assigned to one or more azo bonds (–N=N–) (Sahoo, Gupta, & Pal, 2005).

Wastewater drained from the textile industry is caused the major sources of aromatic amines into the environment. The worldwide production of textile dyes was 280,000 tons by annually because it was more than 10,000 dyes used in textile industry (Tantak & Chaudhari, 2006). Many industries (textile, leather, plastics, paper, food and cosmetics) drain the high amount of water and subsequently came out high volumes of wastewater in dying process. Mostly, wastewater is rich in colour and also contains different dyes. More than one million tons of dyes, especially azo dyes, are obtained every year in worldwide (Divya et al., 2013). About 15% of worldwide production of azo dyes is lost due to the evaluation within synthesis and processing. About half of the textile dyestuffs; large quantities of azo dyes, is produced by worldwide and used in an applications advance. The increased public related to these environmental pollutants and the stringent international environmental standards (ISO 14001, October 1996) have notified to develop the novel treatment methods for transferring organic contaminants, such as dye-containing effluents, to harmless compounds (Maria Stylidi et al., 2003).

The largest group of synthetic dyes is azo dyes and it can be produced 70% of commercial dyes. The connection of highly substituted aromatic rings is characterized by one or more azo group because of their chemical structures. The conventional wastewater treatment processes do not degrade due to the molecules recalcitrant which formed by the substituted ring structures instruction. These dyes occurred both impart colours to water sources and damage living organisms by stopping the re-oxygenation

capacity of water, blocking sunlight, and therefore disturbing the natural growth activity of aquatic life because of releasing into the environment (City, 2010).

2.1.3 Classification of Azo Dye

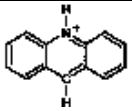
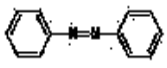
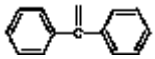
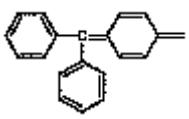
In the ecosystem, dyes release as wastewater is a dramatic source of aesthetic pollution, eutrophication, and perturbations in aquatic life which are important organic pollutants (Zhu, et al., 2010). Azo-aromatic groups are highly dispersible pollutants which involved in dyes. Moreover, they assign and correspond to water toxicity and become increasing danger to the environment and human beings. These effluents discharged to the environment is a considerable source of non-aesthetic pollution since the presence of low concentrations of dyes is visible by completely and also released to various industries such as textile, paper, leather, food are known to be toxic, carcinogenic, mutagenic, teratogenic (Abramian & El-Rassy, 2009a).

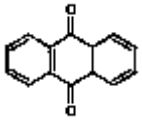
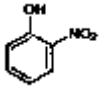
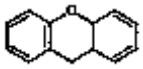
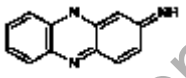
Azo dyes can be formed more than 10,000 dyes, which serve the main group (60–70%) in wastewater which are one of the oldest industrially synthesized organic compounds. The dyes removed colour due to cleavage of the azo bond (–N=N–) which reducing equivalents from an external electron donor (biologically or chemically generated) are transferred to the dye. The formation of aromatic amines, which usually cannot be metabolised anaerobically because of producing the hydroxyl and carboxyl groups that can be fully degraded under methanogenic conditions in the reduction of the azo dyes system (Brás, et al., 2005). Stylidi, et al., (2003) who reported that by having an azo group consisting of two nitrogen atoms which constitute the largest and most important class of commercial dyes used in textile industry. Azo dyes are characterized

by nitrogen to nitrogen double bonds (N=N), that are mostly concerned with the aromatic groups (benzene or naphthalene rings) (M. a. Rauf, Meetani, & Hisaindee, 2011).

The discharge of azo compounds into water streams is defective due to their colour and many azo dyes have become several ecological and environmental problems, because of their toxic, non-biodegradation and potentially carcinogenic (Yang, et al., 2011). Among the classification of dyestuffs, azo-dyes are the most generally utilized and recalcitrant dye, which has been released to produce potential carcinogenic products by reduction under anaerobic conditions (Sun, et al., 2011). Dyes can be divided into various classes such as acridine dyes, azo dyes, arylmethane dyes, anthroqinone dyes, nitro dyes, xanthenes dyes, and quinine–amine dyes, respectively. Table 2.1 showed that the structures of various types of dyes (Rauf et al., 2011).

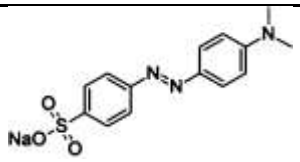
Table 2.1: Classification of dyes based on molecular structure (Rauf et al., 2011)

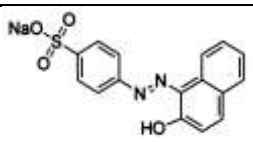
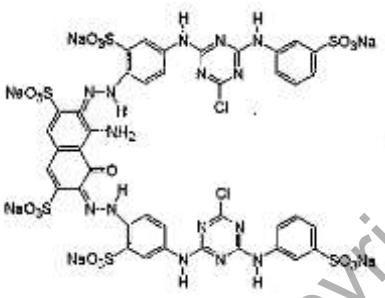
Class	Structure
Acridine	
Azo	
Diarylmethane	
Triarylmethane	

Anthroqinone	
Nitro	
Xanthene	
Quinone-imine	

Azo-dyes have various types, such as direct, acid, base, reactive, disperse, metal- complexes, mordant and sulfur dyes (Ay, Catalkaya, & Kargi, 2009). Based on the number of azo groups in the molecule, azo dye was divided into mono azo (Methyl Orange, Acid orange 7, and etc.) and diazo (Reactive Green 19 and so on.) in this study. Table 2.2 summarized the representative example of mono azo dyes and di azo dye (Rauf et al., 2011).

Table 2.2: Representative example of mono azo dyes and di azo dye (Rauf et al., 2011)

Type	Representative Dye	Structure
Mono azo	Methyl Orange	

Mono azo	Acid Orange 7	
Diazo	Reactive Green19	

Methyl Orange (MO) is a water soluble azo dye that is widely used for textile, printing, paper, pharmaceutical, and food industries and also used as a model dye for studying the effectiveness of UV/H_2O_2 process on the decolorization of dye industrial wastewater (Haji, et al., 2011). The molecular formula of MO was $C_{14}H_{14}N_3NaO_3S$ with the maximum absorption peak (λ_{max}) at 460 nm and the molar mass was 327.3 g/mol. MO is a pH indicator (at pH 3.0(pink) – pH 4.4(yellow)) which was frequently used in titration because it can be easily to recognize the changes of colour. MO was possessed the mutagenic properties because the MO solution was transferred to red colour when its molecule absorbs blue-green light solution. Moreover, MO solutions was changed to yellow colour in alkaline solution (Ocholi et al., 2016).

Acid Orange 7 (AO7) or Orange II can soluble in water, which is a mono azo acidic dye (Daneshvar, et al., 2008). The molecular formula of AO7 was $C_{16}H_{11}N_2NaO_4S$ with the maximum absorption peak (λ_{max}) at 484 nm and the molar mass was 350.32 g/mol. AO7 is not only the representative of a textile type of pollution but also a model compound commonly used for the photodegradation of dyes (Bauer,

Jacques, & Kalt, 1999; Akazdam, Chafi, Yassine, & Gourich, 2017). AO7 has a high photo and thermal stability, which is modified the aquatic life seriously due to the carcinogenic and mutagenic that dye is also one of the organic compounds found in the textile wastewaters (Divya et al., 2013).

Reactive Green 19 (RG19) is reactive dyes and it was using the representative dyes for reactive dyes because it has two azo groups as the chromophoric moiety and two chlorotriazine groups as reactive (Guaratini, Fogg, & Zanoni, 2001). The molecular formula of RG19 is $C_{40}H_{23}C_{l2}N_{15}O_{19}S_6.6Na$ with the maximum absorption peak (λ_{max}) at 630 nm and the molar mass is 1,418.92 g/mol (Zuorro & Lavecchia, 2014). RG19 has six sulfonate groups, one primary and four secondary amino groups, respectively (Yilmaz, Bayramoglu, & Arıca, 2005). RG19 is extensively used in the textile industry because the colour of RG 19 is bright and also its excellent wash and light fastness properties (Zuorro et al., 2013). Moreover, reactive dyes are widely used in textile dyeing because of their superior fastness to the applied fabric, high photolytic stability and recalcitrant to microbial degradation. Reactive dyes perform low levels of addiction with the fiber and up to 10–50 % of total dye used in dying process (Saratale, et al., 2009). Many azo dyes and their cleavage products investigated that toxic to aquatic life, mutagenic/carcinogenic and gentoxic. For this reason, reactive dyes are in the great concern with protecting the water ecosystem (Essawy, Ali, & Abdel-Mottaleb, 2008).

2.2 Wastewater Treatment Methods

The water resource is one of the most important resources for human beings, additionally animals and plants. The released of highly coloured wastewater into the

ecosystem contains aesthetic pollution, which is even a small amount of dye is clearly apparent, and environmental problems are acting as the confusion of aquatic life that are some azo dyes and degradation products are highly carcinogenic (Aguedach, Brosillon, Morvan, & Lhadi, 2008).

The contaminants in a water stream have become an important character of worldwide affair when the developing amounts of chemical pollutants due to the potential health hazards associated with the entry of these compounds into the food chain of humans and animals. Moreover, the possible human health implication occur with the use of these water transfers to drinking-water are mostly hard to assess. The development of effective water treatment processes activated efforts by increasing public concerns and environmental regulations over the presence of recalcinant micro-pollutants in water (Vega, Keshmiri, & Mohseni, 2011). Hence, water consumption and pollution demand the consistent of a wastewater treatment, which could be indirectly amplified (Zahraa et al., 2006). Many researchers are finding to remove pollutants, impurities and to obtain the decolorization of dyehouse effluents by using the proper treatments (Khataee et al., 2009)

Another treatment methods for the removal of dyes in wastewater are physical, chemical and biological processes, such as adsorption, coagulation, oxidation, reduction, filtration, and biological treatment (Abramian & El-Rassy, 2009a). Each method has its own advantages and disadvantages. However, the advanced oxidation processes (AOPs) which is an alternative to conventional methods built not only the generation of very reactive species such as hydroxyl radicals, which have been offered

to oxidize rapidly, but also non-selectively a broad range of organic pollutants (Khataee et al., 2009).

Among the various AOPs, heterogeneous photocatalysis is an attractive method, which has been advised for the treatment of recalcitrant compounds, involves in industrial wastewaters such as dyestuffs and it has been successfully utilized for the degradation of various families of organic pollutants. The photocatalytic process (under solar radiation) is the most useful process which is the environmentally ideal energy source (Maria Stylidi et al., 2003).

2.2.1 Physical Process

There are various physical methods in decolourization, such as precipitation, adsorption, filtration, and reverse osmosis (Sohrabi & Ghavami, 2008). The flocculation, reverse osmosis, membrane filtration and adsorption on activated charcoal are simply transferring the pollutants to other media because of the non-destructive and also secondary pollution will be formed when they transfer organic compounds from water to another phase (Sahoo et al., 2005). The traditional physical techniques (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, and ion exchange on synthetic adsorbent resins) can generally be used efficiently for the removal of dye pollutants. The expensive operations, such as the regeneration of the adsorbent materials and post-treatment of solid-wastes, are needed in this process (Konstantinou & Albanis, 2004).

However, physical process is expensive but it can be studied with many low-cost adsorbents such as sugar cane dust, perlite (a glassy volcanic rock), bagasse pith, sludge, fly ash, coal and natural clay can be used as alternative adsorbents for removing dyes from aqueous solutions. Moreover, the adsorption was performed an important role in wastewater treatment processes. The adsorption process can be used as a promising technique for the removal of contaminants with the selection of a proper adsorbent. Besides, activated carbon has been widely used as an adsorbent for the removal of various pollutants because it has high adsorption capacity.

2.2.2 Chemical Process

Many processes such as reduction, oxidation, complex metric methods, ion exchange and neutralization contains in chemical methods of dye removal. Strong oxidants such as chlorine or ozone has caused more successful results in chemical treatment, but they are not economically viable because of high dosage requirement (Sohrabi & Ghavami, 2008). On the other hand, the environment has been remained the serious problem due to the releasing of chlorinated organic compounds. Ozonation is a very cleaner process, but its needed on-site preparation because of its variety that the preparation contains significant important costs (S. Kaur & Singh, 2007b). Chlorination and ozonation are used for the certain dyes removing but they have usually high operating costs and limited effect on carbon content in slower rates (Konstantinou & Albanis, 2004).

AOPs are the most interested for the effective oxidation of a wide variety of organics and dyes which are almost depended on the photocatalytic degradation and

also the most powerful chemical method. The photocatalytic technique can be promoted as a wastewater purifier because it can be completely degraded organics into water and CO_2, without producing any harmful by-products. Moreover, this technique has been generally utilized for the photo-mineralization of a large number of dyes such as methylene blue, direct and acid dyes, azo dyes and reactive black, respectively (Jain & Shrivastava, 2008). It is found that chemical methods are not economically usable because of the production of large amounts of sludge and high dosage are necessary in this method (Sahoo et al., 2005).

2.2.3 Biological Process

The conventional biological treatment methods are inefficient for decolorization and degradation because it has a large degree of aromatic existence in dye molecules and the stability of modern dyes. Besides, the majority of dyes is only adsorbed on the sludge, but not degraded in this treatment (Konstantinou & Albanis, 2004). Because of their resistance to aerobic degradation, bio-treatment of azo dyes is limited in this process. Additionally, carcinogenic aromatic amines are accomplished by anaerobic degradation of azo dyes (Sahoo et al., 2005). For coloured effluents, these methods have not confirmed to be particularly competent. The main cause is that the dyes are absorbed onto biomass without being accurately degraded. The sludge should be separated in a sustainable manner because the pollution transfer is no more acceptable in this method (Khataee et al., 2009).

Moreover, these methods are ineffective to complete removal of colour and degradation of organics and dyes (Jain & Shrivastava, 2008). It can be organized not