

**SONOCATALYTIC DEGRADATION OF ORGANIC DYE IN THE
PRESENCE OF TiO₂ PARTICLES**

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**A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Engineering
(Hons.) Chemical Engineering**

**Faculty of Engineering and Science
Universiti Tunku Abdul Rahman**

May 2016

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

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SONOCATALYTIC DEGRADATION OF ORGANIC DYE IN THE PRESENCE OF TiO₂ PARTICLES

ABSTRACT

Sonocatalytic degradation of Methylene Blue, Methyl Orange and Rhodamine B in a 40 kHz, 124 W ultrasonic bath was carried out in the presence of titanium dioxide (TiO₂) catalyst. Rhodamine B showed the highest degradation efficiency because it has a relatively larger molecular weight than Methylene Blue and Methyl Orange. The catalysts were subjected to heat treatment from 200 °C to 800 °C for 2 hours to promote phase change in the catalyst and were characterised by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). XRD confirmed that phase change occurred from anatase to rutile phase at 800 °C heat treatment temperature whereas SEM showed that catalysts started to undergo aggregation when the heat treatment temperature was raised to 600 °C. TiO₂ that has more anatase phase showed higher degradation efficiency than TiO₂ with less anatase phase.

The effect of initial dye concentration, catalyst loading, pH and hydrogen peroxide (H₂O₂) concentration on the sonocatalytic activity were carried out at 2.5 mg/L to 12.5 mg/L, 0 g/L to 2.0 g/L, pH 2 to pH 10 and 0.5 to 2.5 mmol/L respectively. The optimum operating conditions discovered are 7.5 mg/L initial dye concentration, 1.0 g/L catalyst loading, pH 8 solution and 1.5 mmol/L H₂O₂ concentration, which successfully removed 75.08 % of Rhodamine B in 60 mins. The sonocatalytic reaction follows the pseudo-first order rate kinetics and the degradation efficiency of the reused catalyst were 56.87 % and 35.72 % in the subsequent usage.

TABLE OF CONTENTS

DECLARATION	i
APPROVAL FOR SUBMISSION	ii
ACKNOWLEDGEMENTS	iv
ABSTRACT	v
TABLE OF CONTENTS	vi
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF SYMBOLS / ABBREVIATIONS	xii

CHAPTER

INTRODUCTION	1
1.1 Global Water Pollution from Textile Industry	1
1.2 Water Pollution in Malaysia	2
1.3 Environmental Impacts of Dyes	4
1.4 Types of Industrial Dye	5
1.5 Problem Statement	7
1.6 Objectives	8
1.7 Scope of Study	9
 LITERATURE REVIEW	 10
2.1 Various Textile Dyeing Wastewater Treatment Methods	10
2.1.1 Physicochemical Methods	10

2.1.2	Membrane Filtration	11
2.1.3	Biological Wastewater Treatment	12
2.1.4	Advanced Oxidation Processes (AOPs)	12
2.2	Theory of Ultrasound	13
2.2.1	Sonochemistry	15
2.2.2	Ultrasonic Reaction Systems	16
2.2.3	Heterogeneous Sonocatalytic Process	18
2.3	Characterization of TiO ₂ catalyst	21
2.4	Parameter Studies	22
2.4.1	Effect Ultrasonic Irradiation on Different Dyes	22
2.4.2	Effect of Heat Treatment of TiO ₂	23
2.4.3	Effect of Initial Dye Concentration	24
2.4.4	Effect of Catalyst Dosage	24
2.4.5	Effect of Initial pH	25
2.4.6	Effect of H ₂ O ₂ Concentration	26
2.5	Reusability Study	27
2.6	Kinetic Study	27

METHODOLOGY **31**

3.1	Materials and Chemicals	31
3.2	Equipments	32
3.3	Overall Research Flow	33
3.4	Experimental Set-up	34
3.5	Experimental Procedures	35
3.5.1	Catalyst Preparation	35
3.5.2	Preparation of Organic Dyes	35
3.5.3	Characterization of Catalyst	35
3.5.4	Parameter Studies	36
3.6	Reusability Study	39
3.7	Kinetic Study	39
3.8	Liquid Sample Analysis	39
3.8.1	UV-Vis Spectrophotometry	40
3.9	Gantt Chart	40

4	RESULTS AND DISCUSSION	42
4.1	Characterizations of TiO ₂ powders	42
4.2	Adsorption and the Effect of Ultrasonic Irradiation on Degradation of Different Dyes	45
4.3	Parameter Studies in Sonocatalytic Process	47
4.3.1	Effect of Heat Treatment of TiO ₂ catalyst	47
4.3.2	Effect of Initial Dye Concentration	49
4.3.3	Effect of Catalyst Loading	50
4.3.4	Effect of Initial Solution pH	52
4.3.5	Effect of H ₂ O ₂ Concentration	53
4.3.6	Reusability of TiO ₂ catalyst	54
4.4	Kinetic Study	55
4.5	Possible Mechanisms for Sonocatalytic Degradation of Rhodamine B	57
5	CONCLUSION	58
5.1	Conclusion	58
5.2	Recommendations	59
	REFERENCES	60
	APPENDICES	65

LIST OF TABLES

TABLE	TITLE	PAGE
1.1	Malaysia Sewage and Industrial Discharge Standards	3
1.2	Industrial Classification of Dyes	7
2.1	Various Research Done on TiO ₂ as the Sonocatalyst	19
3.1	Name, brand and purity and purpose of chemical reagents	31
3.2	Model and functions of instruments	32
4.1	Weight ratio of anatase and rutile phase in various heat treated TiO ₂ powder	42
4.2	Chemical Structure, Type and Molecular Weight of Rhodamine B, Methylene Blue and Methyl Orange	45
4.3	Apparent Rate Coefficients and Regression Constants for the Sonocatalytic Degradation of Rhodamine B	57

LIST OF FIGURES

FIGURE	TITLE	PAGE
1.1	River Water Quality Trend, 2005-2013	2
2.1	Process of bubble formation, growth and collapse after a few acoustic cycle	14
2.2	Growth and implosion of cavitation bubble under ultrasonic irradiation	14
2.3	(a) Reaction zones in the cavitation process	17
2.4	Photocatalytic oxidation of organic molecule	21
2.5	(a) Equilibrium of azo dyes towards the interface before the bubble collapses (b) Sonolysis of azo dyes after the bubble collapses. (-N=N -) refers to azo dye	29
3.1	Overall Flow Diagram of the Research	33
3.2	Experiment Set-up	34
3.3	FYP 1 Schedule	40
3.4	FYP 2 Schedule	41
4.1	XRD patterns for untreated and heat treated TiO ₂ powders	43
4.2	SEM Images (a) Untreated of TiO ₂ Powder and 2 Hours of Heat Treatment at, (b) 200 °C, (c) 400 °C, (d) 600 °C, (e) 800 °C	44
4.3	Adsorption and Sonolysis Efficiencies of Various Dyes on TiO ₂ Powder (Initial Dye	

	Concentration = 10 mg/L, TiO₂ Loading = 1.0 g/L, pH = 6, Reaction Time = 60 minutes)	46
4.4	Effect of Heat Treatment of Catalyst on the Sonocatalytic Degradation of Rhodamine B (Initial Dye Concentration = 10 mg/L, pH = 6, Catalyst Loading = 1 g/L, Reaction Time = 60 minutes)	48
4.5	Effect of Initial Dye Concentration on the Sonocatalytic Degradation of Rhodamine B (pH = 6, Catalyst Loading = 1 g/L, Reaction Time = 60 minutes)	49
4.6	Effect of TiO₂ Catalyst Loading on the Sonocatalytic Degradation of Rhodamine B (Initial Dye Concentration = 7.5 mg/L, pH = 6, Reaction Time = 60 minutes)	51
4.7	Effect of pH on the Sonocatalytic Degradation of Rhodamine B (Initial Dye Concentration = 7.5 mg/L, Catalyst Loading = 1 g/L, Reaction Time = 60 minutes)	52
4.8	Effect of pH on the Sonocatalytic Degradation of Rhodamine B (Initial Dye Concentration = 7.5 mg/L, pH = 8, Catalyst Loading = 1 g/L, Reaction Time = 60 minutes)	54
4.9	Degradation Efficiency of Fresh and Reused TiO₂ Catalysts (Initial Dye Concentration = 7.5 mg/L, pH = 8, Catalyst Loading = 1 g/L, H₂O₂ Loading = 1.5 mmol/L, Reaction Time = 60 minutes)	55
4.10	Reaction Kinetics Graph for Sonocatalytic Degradation of Rhodamine B (Initial Dye Concentration = 7.5 mg/L, pH = 8, Catalyst Loading = 1 g/L, Reaction Time = 60 minutes)	56

LIST OF SYMBOLS / ABBREVIATIONS

C_0	Initial dye concentration of organic dye (mg/L)
C_t	Concentration of organic dye at time t (mg/L)
I_A	Diffraction intensity of anatase phase
I_R	Diffraction intensity of rutile phase
k	Apparent rate constant for the reaction between azo dyes and radicals (mg/L/min)
K	k_1/k_2 , the equilibrium constant of azo dyes diffusing into the interfacial region (L/mg)
k_{app}	Apparent rate constant (min^{-1})
k_1	Rate constant for absorption (min^{-1})
k_2	Rate constant for desorption (mg/L/min)
r	Rate of degradation (mg/L/min)
t	Time (min)
β_A	Proportion of anatase phase
β_R	Proportion of rutile phase
θ	ratio of azo dyes occupied in the effective reaction site
AOP	Advanced oxidation process
BOD	Biological oxygen demand
COD	Chemical oxygen demand
PZC	Point zero charge
SEM	Scanning electron microscopy
TiO ₂	Titanium dioxide
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Global Water Pollution from Textile Industry

One of the most urgent problems on Earth these days is environmental pollution due to human activities. Industrial activities have always been contributing to pollution by generating large amount of wastewater into natural water streams. The textile industry for instance, consumes large quantity of water and produces a huge amount of contaminants which is mainly made up of dyes. Over 280 000 tonnes of textile dyes are discharged into the environment without proper treatment every year (Pereira & Alves, 2012). Dyes that did not bind to the fabric during the dyeing stage are released into the effluent stream. It was estimated that the amount of dye being discharged in wastewater stream varies from 2 % for basic dyes to 50 % for reactive dyes depending on the type of the dye, which results in the contamination of surface and groundwater around the factory (O'Neill, et al., 1999). Almost 1 million ton of synthetic dyes are produced every year and it is estimated that around 100 000 to 150 000 tons of the produced dyes goes into the environment (Zoellinger, 2001).

The textile industry contributes a lot to the economy of Asian countries, especially in countries like China and India. After the termination of the Agreement on Textile and Clothing, the trade in textile and clothing is no longer subjected to quotas. As a result, textile industry in China and India bloomed due to the lower wage rate in those two countries (Martin, 2007).

1.2 Water Pollution in Malaysia

It is undeniable that the industrial development in Peninsular Malaysia has contributed to the overall economic development of the country by generating job opportunities and catalysing the socio-economic and infrastructural development. However, it also brings adverse effects on the environment of the country. Industrial effluents that contain heavy metals, organic compounds, phosphorous, suspended solids, colour and other compounds are discharged into river streams.

According to Figure 1.1, the number of rivers that are clean has slightly decreased from 368 to 275 since the year 2007 while the number of slightly polluted rivers increases from 150 to 175 since the year 2011. The number of polluted river has decreased from 74 to 25 since 2010. This could be due to the result of more stringent environmental regulations imposed by the government on the factories in Malaysia. The sewage and industrial discharge standards are shown in Table 1.1.

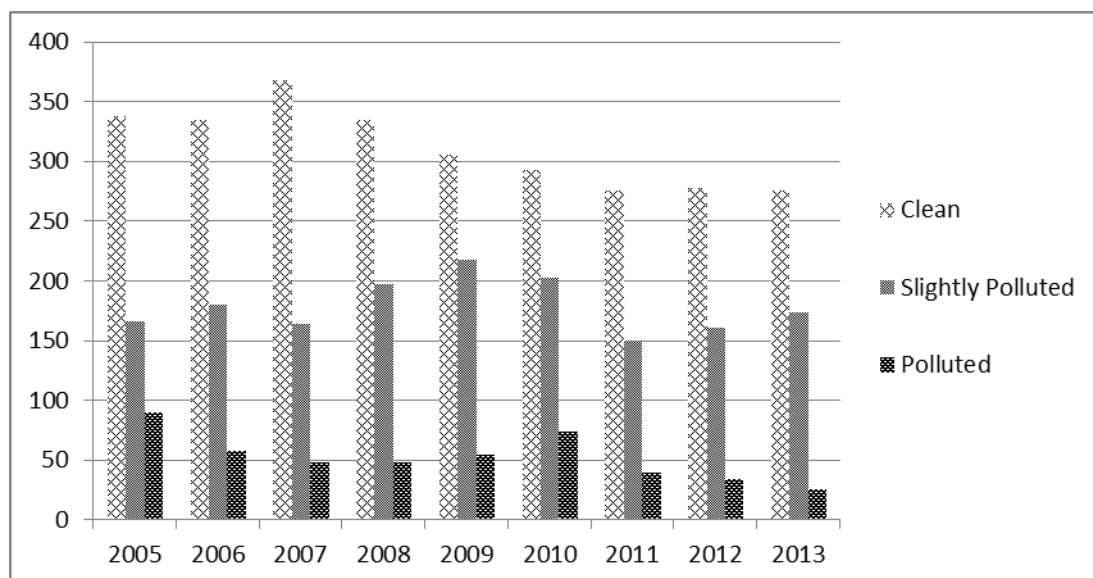


Figure 1.1: River Water Quality Trend, 2005-2013 (Department of Environment, 2014)

Table 1.1: Malaysia Sewage and Industrial Discharge Standards (Department of Environment, 2010)

Parameter	Unit	Standard	
		A	B
Temperature	°C	40	40
pH Value		6.0-9.0	5.5-9.0
BOD ₅ at 20°C	mg/L	20	50
COD	mg/L	50	100
Suspended Solids	mg/L	50	100
Mercury	mg/L	0.005	0.05
Cadmium	mg/L	0.01	0.02
Chromium, Hexavalent	mg/L	0.05	0.05
Arsenic	mg/L	0.05	0.1
Cyanide	mg/L	0.05	0.1
Lead	mg/L	0.10	0.5
Chromium, Trivalent	mg/L	0.20	1.0
Copper	mg/L	0.20	1.0
Manganese	mg/L	0.20	1.0
Nickel	mg/L	0.20	1.0
Tin	mg/L	0.20	1.0
Zinc	mg/L	1.0	1.0
Boron	mg/L	1.0	4.0
Iron	mg/L	1.0	5.0
Phenol	mg/L	0.001	1.0
Free Chlorine	mg/L	1.0	2.0
Sulphide	mg/L	0.5	0.5
Oil and Grease	mg/L	-	10.0

Standard A applies to discharges into inland waters that are located within catchment areas as listed in the Third Schedule whereas Standard B is applicable to any other Malaysian waters.

In Malaysia, synthetic textile fiber is a very popular and important industry especially in West Malaysia. Approximately 400 000 tons of man-made fiber such as staple, nylon, etc. is produced each year and in the year 2008, the man-made fiber produced in Malaysia made up to 1.03 % of the global production (Pang & Abdullah, 2013). In the year 2013, the textile industry became Malaysia's 9th largest export earner with a total export of RM 10.3 billion. Under the Third Industrial Master Plan, the textile industry in Malaysia is expected to gain a tremendous growth in export (Malaysian Investment Development Authority, 2014).

The main source of water pollution in Malaysia is sewage treatment plants, manufacturing industry, agricultural industry and animal farming. Of all the wastewater generated, textile finishing wastewater makes up to 22 vol % of the total industrial wastewater generated in Malaysia (Pang & Abdullah, 2013). According to them, the wastewater generated by textile industry which contains either organic or synthetic dyes has been increasing tremendously from 744 tons in 2007 to 1559 tons in 2009 and the consumption of water can reach up to 3000 m³ every day.

1.3 Environmental Impacts of Dyes

Different dyes have different degree of fixation to fibers. The degree of fixation of dyes is different based on the type of fibre, shade and dyeing parameters. To approximate the amount of dyes released after processing into the wastewater stream, factories often use the dye fixation rate values. These losses are less than 2 to 10 % for direct, disperse and basic dyes. However, it could achieve up to 50 % for reactive dyes. Reactive dyes can be hydrolysed to form dyes that have no or very low affinity to the fibres, resulting in the drop of the fixation ability of dyes and the dyes are washed into wastewater streams (Hao, et al., 2000). However, they are gaining popularity due to a better shade and dyeing parameters.

Being a recalcitrant pollutant, organic dye remain in the environment for a long time and they affect aquatic organisms living in the water where industrial effluents are discharged. Organic dyes adsorb and reflect sunlight penetrating into rivers. As a result, photosynthetic activities of aquatic plants are disrupted which in turn affects the food chain in the river. Besides that, dyes discharged into rivers will form a thin layer over the surface of water (Pereira & Alves, 2012). They decrease the level of dissolved oxygen in the water which further affects the marine organisms living in the receiving water. Organic dyes also increase the biological oxygen demand (BOD) and chemical oxygen demand (COD) of water.

Another important reason to remove organic dyes from water is to remove the toxicity of water. Living organisms that are exposed to organic dyes face the risk of

getting either acute or chronic health effects depending on how long it has been exposed and the concentration of the dye. It was estimated that about 10 % of dyes that were manufactured in the world end up in the environment through industrial effluent streams (O'Neill, et al., 1999).

Throughout the wet-processing steps, toxic compounds are often used which will harm aquatic life. The toxic compounds include heavy metals, surfactants, detergents for fabric rinsing & washing and additives which include sodium sulphate, salt and sulphuric acid. Dyeing bath is often carried out in extreme pH conditions of either alkaline or acidic and at a high temperature. This produces wastewater streams that have high COD & BOD, suspended solid and toxic organic compounds. Even though regulations have been set, some factories still failed to comply with the discharge limits (Pang & Abdullah, 2013).

Azo dyes make up the largest group of synthetic dyes and they are one of the most commonly used industrial dyes. Subsequently, they are also the most commonly found synthetic dyes that are discharged into the environment (Pereira & Alves, 2012). When azo compounds undergo anaerobic reduction, aromatic products which can be harmful are formed. Scientists have found a relationship between this to bladder cancer because an increased number of bladder cancer has been reported on dye workers that were exposed to huge quantity of azo dyes (Puvaneswari, et al., 2006). Azo dyes have the tendency to cleave reductively to generate aromatic amines, which are carcinogenic (Chequer, et al., 2011).

1.4 Types of Industrial Dye

In the industry, dyes are usually classified based on their usage and their chemical properties. Table 1.2 shows the type of dye, a brief description of the dye and its application in the industry.

The first type of dye is acid dyes. They contain sulfonic or carboxylic acid salt functional group. They have to be used in an acid solution because they need the

positive charge developed within the fiber in the acid solution to act as the driving force to improve the diffusion of dye into the fiber. Fibers that develop positive charge in acid solution like wool, silk, nylon and protein fibers can be easily dyed by acid dyes. Basic dyes are also called cationic dyes and they usually contains amine derivatives. Unlike acid dyes, cationic dyes are attracted to negative charges in fibers. Application of the dye includes dyeing protein, cellulosic fibers nylon (Hunger, 2003).

Solvent dyes are insoluble in water but soluble in organic solvents. They lack polar solubilizing groups like carboxylic acid, quaternary ammonium and sulphonic acid. They are usually used to make printer inks and pigments. Direct dyes are water-soluble anionic dyes and they are often used in dyeing cellulosic fibers, nylon and cottons. They often require post-treatments such as chelation with metal salts to enhance the dyeing properties (Pereira & Alves, 2012).

Disperse dyes are mostly applied to hydrophobic fibers because they are water-insoluble. They are frequently used on polyester and they require a very high temperature dyebath. Reactive dyes are dyes that form covalent bonds with the fiber it is applied to. It produces very good dyeing properties on cotton and the dyeing process is very simple (Hunger, 2003).

Sulphur dyes are applied to cotton together with sodium sulphide as the reducing agent in an alkaline bath. They are very cheap and the dyeing properties are very good, which makes the dye very attractive economically. They are usually used in dyeing cellulosic fibers and cotton. Lastly, vat dyes are insoluble in water and they are also applied mostly onto cellulosic fibers and cottons.

Table 1.2: Industrial Classification of Dyes (Hunger, 2003)

Dye Type	Description	Application
Acid	Water soluble, surface affinity depends on salt formation of anionic and cationic groups, uses acid dye bath	Silk, paper, wool, leather
Basic	Water soluble, surface affinity depends on salt formation of anionic and cationic groups, uses basic dye bath	Silk, paper, cotton, wool
Solvent	Insoluble in water, toxic, fibre has to be pre-treated for the dye to have better affinity	Printer inks, pigments
Direct	Uses alkaline dyebath	Cellulosic fibre, nylon, cotton
Disperse	Water soluble, dyebath is required to be high in temperature	Polyester
Reactive	Very permanent dye, chromophore reacts directly with substrate	Cellulosic fibre
Sulphur	Usually dark in colour	Cotton, cellulosic fibre
Vat	Insoluble in water, cheap	Cotton, cellulosic fibre

1.5 Problem Statement

Having an access to safe potable water is essential in order for people to survive. As the human population on Earth grows, the demand for clean water also increases. The World Health Organisation (WHO) approximated that nearly 748 million people have no access to potable water even though various efforts have been carried out to provide water supply to people living in rural areas (World Health Organisation, 2014).

On the other hand, industrial activities have dramatically increased and large amount of industrial wastewater is being generated every day. Even though legislative regulations have been set up by countries of the world, industrial wastewater that contains pollutants above the permissible value is still being

discharged into the environment every day. This contradicts with the effort of WHO and many other Non-Governmental Organisations (NGOs) to provide clean safe drinking water to everyone in the world.

However, industrial growth is inevitable as it contributes to the profit of a country, creates job opportunities and satisfies the demand of the people on Earth. The textile industry, for instance, has generated billions in profit for our country, but it has also generated tons of pollutants such as organic dyes that end up in natural water streams. This happens because firstly, the government in Malaysia is not very strict when it comes to implementation of environmental regulations. As a result, factories have been disposing wastewater with pollutants above the allowable limit into rivers and seas illegally. On top of that, conventional wastewater treatment of organic dyes such membrane filtration could be costly and generates huge amount of sludge, which is another form of waste that has to be removed.

To overcome this problem, researchers have been searching for a better alternative and one of the alternatives is sonocatalytic degradation of organic dyes. Since this method is relatively new compared to other wastewater treatment techniques, various researches have to be carried out to identify the optimal operating conditions and maximize the potential this method holds.

1.6 Objectives

The research objectives are:

- To prepare and study the characteristics of TiO_2 catalyst used for sonocatalytic degradation such as particle size, surface morphology, phase composition and surface area.
- To measure the efficiency of sonocatalytic degradation under different conditions, such as the heat treatment TiO_2 catalyst, different initial dye concentration, amount of catalyst, pH value, and hydrogen peroxide concentration.
- To study the reusability of the catalyst.

- To study the reaction kinetic on the sonocatalytic degradation reaction of organic dyes using TiO_2 catalyst.

1.7 Scope of Study

Titanium dioxide (TiO_2) will be used as the sonocatalyst is because of its chemical stability, availability, high catalytic activity and suitable flat band potential (Zangeneh, et al., 2015). TiO_2 powder at various heat treatment temperature will be characterized by using X-ray diffraction (XRD) and scanning electron microscopy (SEM) for its composition and surface properties respectively.

After that, experiments will be carried out to determine the difference in degradation efficiency under different conditions. The effect of heat treatment temperature, initial concentration of organic dyes, initial pH values of the dye solution, the amount of TiO_2 powder used and the concentration of hydrogen peroxide will be studied. Then, a reusability study on the catalyst will be studied.

Furthermore, a suitable kinetic on sonocatalytic degradation reaction of organic dyes using TiO_2 powder will be proposed. In the end, the results obtained will help in the identification of the optimum operating parameters for sonocatalytic degradation of organic dyes using TiO_2 powder as the catalyst.

CHAPTER 2

LITERATURE REVIEW

2.1 Various Textile Dyeing Wastewater Treatment Methods

In order to find a more economic and effective method to treat textile wastewater, different methods have been developed in the last decade. The methods developed include physicochemical treatment, biological treatment and other methods.

2.1.1 Physicochemical Methods

Physicochemical wastewater treatment is one of the most commonly used methods in wastewater treatment plants especially for water which has large amount of suspended substances, even though it has a very low COD removal. A typical physicochemical treatment method is coagulation flocculation sedimentation (Wang, et al., 2011).

Coagulation destabilizes the electrostatic interactions between the molecules of water and dyes by the addition of coagulant (Allegre, et al., 2005). Usually, coagulation is used together with sedimentation or flocculation. Flocculation reagents used for the removal of dye effluents can be large, linear synthetic polymers or co-polymers such as ethylenedichloride and hexamine (Anjaneyulu, et al., 2005). The removal of colour is achieved by aggregating and sorption of dye molecules on the coagulants, forming flocs. Flocs are then removed by sedimentation.

This method is very effective in removing insoluble dyes such as disperse dyes. However, it produces a huge volume of sludge which leads to extra disposal and treatment cost (Hao, et al., 2000). Another disadvantage of this method is the high cost needed to buy chemicals for pH adjustment and precipitation.

2.1.2 Membrane Filtration

Membrane filtration utilizes a permeable or semi-permeable membrane to act as a selective barrier that only allows some components in the water to pass through while hindering the other component (Pereira & Alves, 2012). At present, the membrane separation techniques that are applied in the treatment of textile wastewater are reverse osmosis, microfiltration, nanofiltration and ultrafiltration (Wang, et al., 2011).

An advantage of using membrane filtration is that it can recover the dyes in wastewater to be reused. Besides that, it can remove almost all type of dye. Membranes can filter solutes with different molecular weight by using different pore size.

The disadvantage of this process is its high cost of labour and replacement of membrane because membranes have the tendency to be clogged and is prone to fouling (Ahmad, et al., 2002). It is economically not viable to pay high labour and energy cost to change or regenerate the membranes. On top of that, dye molecules are not destroyed but concentrated on top of the membrane, and the concentrated dyes creates new disposal problems. Therefore, membrane filtration is only suitable for lower dye concentration treatment and not a good method for industrial wastewater treatment.

2.1.3 Biological Wastewater Treatment

Biological treatment processes uses the biochemical reactions that are carried out in microorganisms or the enzymes they produce to degrade dye pollutants. Depending on the oxygen requirements of the bacteria, they are categorized into aerobic, anaerobic and facultative bacteria. Biological treatment is usually the most economical method to treat textile wastewater if compared to physical or chemical processes (Wang, et al., 2011). The disadvantages are the need for a large land area, less flexibility in operation and design, and some chemicals are toxic to the microbes (Pereira & Alves, 2012).

2.1.4 Advanced Oxidation Processes (AOPs)

Advance oxidation process (AOP) is a type of chemical treatment process created to remove organic compounds like organic dyes in water and wastewater through oxidation by hydroxyl radicals ($\bullet\text{OH}$) (Glaze, et al., 1987). AOP relies on the site generation $\bullet\text{OH}$ of highly reactive to oxidise any compound found in the wastewater. When OH radicles are formed, they react unselectively and contaminants will be efficiently broken down and converted into small molecules that is safe to be discharged into the environment in a very short amount of time. Hydroxyl radicals are usually produced using strong oxidants such as hydrogen peroxide and ozone, along with energy sources such as electrolysis, ultrasonic waves, ultraviolet light or catalysts like iron oxide and titanium dioxide.

$\bullet\text{OH}$ radicals degrade organic compounds by removing a hydrogen atom from the molecule (Hao, et al., 2000). The common degradation pathways of organic molecules by $\bullet\text{OH}$ radicals are as follows:





Where R represents hydrocarbon compound

The advantages of AOP in wastewater treatment are:

- It can eliminate organic compounds effectively rather than transferring the organic compounds into another phase.
- AOPs can be applied in many situations where a huge amount of organic contaminants are needed to be removed because of the high reactivity of OH radicles used in AOPs.
- It could remove heavy metals in the form of precipitated $M(OH)_x$, where M represents the metal and x represents the number of hydroxide molecule in the precipitate.
- Theoretically, AOPs will not produce new hazardous pollutants into the water because the complete reduction product of OH is water (H_2O) and carbon dioxide (CO_2).

2.2 Theory of Ultrasound

Recently, researchers worldwide have grown interest in the use of ultrasound to treat pollutants from wastewater (Villaroel, et al., 2014). Ultrasound is sound wave that has frequency range from 18 kHz to 10MHz with associated acoustic wavelengths of 10 – 0.01 cm (Abbasi & Asl, 2008). Ultrasonic waves consisting of compression and expansions are able to produce acoustic cavitation as shown in Figure 2.1 (Leong, et al., 2011).

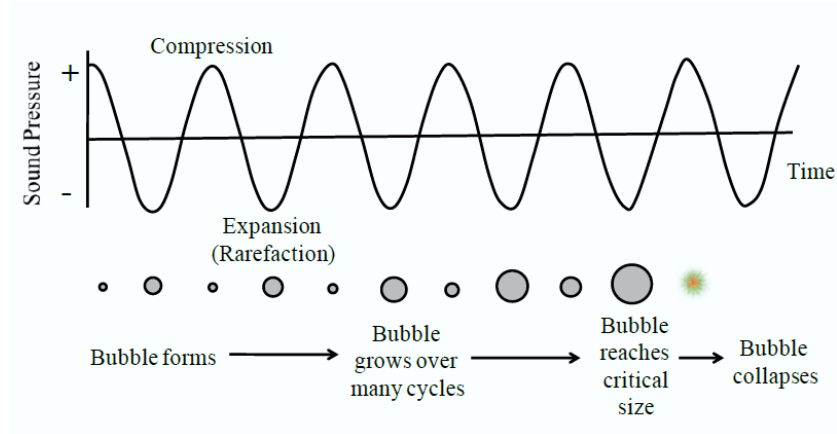


Figure 2.1: Process of bubble formation, growth and collapse after a few acoustic cycle (Leong, et al., 2011)

When cavitation bubble grows, cavitation bubbles will trap vapor of volatile species from the liquid medium until they reach their critical size before they collapse and it is represented in Figure 2.2 (Suslick, 1989). The critical size of the bubble is determined by the ultrasonic frequency. When the bubble collapses, the implosion will generate a huge amount of heat that the temperature and pressure will be increased to a few thousand degrees Kelvin and a few hundred times the atmospheric pressure (Leong, et al., 2011).

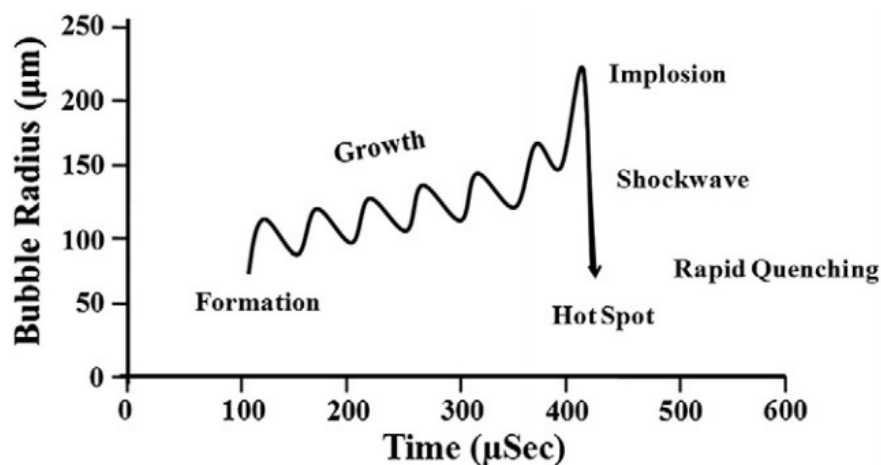


Figure 2.2: Growth and implosion of cavitation bubble under ultrasonic irradiation (Abbasi & Asl, 2008)

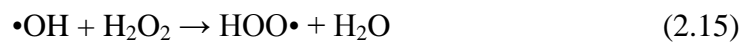
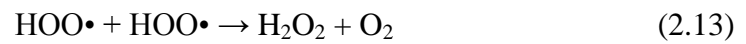
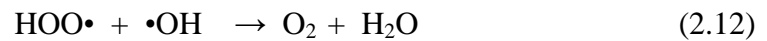
Cavitation bubbles may collapse in two different ways. If the bubbles collapse in a single acoustic cycle violently, it is termed transient cavitation whereas if the bubbles remain in their critical size for many cycles, it is termed stable cavitation (Leong, et al., 2011). The violent transient collapse of the bubble can sometimes emit light and this is called sonoluminescence. When the bubble undergoes the compression stage, the contents are heated and this excites the gas species in the bubble, resulting in the formation and recombination of excited species (Jarman, 2005). Yasui, et al. (2008) discovered that the light emitted in sonoluminescence is actually bremsstrahlung radiation that occurs in the weak ionized plasma that is formed inside the heated bubble. Bremsstrahlung radiation is produced when an electron accelerated by the collision with a neutral atom or ion.

2.2.1 Sonochemistry

Sonochemistry is the area of chemistry where chemical reactions are induced by ultrasound (Leong, et al., 2011). The cavitation induced by ultrasound can be a very useful tool in carrying out chemical reactions.

Ultrasound irradiation (sonolysis) is also accepted as a type of AOP because it generates reactive radical species by pyrolysis of water molecules during cavitation. The extreme conditions generated by a collapsing bubble leads to the formation of radical chemical species. Dissolved oxygen and water vapour in the water undergo bond rupture under such extreme conditions to produce hydroxyl and perhydroxyl radicals (Villaroel, et al., 2014). The involved chemical reactions are shown in equations (2.5) to (2.16):





Equation (2.5) to (2.9) represents the thermal dissociation of water and oxygen inside the bubble and in the interfacial region. Equations (2.9) to (2.12) show the chemical reactions that take place at the interface and in the liquid bulk by the reactive radicals. The radicals that have yet to react with the substrate will be diffused into the solution to produce hydrogen peroxide as shown in equation (2.13) and (2.14). The generated H_2O_2 can further react with $\cdot\text{OH}$ and $\cdot\text{H}$ radicals to produce more $\text{HOO}\cdot$ and $\cdot\text{OH}$ radicals via equations (2.15) and (2.16).

2.2.2 Ultrasonic Reaction Systems

In the sonolysis of liquid, there are three reaction zones associated with a cavitation bubble as shown in Figure 2.3 (Chen, 2012). The first zone is the hot spot at the center of the cavitation bubble where the temperature and pressure can reach up to

5000 K and 500 atm when the bubble collapses. In this zone, water molecules pyrolyse into $\bullet\text{H}$ and $\bullet\text{OH}$ radicals while in the gas phase. The pollutant will either undergo pyrolysis or react with $\bullet\text{OH}$ radicals.

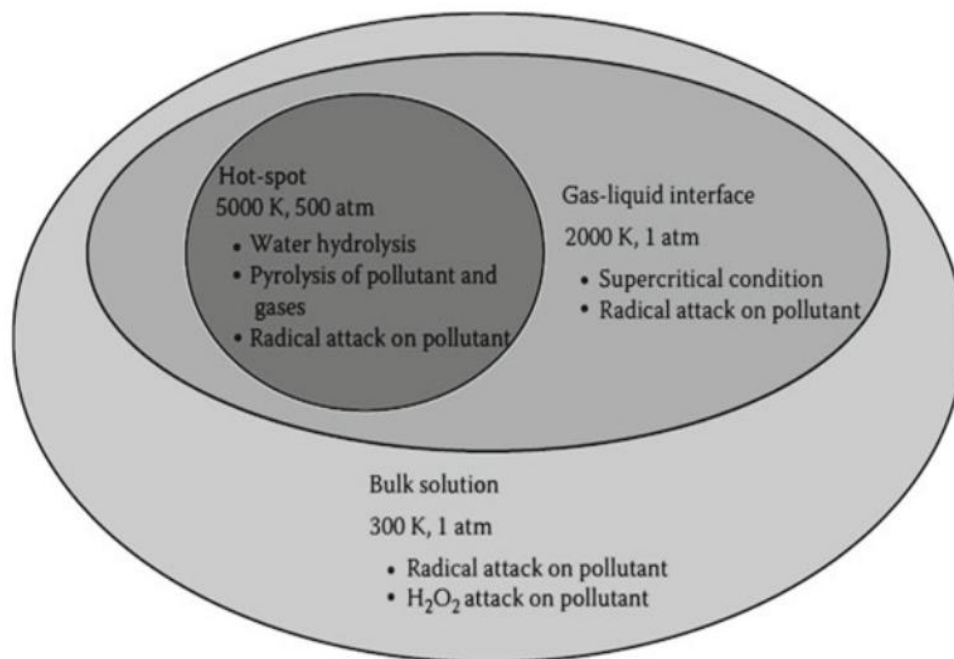


Figure 2.3: (a) Reaction zones in the cavitation process (Chowdhury & Viraraghavan, 2009)

The second reaction zone is the interfacial region between the bulk liquid and cavitation bubble where reaction in the first zone takes place but in aqueous phase. The temperature is very high in the interface but the pressure is at atmospheric pressure. In this region, $\bullet\text{OH}$ radicals would recombine to form H_2O_2 .

The third region is the bulk region. In this region, temperature and pressure are the same as the atmospheric environment. The reaction that occurs here are mostly between the pollutant H_2O_2 and $\bullet\text{OH}$.

Degradation of organic pollutants can occur via thermal decomposition which takes place inside the cavitation bubble and in the interfacial region between the bulk solution and cavitation bubble or by reactions with radicals and hydrogen peroxide at the interface and in the liquid bulk. Where the pollutants are degraded depends on

the hydrophobicity of the pollutant. If the pollutant is hydrophobic, the decomposition will take place at the interfacial region of cavitation whereas if the pollutant is hydrophilic, the decomposition will take place in the bulk solution (Son, et al., 2012).

2.2.3 Heterogeneous Sonocatalytic Process

Ultrasonic irradiation in the presence of heterogeneous catalyst was found to be a very promising method in the elimination of dyes and phenols (Nikolopoulos, et al., 2006). The presence of solid particles provides weak points for nucleation of the cavitation bubble formation and thus increasing the numbers of cavitation occurring in the reactor (Bagal & Gogate, 2014). Therefore, sonocatalysts that are present in the system could promote the process of cavitation and produce the effect of intensifying the cavitation activity in the reactor.

Titanium dioxide (TiO_2) has been used mainly in the catalysis processes to treat wastewater. This is because of its chemical stability, availability, biologically inert, low operation temperature, high chemical stability, high catalytic activity, suitable flat band potential, low energy consumption and insolubility in water under most normal conditions (Zangeneh, et al., 2015).

Titanium dioxide has also been used with ultrasound in heterogeneous sonocatalytic degradation. In a work done by Wang, et al. (2005) in which they investigated the degradation of Methyl Orange with anatase and rutile TiO_2 as the sonocatalyst, and they reported that the ultrasonic degradation of Methyl Orange was more effective and distinct in the presence of rutile TiO_2 than in anatase TiO_2 and the degradation is the least effective in conditions where no TiO_2 catalyst was added. Having catalyst such as TiO_2 in the solution increases the number of free radicals generated, therefore increasing the rate of organic pollutants degradation. Table 2.1 summarizes different research done by researchers on sonocatalytic degradation of pollutants using TiO_2 as the catalyst.

Table 2.1: Various Research Done on TiO₂ as the Sonocatalyst

No	Organic Pollutant	Catalyst	Optimum Conditions	Important Findings	References
1	Congo Red	Nanometer rutile TiO ₂ powder	30 – 40 kHz frequency; 40 – 50 W; 0.5 g/L TiO ₂ ; 50 °C; pH 3 – 5; 25 mg/L dye; 180 min	(i) Degradation efficiency with nanometer rutile TiO ₂ powder is significantly higher than ultrasound alone	(Wang, et al., 2007b)
2	Acid Red B	(i) Nanometer rutile TiO ₂ (ii) Nanometer anatase TiO ₂	40 kHz frequency; 30 W; 1.5 g/L nanometer anatase TiO ₂ ; pH 3; 10 mg/L dye; 150 min	(i) Nanometer anatase TiO ₂ shows a better degradation efficiency than nanometer rutile TiO ₂	(Wang, et al., 2007a)
3	Rhodamine B	TiO ₂ /AC	30 kHz frequency; 5 g/L TiO ₂ /AC; pH 6; 60 mins reaction time	(i) Achieved 82.21 % degradation efficiency	(Tang, et al., 2012)
4	Basic Blue 41	Nano TiO ₂	35 kHz frequency; 160 W; 0.01 g/L TiO ₂ ; 15 mg/L dye; 3 hours	(i) Addition of H ₂ O ₂ improved the degradation efficiency from 18 to 62 % (i) Pseudo-first order kinetics	(Abbasi & Asl, 2008)
5	Methyl Orange	(i) Rutile TiO ₂ (ii) Anatase TiO ₂	40 kHz frequency; 50 W; 500 mg/L rutile TiO ₂ ; 40 °C; pH 3; 150 min	(i) Rutile TiO ₂ powder has better sonocatalytic activity than anatase TiO ₂ powder (i) Recycled rutile TiO ₂ has higher activity than fresh TiO ₂	(Wang, et al., 2005)

Table 2.1: Continued

No	Organic Pollutant	Catalyst	Optimum Conditions	Important Findings	References
6	Methyl Orange	(i) Rutile TiO ₂ powder (ii) Transition crystal rutile with 3.6 % anatase TiO ₂	40 kHz frequency; 50 W; 1 g/L transition crystal TiO ₂ ; 50 °C; 10 mg/L dye; 80 min	(i) Degradation efficiency transition crystal rutile TiO ₂ powder is over 75 % (ii) Transition crystal rutile TiO ₂ powder can prevent the recombination of electron-hole pairs produced from sonoluminescence and “hot spot”	(Wang, et al., 2007c)
7	Congo Red; Methylene Blue; Methyl Orange	(i) Original TiO ₂ powder (ii) Heat treated TiO ₂ powder at 400 °C, 600 °C, 800 °C and 100 °C for 2 hours respectively (iii) Heat treated TiO ₂ powder at 800 °C and 1000 °C respectively	20 kHz frequency; 200 W; 1.5 g/L TiO ₂ ; 10 mg/L dye; 180 min; 450 mg/L H ₂ O ₂	(i) Phase transformation of rutile phase from anatase phase by heat treatment started to occur at 800 °C. (ii) Congo red is less stable and prone to degradation by •OH due to its 2 azo bonding (iii) Reused TiO ₂ has its removal efficiency of congo red reduced by around 10 % (iv) Sonocatalytic degradation follows pseudo-first order kinetics	(Abdullah & Pang, 2010)

Although the mechanism explaining the sonocatalytic degradation of organic pollutants using TiO_2 powder as the catalyst is not yet proven, researchers believe that the phenomenon can be explained by sonoluminescence and “hot spot”. Ultrasonic irradiation has the ability to induce the formation of light with a very wide range of wavelength. (Wang, et al., 2007c). Among those lights, those wavelengths that are lower than 375 nm are able to excite TiO_2 catalyst, making some electrons to be transferred from the valence band to the conduction band, which results in the formation of a hole-electron pair (Wang, et al., 2005). The electrons and holes react with H_2O to produce $\cdot\text{OH}$ radicals, and O_2 to produce $\cdot\text{O}_2^-$ which are both very reactive species that will degrade organic pollutants and the reaction process is represented in Figure 2.4 (Nosaka, et al., 2014). The temperature of the “hot spot” generated when the acoustic cavitation collapses is so high that the temperature brings a lot of cavities on TiO_2 surface to produce $\cdot\text{OH}$ radicals.

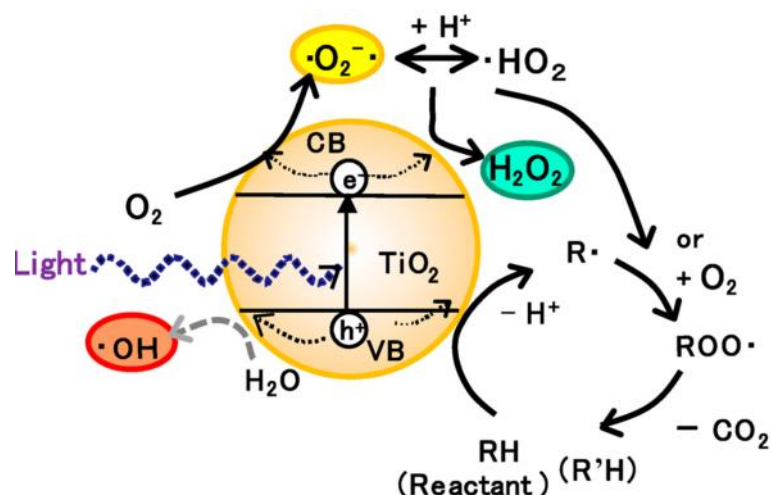


Figure 2.4: Photocatalytic oxidation of organic molecule (Nosaka, et al., 2014).

2.3 Characterization of TiO_2 catalyst

It is important to understand the characteristics of the catalyst because it provides an understanding of the catalytic act on a molecular level, a clear picture of the nature of the catalysts and of their interaction among themselves and their reactants (Haensel & Haensel, 1989). To understand the morphologies and dimensions of TiO_2 catalyst,

scanning electron microscopy (SEM) is often used. SEM utilises a heated filament to generate streams of electrons to examine sample surface at tiny scale. When electrons interact with the specimen, signals such as backscattering of electrons, Auger electrons and others will be produced and will help generate an image of the scanned surface.

X-ray powder diffraction (XRD) is a quick analytical technique used to identify phases of a crystalline material and crystalline structure present in the catalyst. To determine the crystalline phase of the TiO₂ powder, the intensity of the XRD patterns are used.

2.4 Parameter Studies

Sonocatalytic activity can be affected by factors such as the initial concentration and types of organic dyes, the amount of catalyst loading, pH of the dye solution, amount of H₂O₂ added and the heat treatment of the catalyst. These are the parameters that are known to affect the degradation process and will be studied.

2.4.1 Effect Ultrasonic Irradiation on Different Dyes

According to Abdullah & Pang (2010), the types of bond present in the dye and the molecular weight determines the stability of the dye. According to a study carried out by Inoue, et al. (2006), Rhodamine B which has molecular weight of 479.02 g/mol were completely degraded in 2 hours under ultrasonics irradiation whereas Orange II with molecular weight of 350.32 g/mol only completely degraded after 5 hours at 41.5 W ultrasonic power and 404 kHz frequency. Rhodamine B degraded faster than Orange II even though Orange II has an azo group, which is more susceptible to free radical attacks. This shows that larger molecular weight decreases the stability of the dye, making it easier to be degraded.

The type of bond in a dye molecule also plays an important role in determining its stability (Abdullah & Pang, 2010). Congo red, for example, has a very low stability due to it having 2 azo group which is very susceptible to attacks by free radicals (Hachem, et al., 2001).

2.4.2 Effect of Heat Treatment of TiO₂

Heat treatment of TiO₂ will change the phase composition of the catalyst and by increasing the temperature and time of the heat treatment, the phase transformation of anatase TiO₂ to rutile TiO₂ would be promoted (Abdullah & Pang, 2010; Wang, et al., 2007a).

Some researchers believe that similar to photocatalytic process, anatase TiO₂ powder usually produces better degradation results as compared to rutile TiO₂ powder in or sonocatalytic process. This statement is supported by research done by Wang, et al. (2007a), where they found out that Methyl Orange degraded by 96.50 % when a transitional TiO₂ is used with 3.6 % anatase phase and 96.4 % rutile phase whereas the degradation ratio achieved by the original rutile TiO₂ catalyst without any anatase phase is only 65.30 %.

In addition, Wang, et al. (2007b) also discovered that nanometer anatase TiO₂ powder performs better than nanometer rutile TiO₂ powder in degrading acid red B. According to the report, they proposed that acid red B was mostly oxidised on the surface hole of the nanometer anatase TiO₂ catalyst because there was barely any intermediate products of degradation, which means that the whole dye molecule was oxidized in a single step. Whereas for nanometer rutile TiO₂ powder, different intermediate products of degradation were formed such as methoxy phenyl oxime and phthalic anhydride. The degradation of azo bond takes place first followed by the degradation of naphthyl ring.

However, there are also studies that claim that rutile TiO₂ gives better degradation results than anatase TiO₂. Wang, et al. (2005c) found out that the

sonocatalytic degradation of rutile TiO₂ powder is better than anatase TiO₂ powder with degradation ratio of about 60 % and 19 % respectively. Abdullah & Pang (2010) also supported the claim because according to them, rutile TiO₂ has the ability of avoiding hole-electron recombination, thus, anatase TiO₂ with some rutile phase TiO₂ showed a better sonocatalytic activity than pure anatase TiO₂.

2.4.3 Effect of Initial Dye Concentration

Usually the sonocatalytic activity increases as the initial concentration of dye increases until a certain concentration where any further increase in the concentration will result in a decrease in sonocatalytic activity (Wang, et al., 2005). When the initial concentration increases, the probability of •OH radicals reacting with dye molecules on the surface of the catalyst also increases and therefore, increasing the degradation rate.

After the optimum concentration, the degradation efficiency of dye is inversely proportional to the initial dye concentration (Shimizu, et al., 2007). The degradation efficiency decreases due to the screening effect between high concentration of organic dye and the amount of •OH radicals produced on the catalyst surface are not enough to degrade the huge amount of organic dyes (Wang, et al., 2005). Another factor that contributes to the decrease in degradation efficiency is due to the huge amount of organic dyes that adsorb onto the catalyst surface at high concentration (Abdullah & Pang, 2010).

2.4.4 Effect of Catalyst Dosage

The optimum amount catalyst loading is a very important parameter as it affects the cost of the water treatment process. The increase in amount of TiO₂ catalyst will increase the degradation rate until a certain optimum point (Wang, et al., 2007b; Tang, et al., 2012). This is because the increase in sonocatalyst in the dye solution increases the nucleation sites for cavity formation to take place. Besides that, the

sonocatalyst also acts as a catalyst to promote water dissociation reaction to generate $\cdot\text{OH}$ radicals (Tang, et al., 2012).

However, a further increase in catalyst loading after the optimum point will lead to mutual screening effects of the sonocatalyst which will slow down the degradation rate by preventing the dye molecules from receiving the energy from the ultrasound wave (Wang, et al., 2007a).

2.4.5 Effect of Initial pH

The effect of initial pH varies according to the charge of dye molecules as well as the surface charge of the catalyst at different pH. This phenomenon can be explained by the point of zero charge (PZC) TiO_2 catalyst surface which is report to be around pH 6.8 by Wang, et al. (2007a) and Shimizu, et al. (2007). When pH is above 6.8, the surface of TiO_2 becomes negatively charged, whereas when pH is below 6.8, the surface of TiO_2 becomes positively charged (Shimizu, et al., 2007).

At pH above 6.8, cationic compound like Methylene Blue can easily adsorb onto the surface of TiO_2 catalyst, thus increasing the degradation efficiency. At pH below 6.8, a cationic compound will experience strong electrostatic repulsion with TiO_2 catalyst, which will hinder the adsorbtion of the compound onto the catalyst surface. Due to the fact that $\cdot\text{OH}$ radicals have a very short lifetime and they seldom diffuse far from TiO_2 surface, the degradation efficiency of the compound will be severely reduced (Shimizu, et al., 2007). Anionic compounds behave in the opposite manner.

Furthermore, OH^- anions can form $\cdot\text{OH}$ radicals after losing one electron at the surface of TiO_2 catalyst and these radicals will contribute in degrading more organic compounds (Wang, et al., 2007b). It is important to make sure that the adsorption of organic compound on the catalyst surface is not too strong because that will reduce the surface area available for $\cdot\text{OH}$ radical generation (Bejarano-Perez & Suarez-Herrera, 2007).

2.4.6 Effect of H₂O₂ Concentration

H₂O₂ is a strong oxidizing agent and the loading of hydrogen peroxide plays an important part in the determination of the overall efficiency of the degradation process in a sonocatalytic process. The optimum loading of hydrogen peroxide is determined based on the type of pollutant to be degraded, operating conditions as well as the type of the sonochemical reactor (Bagal & Gogate, 2014).

If H₂O₂ is added externally to the medium, the degradation rate of organic dyes should be enhanced due to the ability of H₂O₂ to generate more •OH radicals by self-decomposition of H₂O₂ under ultrasonic irradiation as well as reduction by •OH or H• radicals (Abdullah & Pang, 2010). The reactions are represented in equations (2.15), (2.16) and the self-decomposition of H₂O₂ is shown below.



It is also important to note that excess concentration of H₂O₂ in the medium would have adverse effect on degradation of pollutants because HO• radicals generated by either Fenton reactions or cavitation bubbles could be converted into molecular species because of the scavenging effect of H₂O₂ (Abbasi & Asl, 2008). The reactions are represented by equations (2.12) and (2.15)

The amount of H₂O₂ have to be adjusted to make sure that all the H₂O₂ is utilized in the process because residual hydrogen peroxide increases the COD level in water and it is also harmful to micro-organisms (Chakinala, et al., 2008). It is important to ensure that COD of the treated water is reduced to the required concentration before the water is discharged into the environment or used as a pre-treatment to biological methods.

2.5 Reusability Study

The reusability of the catalyst plays an important role in determining the cost of the application if the catalyst were to be used in the industry. If a catalyst can be used for a few times before being deactivated, it will be more commercially viable for the industry to use the catalyst because it will save them cost from buying fresh catalyst. Besides that, a reusable catalyst reduces the amount of waste generated. Ultrasonic irradiation can change the size and increase the surface area of the catalyst for a better sonocatalytical activity or it can also destroy the surface of the catalyst and reduce its sonocatalytical performance (Wang, et al., 2005).

Besides that, Wang, et al. (2005) investigated the reusability of rutile and anatase TiO₂ catalyst in the degradation of Methyl Orange. They found out that the degradation efficiency for a reused rutile TiO₂ catalyst improves when it was used for the second time, but the degradation efficiency drops after that. The degradation efficiency of anatase TiO₂ catalyst shows gradual decrease in degradation efficiency.

2.6 Kinetic Study

In order to predict the rate of degradation of organic compounds in a sonocatalytic reaction, kinetic model has been studied and developed. The kinetics of pollutant degradation using sonocatalytical method can be explained by pseudo-first order kinetic model (Abbasi & Asl, 2008).

The rate constant k' can be determined by:

$$-r = \frac{d[\text{Organic Dye}]}{dt} = k' [\text{Organic Dye}] [\bullet \text{OH}] \quad (2.18)$$

Because $\bullet\text{OH}$ radicals are a very reactive species, its concentration is assumed to be a constant. Therefore, Eq. (4.2) can be simplified into a pseudo-first order equation and $k'[\bullet\text{OH}]$ becomes apparent pseudo-first order constant k_{app} .

$$-r = \frac{d[\text{Organic Dye}]}{dt} = k_{app} [\text{Organic Dye}] \quad (2.19)$$

where

$$k_{app} = k'[\bullet\text{OH}]$$

After integrating Eq. (2.19), a equation that relates the dye concentration to the time of reaction can be obtained and it is given below:

$$\ln C_0/C_t = k_{app} t \quad (2.20)$$

where

C_0 = initial dye concentration of organic dye (mg/L)

C_t = concentration of organic dye at time t (mg/L)

k_{app} = apparent rate constant (min^{-1})

t = time (min)

Another kinetic model that can be used to describe a sonocatalytic degradation of organic compounds is the Langmuir-Hinshelwood kinetic model (Okitsu, et al., 2005). In their study, they assumed that the concentration of $\bullet\text{OH}$ radicals exists at a very high concentration at the interface region of the collapsing bubble where organic dyes decompose by oxidation via the reaction with $\bullet\text{OH}$ radicals. Figure 2.5 shows the outline of the model proposed where the most reactive area of degradation happens in the region surrounding the cavitation bubble.

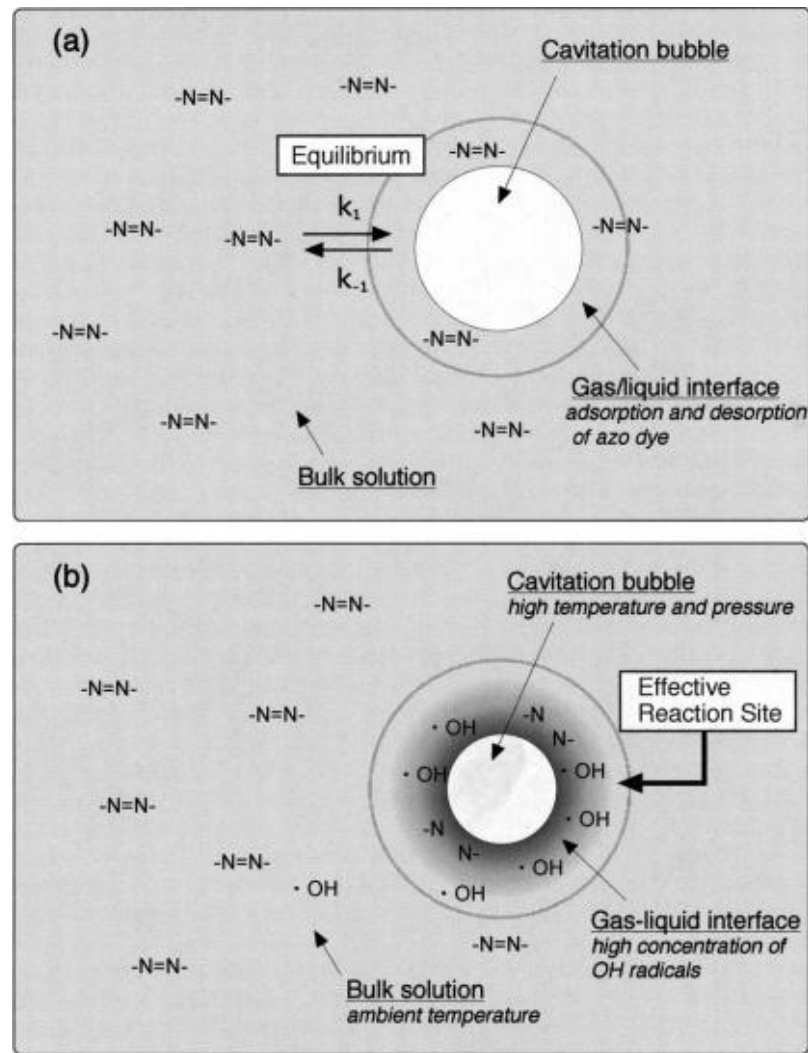


Figure 2.5: (a) Equilibrium of azo dyes towards the interface before the bubble collapses (b) Sonolysis of azo dyes after the bubble collapses. ($-N=N-$) refers to azo dye (Okitsu, et al., 2005).

This kinetics in their study assumes that the rate of adsorption, r_1 , of azo dyes molecules from the bulk solution to the interface region of the collapsing bubble is proportional to the concentration of the azo dyes in the bulk solution and $(1-\theta)$, where θ is correspondent to the ratio of azo dyes occupied in the effective reaction site. On the other hand, the rate of desorption, r_{-1} , is proportional to θ . Therefore, the rate of r_1 and r_2 is expressed by use of the rate constant k_1 for absorption and k_2 for desorption in the equations below

$$r_1 = k_1[\text{azo dye}](1-\theta) \quad (2.21)$$

$$r_2 = k_2\theta \quad (2.22)$$

where

k_1 = rate constant for absorption (min^{-1})

k_2 = rate constant for desorption (mg/L/min)

When a pseudo-steady state is achieved,

$$k_1[\text{azo dye}](1-\theta) = k_2\theta \quad (2.23)$$

Therefore,

$$\theta = \frac{K[\text{azo dye}]}{1 + K[\text{azo dye}]} \quad (2.24)$$

They also assumed that all azo dyes existing in the reaction site are decomposed by $\bullet\text{OH}$ radicals when the bubble collapses with the apparent constant of k . The decomposition rate of the azo dyes, r , are be represented by the equation below

$$r = k\theta = \frac{kK[\text{azo dye}]}{1 + K[\text{azo dye}]} \quad (2.25)$$

where

r = rate of degradation (mg/L/min)

k = apparent rate constant for the reaction between azo dyes and $\bullet\text{OH}$ radicals (mg/L/min)

$K = k_1/k_2$, the equilibrium constant of azo dyes diffusing into the interfacial region (L/mg)

CHAPTER 3

METHODOLOGY

3.1 Materials and Chemicals

The materials and chemicals used are presented in Table 3.1. Titanium dioxides were used as the catalyst for the degradation of dyes whereas hydrogen peroxide will be used as the oxidising agent. The pH of the liquid will be adjusted using hydrochloric acid and sodium hydroxide. The model pollutants used were Methylene Blue, Methyl Orange and Rhodamine B.

Table 3.1: Name, brand and purity and purpose of chemical reagents

Chemical Reagents	Brand	Purity	Purpose
Titanium dioxide, TiO₂	Friedemann Schmidt	99 %	Catalyst
Hydrogen peroxide H₂O₂	Merck	35 %	Oxidising agent
Sodium hydroxide, NaOH	Merck	50 %	pH adjustment
Hydrochloric Acid, HCL	Merck	37 %	pH adjustment
Methylene Blue	R & M	82 %	Model pollutant
Methyl Orange	R & M	85 %	Model pollutant
Rhodamine B	Sigma-Aldrich	95 %	Model pollutant

3.2 Equipments

The instruments and equipments needed for this study are tabulated in Table 3.2 together with their brand/model and their purpose. A furnace was used to heat treat TiO₂ at 200 °C, 400 °C, 600 °C, 800 °C. After heat treatment, the powders were characterized using XRD and SEM for their phase composition, crystalline size and their surface morphology respectively. A pH meter was used to measure the pH when adjusting the pH of the dye solution. An ultrasonic water bath was used to provide ultrasonic irradiation at 40 kHz and 124 W. Syringe filters were used to separate out TiO₂ powder from the dye solution before liquid sample analysis were carried out. The degradation of organic dyes was measure using a UV-vis spectrophotometer.

Table 3.2: Model and functions of instruments

Instruments	Brand	Purpose
Furnace	Carbolite RHF 1500	To calcine TiO ₂ at 200 °C, 400 °C, 600 °C, 800 °C.
pH meter	Eutech PC-300	To measure pH of solutions
UV-vis spectrophotometer	Jenway 6320D	To measure concentration of dye
Scanning electron microscope (SEM)	Hitachi Model S-3400N	To examine morphology of TiO ₂ powder
X-ray diffraction	LabX XRD-6000	To perform phase identification of crystalline
Syringe filter	Cole Parmer 0.45 micron	To separate TiO ₂ from dye solution
Ultrasonic bath	WiseClean WUC-A03H	Source of ultrasound and water bath

3.3 Overall Research Flow

Figure 3.1 shows the overall research flow chart. Firstly, TiO₂ catalyst was heat treated at various temperature followed by the preparation of organic dyes. After that, the catalysts will be characterised using XRD and SEM. The catalysts were then used for parameter studies and the used catalysts were kept for reusability study. The liquid samples from both parameter studies and reusability study were analysed using UV-Vis spectrophotometer. Lastly, the kinetic study for the sonocatalytic degradation of dye was carried out.

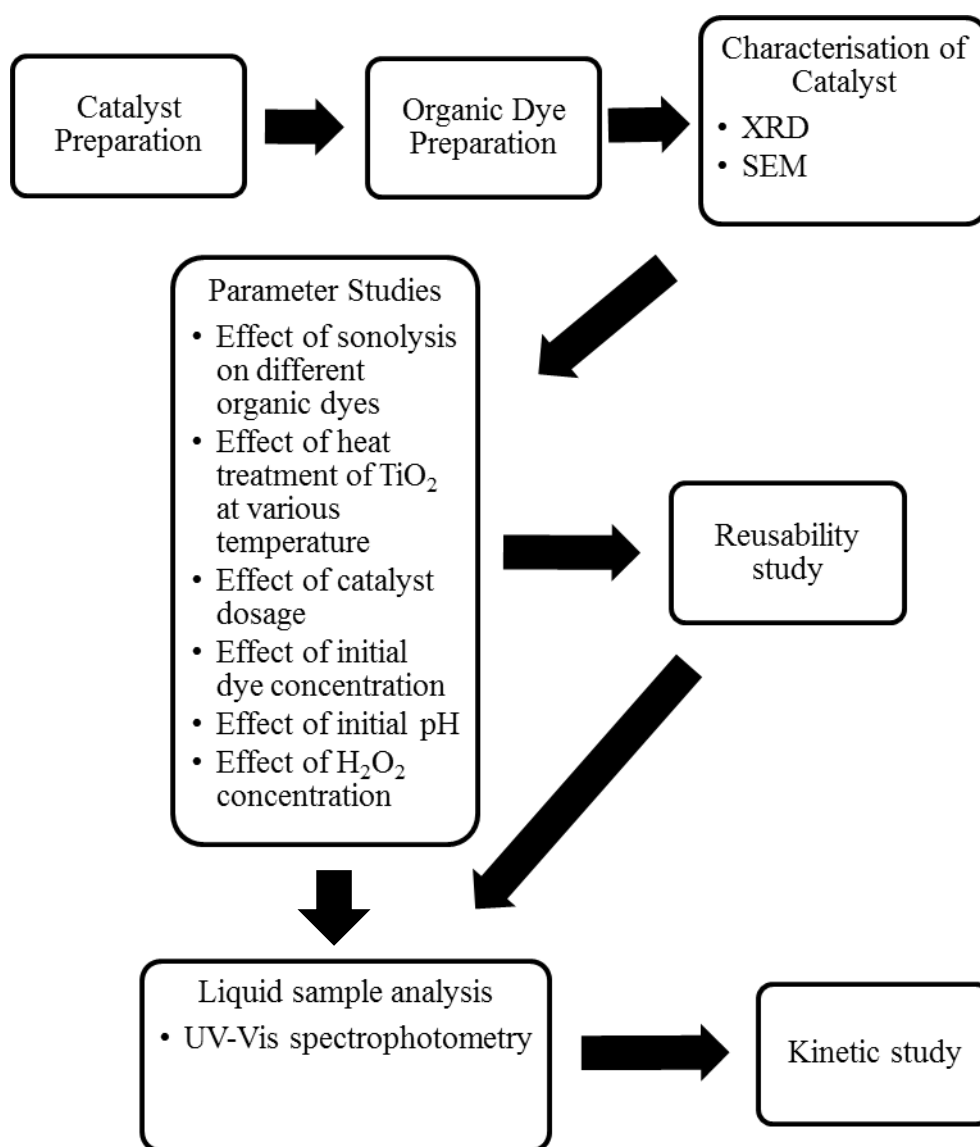


Figure 3.1: Overall Flow Diagram of the Research

3.4 Experimental Set-up

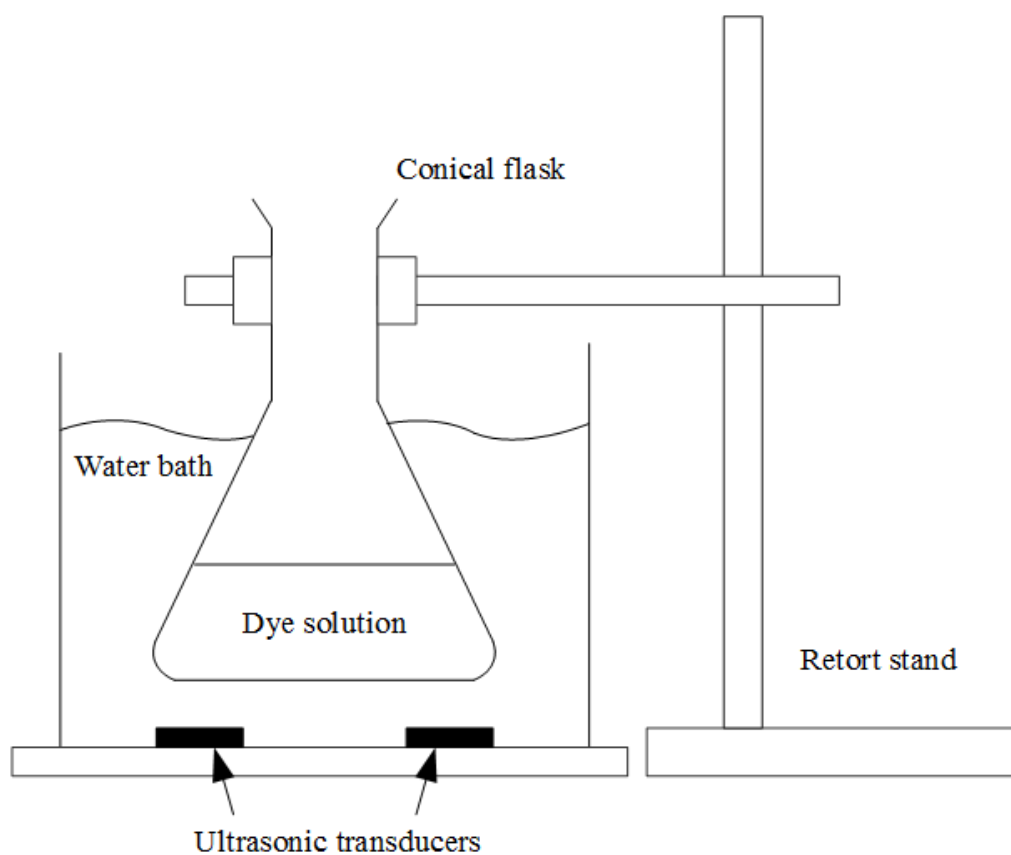


Figure 3.2: Experiment Set-up

The experiment was carried out in an ultrasonic bath manufactured by WiseClean and the model is WUC-A03H. The ultrasonic bath produces ultrasonic waves at 40 kHz and with 124 W power. A retort stand and a clamp is used to hold the conical flask containing the dye solution in place. The conical flask is placed directly in between the two ultrasonic transducers so that the dye solution can absorb most of the ultrasonic irradiation.

3.5 Experimental Procedures

3.5.1 Catalyst Preparation

TiO₂ powder will be heat treated at 200 °C, 400 °C, 600 °C, 800 °C for 2 hours to study the effects of the heat treatment temperature on the degradation efficiency of organic dyes. After cooling down to room temperature, the heat treated TiO₂ powders are kept in a dry environment using silica gels.

3.5.2 Preparation of Organic Dyes

Organic dye solutions are prepared by adding 0.5 g of dye powder into a 1 L de-ionised water to obtain a stock solution of dye concentration 500 mg/L. The stock solutions will be diluted according to the concentration needed during parameter studies.

3.5.3 Characterization of Catalyst

Catalyst characterization is a very important step in understanding the nature of the catalyst. It allows an insight to the catalyst composition, chemical structure and chemical properties of the catalyst. By understanding the characteristics of the catalyst, the performance of the catalysts can be explained. In this research, the catalysts were characterized by XRD and SEM.

XRD was used to study the crystalline phases, crystalline structure and crystalline size present in the non-heat treated and heat treated TiO₂ powders. The test was carried out using LabX XRD-6000 at room temperature and Cu K α radiation. The XRD patterns were collected at 100 mA and 40 kV. The measurements starts at $2\theta = 10^\circ$ and ends at 80° with a scanning speed of 2 °/min. The ratio of the anatase

and rutile phases were calculated using Equation 3.1 and Equation 3.2 respectively (Wang, et al., 2007c).

$$\beta_A = [1 + 1.26(I_R/I_A)]^{-1} \quad (3.1)$$

$$\beta_R = [1 + 0.8(I_A/I_R)]^{-1} \quad (3.2)$$

where

β_A = Proportion of anatase phase

β_R = Proportion of rutile phase

I_A = Diffraction intensity of anatase phase

I_R = Diffraction intensity of rutile phase

SEM is used for the surface morphology analysis of the catalyst by producing high resolution images of surface topography. The model of the equipment used for SEM is Hitachi Model S-3400N.

3.5.4 Parameter Studies

All experiments were carried out in a batchly manner. The amount of dye solutions used for each experiment was 100 mL and the pH of the solutions was adjusted using 0.1 M HCl or 0.1 M NaOH to the desired pH using pH meter Eutech PC-300. After that, the catalysts were added in the 100 mL dye solution. The ultrasonic wave frequency was 40 kHz and the irradiation power was 124 W. Samples were taken out in a 10 min interval and the catalyst was separated by a syringe filter. The concentration of residual dye in the sample was measured using UV-Vis spectrophotometer to calculate the degradation of dye. The used catalysts were collected for reusability studies.

3.5.4.1 Effect of Type of Organic Dyes on Adsorption

The effect adsorption of different organic dyes on TiO₂ powder was investigated using Methylene Blue, Methyl Orange and Rhodamine B without ultrasonic wave. The experiment was carried out under initial dye concentration of 10 mg/L for all types of dye, 0.1 g/L of TiO₂ powder in 100 mL dye solution. The initial pH of the solution is adjusted using 0.1 M HCl and 0.1 M NaOH to pH 6.

3.5.4.2 Effect Ultrasonic Irradiation on Different Dyes

The effect of ultrasonic irradiation on different dyes was studied to understand the sonolysis of Methylene Blue, Methyl Orange and Rhodamine B. The experiment was carried out without TiO₂ powder, pH 6, initial dye concentration of 10 mg/L, ultrasonic wave frequency of 40 kHz and irradiation power of 124 W. The dye with the best degradation efficiency was chosen to be used in further studies.

3.5.4.3 Effect of Heat Treatment of Catalyst

The effect of heat treatment of catalyst on the degradation efficiency of dye under ultrasonic irradiation was investigated using non-treated TiO₂ powder and TiO₂ powders that were heat treated at 200 °C, 400 °C, 600 °C and 800 °C under ultrasonic irradiation of 40 kHz and 124 W. The concentration of catalysts used was 0.1 g/L. The initial pH was pH 6 and the concentration of the dye used was 10 mg/L. The catalyst that performed with the highest degradation rate was chosen to be used in the following experiments.

3.5.4.4 Effect of Initial Dye Concentration

The effect of initial dye concentrations on the dye degradation efficiency under ultrasonic irradiation was studied by carrying out experiments with initial dye concentrations of 2.5 mg/L, 5.0 mg/L, 7.5 mg/L, 10.0 mg/L and 12.5 mg/L. It was carried out at pH 6, 1 g/L catalyst loading and under ultrasonic irradiation of 40 kHz and 124 W. The type of organic dye and catalyst used was determined in the previous experiments. The initial concentration that had the best degradation efficiency was carried forward to the following experiments.

3.5.4.5 Effect of Catalyst Loading

The effect of catalyst loading on the degradation efficiency of dye was studied using 0 g/L, 0.5 g/L, 1.5 g/L and 2 g/L of TiO₂ catalyst under ultrasonic irradiation of 40 kHz and 124 W. The initial pH was pH 6 and the initial concentration of the dye used was determined in the previous parameter study. The optimum catalyst loading was carried forward to be used in the following experiments.

3.5.4.6 Effect of Initial pH

The optimum pH for degradation of organic dye under ultrasonic irradiation was carried out and the pH studied pH 2, pH 4, pH 6, pH 8 and pH 10 under ultrasonic irradiation of 40 kHz and 124 W. The concentration of the dye and the catalyst dosage were determined in the previous experiments. The optimal pH value for degradation of dye was carried forward and used in the following experiments.

3.5.4.7 Effect of H₂O₂ Concentration

The effect of H₂O₂ concentrations on the degradation of organic dye were carried out using concentrations of 0.5 mmol/L, 1.0 mmol/L, 1.5 mmol/L, 2.0 mmol/L, 2.5 mmol/L under ultrasonic irradiation of 40 kHz and 124 W. The other operating parameters such as the initial dye concentration, catalyst dosage and pH were determined in the previous experiments. The optimal H₂O₂ concentration was obtained and used in the following experiment.

3.6 Reusability Study

The catalysts used were rinsed using distilled water for a few times and dried before being used again for degradation of dye. The organic dye degradation rate and efficiency of the used catalyst for each test were computed and compared with the activity of a fresh catalyst.

3.7 Kinetic Study

The kinetic study on the degradation of the organic dye was investigated using developed mathematical kinetic models. The developed kinetic model used was the pseudo-first order kinetic model represented in Equation (2.20).

3.8 Liquid Sample Analysis

The liquid samples from each experiment were tested for the concentration of organic dye using UV-vis spectrophotometry.

3.8.1 UV-Vis Spectrophotometry

UV-Vis spectrophotometry is used to identify the remaining dye concentration in the sample. Before the experiment was carried out, a calibration curve of absorbance versus concentration was plotted using initial known dye concentrations. As stated in Beer-Lambert Law, the absorbance of a substrate is directly proportional to substrate concentration. The absorbance of the dye solution was measured to determine the concentration of dye. The determined absorption was converted to a concentration through the calibration curve plotted. The degradation percentage and degradation of dye were defined by the following equation.

$$\text{Dye degradation efficiency (\%)} = (C_0 - C_t) / C_0 \times 100 \% \quad (3.3)$$

where C_0 = Initial dye concentration

C_t = Dye concentration at time t

3.9 Gantt Chart

The schedule for final year project part 1 was represented in Figure 3.3.

Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Title Registration	■													
Literature Study		■	■	■										
Chapter 1					■	■								
Chapter 2							■	■	■					
Chapter 3										■	■	■		
Compilation													■	
Presentation														■

Figure 3.3:: FYP 1 Schedule

The schedule for final year project part 2 was represented in Figure 3.4.

Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Catalyst Preparation	■													
Dye Preparation	■													
Characterisation of Catalyst		■												
Parameter Study			■	■	■									
Reusability Study						■	■	■						
Kinetic Study									■					
Result Analysis										■	■	■		
Report Writing											■	■	■	
Presentation														■

Figure 3.4:: FYP 2 Schedule

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterizations of TiO₂ powders

A clearer information on the weight proportions of anatase and rutile phases for untreated and treated TiO₂ powders are shown in Table 4. The weight proportions of anatase and rutile phase for untreated catalyst and catalysts treated at 200 °C, 400 °C and 600 °C are almost similar whereas TiO₂ powder that was heat treated at 800 °C showed an increase in rutile phase.

Table 4.1: Weight ratio of anatase and rutile phase in various heat treated TiO₂ powder

Catalyst	Weight proportions	
	Anatase	Rutile
Untreated	0.125	0.875
200 °C	0.132	0.868
400 °C	0.127	0.873
600 °C	0.125	0.875
800 °C	0.042	0.958

Figure 4.1 shows the XRD patterns of the untreated TiO₂ powder as well as all the heat treated TiO₂ powders and Table 4.1 shows the weight proportions of anatase and rutile phase for the all the TiO₂ powders. The results show that the

untreated TiO_2 comprises mainly of rutile phase with some of anatase phase and there were no observable changes in the phases when TiO_2 powders were heat treated at 200 °C, 400 °C and 600 °C for 2 hours. However, the amount of anatase phase decreases while the amount of rutile phase increases for TiO_2 powder when it was heat treated at 800 °C for 2 hours. This happened because of the transformation of metastable anatase phase to stable rutile that took place when TiO_2 are heated to temperature above 600 °C (Hanaor, et al., 2012).

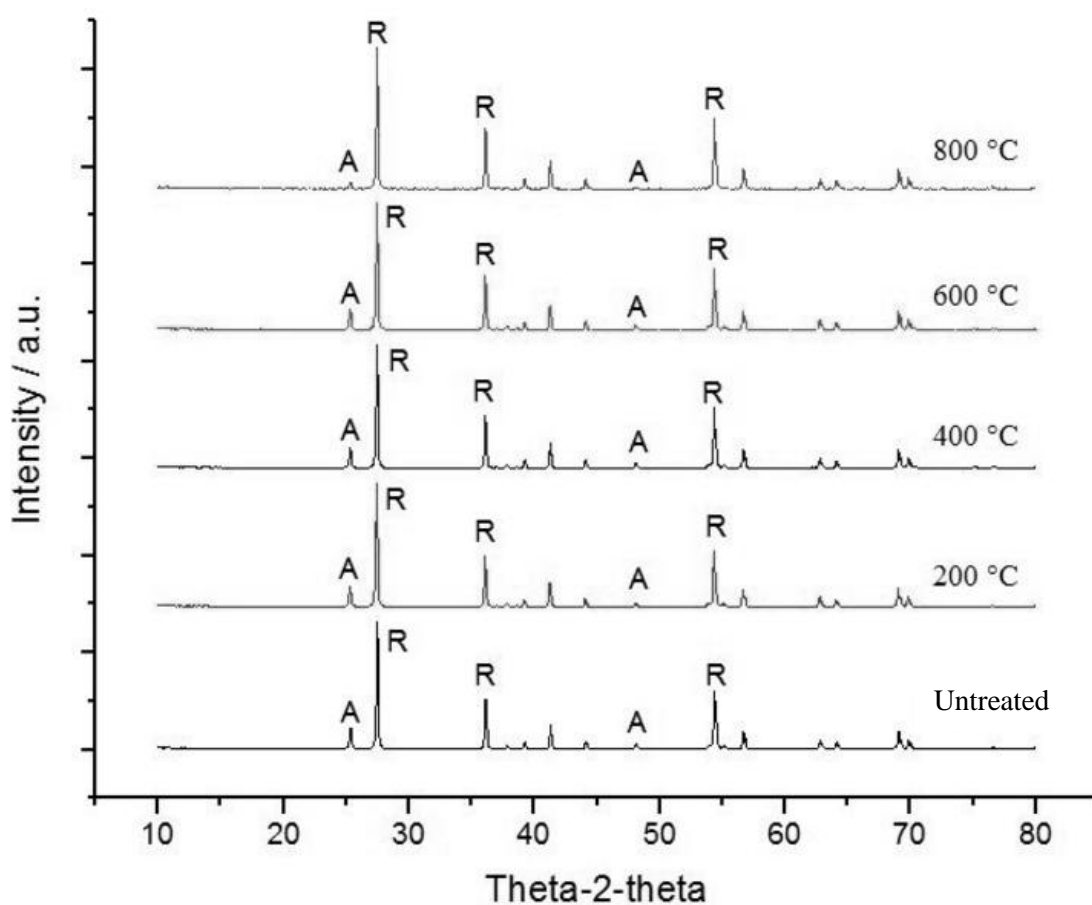


Figure 4.1: XRD patterns for untreated and heat treated TiO_2 powders

The morphology of untreated and heat treated TiO_2 catalysts were studied using SEM and Figure 4.2 shows the SEM images of the powders. All TiO_2 powders exhibit similar appearance and grain size except for TiO_2 powders that were heat treated at 600 °C and 800 °C. According to the SEM images, all the TiO_2 catalysts are shows similar characteristics except for TiO_2 powders that were heated to 600 °C and 800 °C. They show signs of agglomeration as their surface becomes smoother

and the grain size of the particles becomes larger. This is finding consistent with findings by Behnajady, et al. (2013) in which he reported that there was an increase in the crystal size of TiO_2 particles when the particles are heated at $600\text{ }^\circ\text{C}$ for 2 hours which resulted in a reduction in surface area of the catalyst.

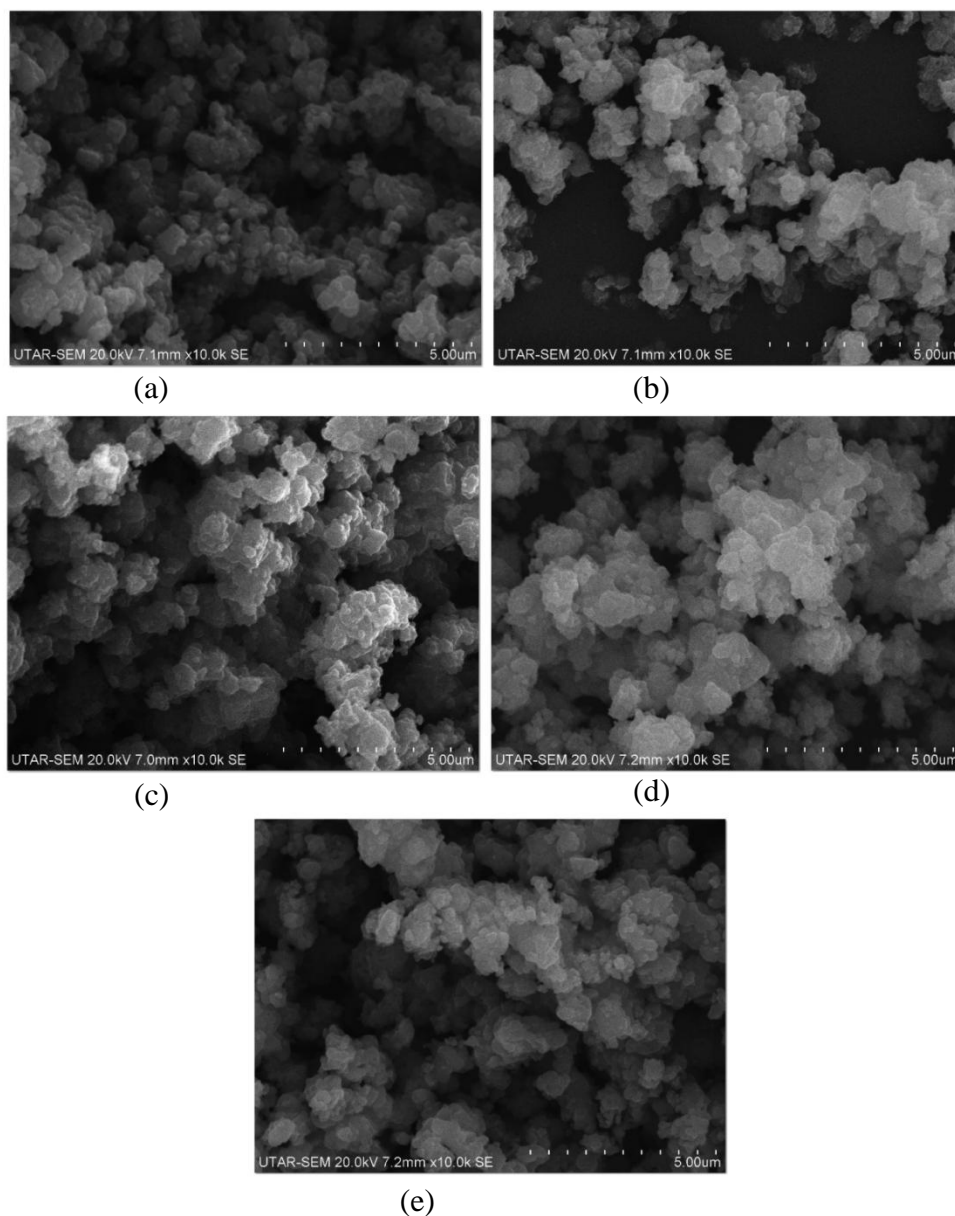
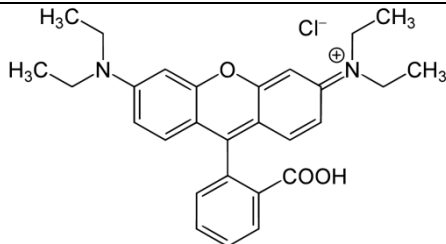
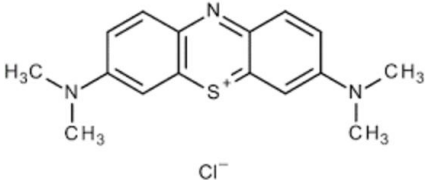
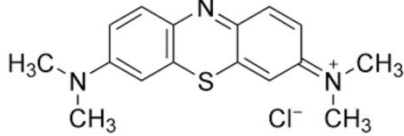


Figure 4.2: SEM Images (a) Untreated of TiO_2 Powder and 2 Hours of Heat Treatment at, (b) $200\text{ }^\circ\text{C}$, (c) $400\text{ }^\circ\text{C}$, (d) $600\text{ }^\circ\text{C}$, (e) $800\text{ }^\circ\text{C}$

4.2 Adsorption and the Effect of Ultrasonic Irradiation on Degradation of Different Dyes

In this study, the adsorption of different dyes on TiO₂ powder was studied using Rhodamine B, Methylene Blue and Methyl Orange. Table 4.2 shows the chemical structure, type and molecular weight of the dyes. The adsorption efficiencies of the three types of dye are shown in Figure 4.3. The highest adsorption efficiency was achieved by Methyl Orange at 7.8 %, followed by Methylene Blue and Rhodamine B with adsorption efficiencies of 2.16 % and 1.62 % respectively. This can be explained by the point of zero charge (PZC) TiO₂ powder surface and the type of the dye used.

Table 4.2: Chemical Structure, Type and Molecular Weight of Rhodamine B, Methylene Blue and Methyl Orange

Dyes	Chemical Structure	Type (Cationic/Anionic)	Molecular Weight (g/mol)
Rhodamine B		Cationic	479.02
Methylene Blue		Cationic	319.85
Methyl Orange		Anionic	327.33

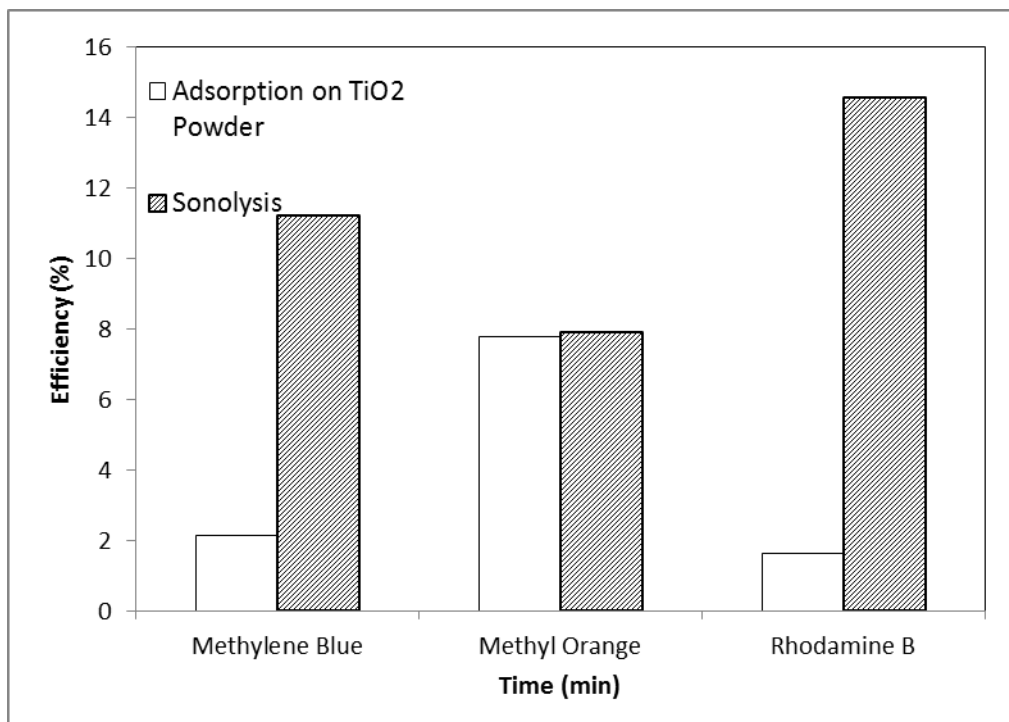


Figure 4.3: Adsorption and Sonolysis Efficiencies of Various Dyes on TiO₂ Powder (Initial Dye Concentration = 10 mg/L, TiO₂ Loading = 1.0 g/L, pH = 6, Reaction Time = 60 minutes)

It is reported that the PZC of TiO₂ is around pH 6.8 (Wang, et al., 2007a; Shimizu, et al., 2007). When the pH value of the dye solution is above 6.8, the charge on the surface of TiO₂ becomes negatively, whereas when pH is reduced to below 6.8, the surface of TiO₂ becomes positively charged (Shimizu, et al., 2007).

Since the test was carried out at pH 6, the surface of TiO₂ catalyst was positively charged. Being an anionic dye, Methyl Orange can adsorb onto the surface TiO₂ powder at a higher efficiency due to electrostatic attraction. On the other hand, Rhodamine B and Methylene Blue are cationic dye. Electrostatic repulsion between TiO₂ powder and the two organic dyes resists the adsorption and therefore resulting in a lower adsorption efficiency of the dyes.

The effects of ultrasound on the dyes were also carried out to understand the effects of sonolysis on different dyes and the result is represented in Figure 4.3. After one hour of reaction time, Rhodamine B showed the highest degradation efficiency

of 14.57 %, followed by Methylene Blue and Methyl Orange with 11.23 % and 7.93 % degradation efficiency respectively.

According to Abdullah & Pang (2010), the types of bond present in the dye and the molecular weight determines the stability of the dye. Rhodamine B has a higher degradation efficiency because it has the largest molecular weight. The effect of molecular weight on the stability of dye was shown in a study carried out by Inoue, et al. (2006), where Rhodamine B which has molecular weight of 479.02 g/mol were completely degraded in 2 hours under ultrasonics irradiation whereas Orange II with molecular weight of 350.32 g/mol only completely degraded after 5 hours at 41.5 W ultrasonic power and 404 kHz frequency. Rhodamine B degraded faster than Orange II even though Orange II has an azo group, which is more susceptible to free radical attacks.

Methylene Blue and Methyl Orange have very similar molecular weights, so the stability of the dyes under ultrasonic irradiation is determined by the bonds present in their structures. Methylene Blue possess lower stability under ultrasonic irradiation because of the position of the one charged sites which is located in the ring whereas the charge of Methyl Orange is located at the external part of the ring.

4.3 Parameter Studies in Sonocatalytic Process

4.3.1 Effect of Heat Treatment of TiO₂ catalyst

The effect of heat treatment of TiO₂ catalyst on the degradation of Rhodamine B was carried out with initial dye concentration of 10 mg/L and catalyst loading of 1 g/L. Figure 4.5 shows that TiO₂ catalysts that were heat treated at 200 °C, 400 °C, and 600 °C have very similar phase composition with the TiO₂ catalyst that was not heat treated. The degradation efficiencies are 26.16 %, 25.52 %, 24.62 % and 23.71 %. However, TiO₂ catalyst that was heat treated at 800 °C showed a lower degradation efficiency of 17.65 %.

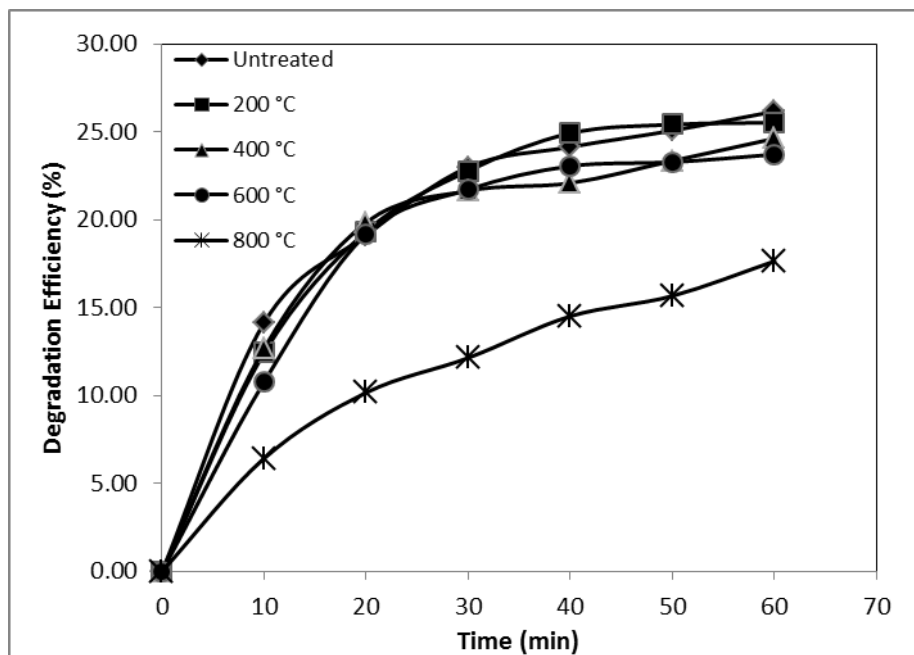


Figure 4.4: Effect of Heat Treatment of Catalyst on the Sonocatalytic Degradation of Rhodamine B (Initial Dye Concentration = 10 mg/L, pH = 6, Catalyst Loading = 1 g/L, Reaction Time = 60 minutes)

This phenomenon can be explained by the phase composition of the catalysts which is shown in Table 4.1. Three samples contain more anatase phase as compared to the catalyst that underwent heat treatment at 800 °C because almost all of the anatase phase had already been transformed to rutile phase. This shows that rutile TiO₂ with anatase TiO₂ performs better than rutile TiO₂ alone. This is because ultrasonic irradiation can lead to the formation of light with a relatively wider wavelength range which are below 375 nm. Due to the low energy band gap of rutile TiO₂ particles, they can absorb light in a wider range of wavelength to photogenerate a lot of electron-hole pairs. Instead of acting as a catalyst to produce more •OH radicals through photocatalytic means, the electron and holes just recombine and lose the ability to produce •OH radicals. However, TiO₂ particles with rutile and anatase phase can restrain the recombination of electron and hole, thus improving the degradation efficiency (Wang, et al., 2007c). Since untreated TiO₂ catalyst without heat treatment does not need extra work to prepare and it has almost the same degradation efficiency as catalysts that were heat treated at 200 °C, 400 °C, and 600 °C, it was chosen to be used for further parameter studies.

4.3.2 Effect of Initial Dye Concentration

The initial dye concentration of Rhodamine B was varied from 2.5 mg/L to 12.5 mg/L with 1 g/L of catalyst loading to study the effects of initial dye concentration on the degradation efficiency and the results are shown in Figure 4.6. The degradation efficiency increases with the increase in initial dye concentration from 2.5 mg/L until 7.5 mg/L. Further increase in the concentration from 7.5 mg/L until 12.5 mg/L shows a decrease in degradation efficiency.

In a low dye concentration condition, $\bullet\text{OH}$ radicals are present in excess. So an increase in the initial dye concentration increases the probability of the dye molecules to react with $\bullet\text{OH}$ radicals, thus the sonocatalytic activity improves which leads to a higher degradation efficiency until a certain optimum initial concentration (Wang, et al., 2005).

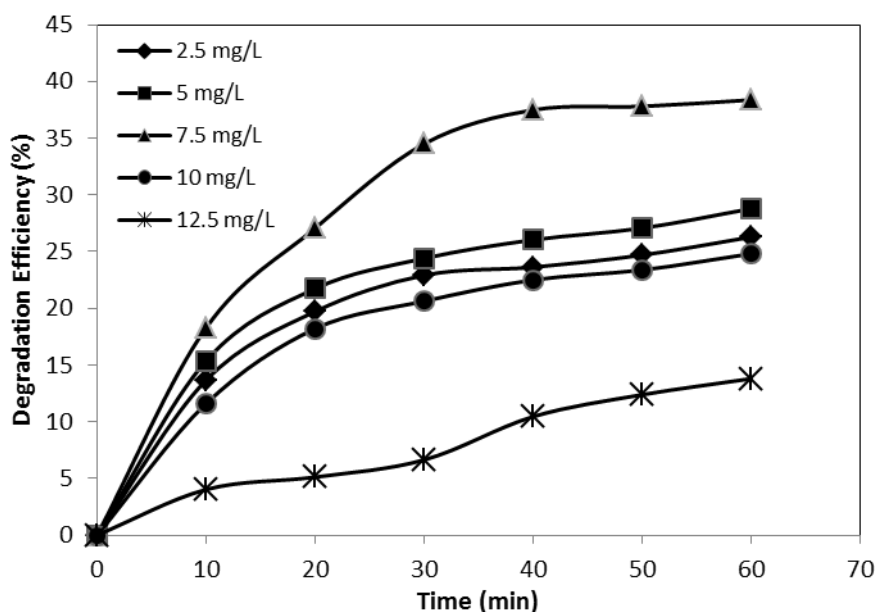


Figure 4.5: Effect of Initial Dye Concentration on the Sonocatalytic Degradation of Rhodamine B (pH = 6, Catalyst Loading = 1 g/L, Reaction Time = 60 minutes)

As the initial concentration of dye continues to increase after the optimum point, the amount of $\bullet\text{OH}$ radicals becomes the limiting factor because the $\bullet\text{OH}$

radicals produced are not sufficient to degrade all the dye molecules (Khataee, et al., 2016). Besides that, at a higher concentration the surface of the catalyst is adsorbed with a lot of dye molecules which will decrease the surface area of the catalyst (Abdullah & Pang, 2010). Mutual screening effect between the dye molecules and TiO₂ particles also increases with the increase in the concentration of dye (Wang, et al., 2005; Abdullah & Pang, 2010). Due to that, the generation •OH radicals will be limited and subsequently the degradation efficiency also drops. Rhodamine B concentration of 7.5 mg/L was used in further experiments because it gives the best sonocatalytic degradation among all the different initial concentrations.

4.3.3 Effect of Catalyst Loading

The optimum TiO₂ loading was investigated by carrying out experiments with loading from 0 g/L until 2.0 g/L and the result is shown in Figure 4.6. It is shown that the degradation of Rhodamine B increases significantly from no catalyst to 1.0 g/L of catalyst loading. The degradation efficiency increases from 12.02 % to 38.44 %. After that, further increase in the catalyst loading after 1.0 g/L decreases the degradation efficiency of Rhodamine B to 29.72 %.

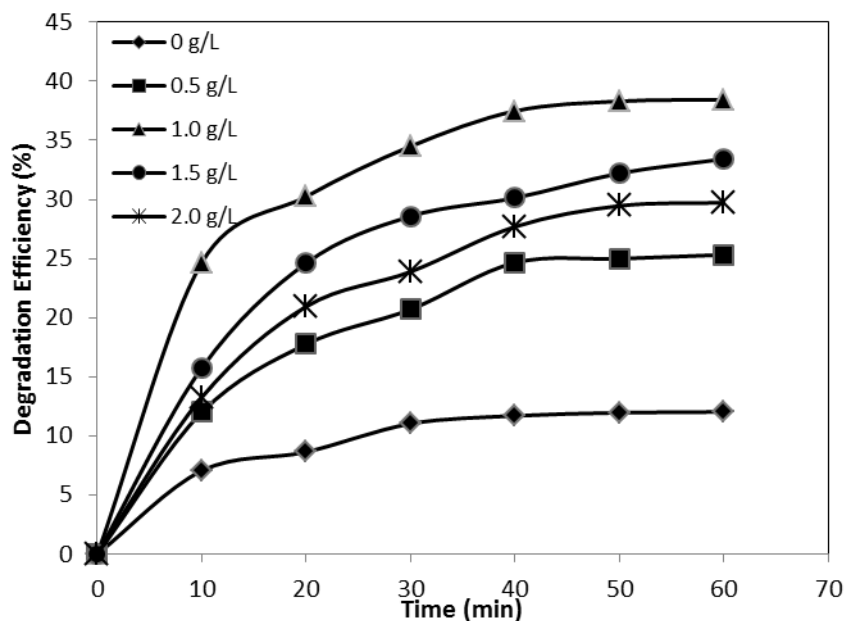


Figure 4.6: Effect of TiO₂ Catalyst Loading on the Sonocatalytic Degradation of Rhodamine B (Initial Dye Concentration = 7.5 mg/L, pH = 6, Reaction Time = 60 minutes)

The increase in degradation efficiency with higher loading is because TiO₂ acts as additional nucleation sites for bubble cavity to form and it also catalyses water dissociation reaction to form $\cdot\text{OH}$ radicals (Tang, et al., 2012). So an increase in the catalyst loading will increase the formation of more $\cdot\text{OH}$ radicals that will enhance sonocatalytic degradation of Rhodamine B up until an optimum point. The degradation efficiency decreases with the increase in catalyst loading after the optimum point happens. The further increase in catalyst loading after the optimum point would lead to mutual screening effects of TiO₂ catalyst. This will slow down the degradation rate by preventing the dye molecules from receiving the energy from the ultrasound wave (Wang, et al., 2007a). Besides that, when the TiO₂ catalyst loading is high, those TiO₂ particles that did not adsorb Rhodamine B dye will still absorb the heat and light energy produced from the ultrasonic waves and that will reduce the energy actually received by TiO₂ particles that have dye molecules to degrade (Wang, et al., 2006).

4.3.4 Effect of Initial Solution pH

Figure 4.8 shows the effect of solution pH on the degradation efficiency of Rhodamine B in the presence of TiO_2 catalyst. The pH of solution studied were pH 2, pH 4, pH 6, pH 8 and pH 10. It is shown that the degradation efficiency was the lowest at pH 2 with only 15.5 % and the degradation improves when the pH increases from pH 2 until pH 8 which is 42.92 %, and then it experienced a drop in degradation efficiency to 34.26 % when pH is increased to 10.

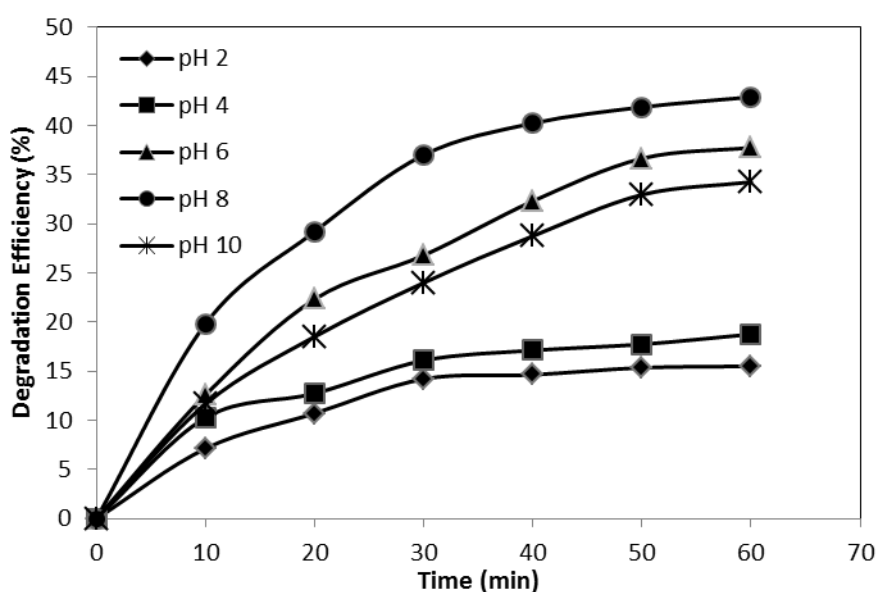


Figure 4.7: Effect of pH on the Sonocatalytic Degradation of Rhodamine B (Initial Dye Concentration = 7.5 mg/L, Catalyst Loading = 1 g/L, Reaction Time = 60 minutes)

The effect of initial solution pH will affect the charge of dye molecules as well as the surface charge of the catalyst. This can be explained by the PZC of TiO_2 catalyst surface which is reported to be around pH 6.8 by Wang, et al. (2007a) and Shimizu, et al. (2007). When pH is above 6.8, the surface of TiO_2 becomes negatively charged, whereas when pH is below 6.8, the surface of TiO_2 becomes positively charged (Shimizu, et al., 2007).

At pH below 6.8, Rhodamine B molecules will experience strong electrostatic repulsion with TiO₂ catalyst, which will hinder the adsorption of the compound onto the catalyst surface. The repulsion force increases with the increase in acidity of the medium. Since •OH radicals have a very short lifetime and they seldom diffuse far from TiO₂ surface, which leads to the decrease in the degradation efficiency (Shimizu, et al., 2007).

Since Rhodamine B is a cationic dye, it can easily adsorb onto the surface of TiO₂ catalyst in basic liquid medium due to electrostatic attraction, thus increasing the degradation efficiency. On top of that, OH⁻ anions can form •OH radicals after losing one electron at the surface of TiO₂ catalyst (Wang, et al., 2007b). The decrease in degradation efficiency when the pH of the medium was increased to pH 10 is because the basicity of the medium is too strong, the adsorption of Rhodamine B on the surface of TiO₂ is too strong, which leads to a decrease in surface area available for •OH radical generation (Bejarano-Perez & Suarez-Herrera, 2007). Subsequent experiments were conducted using dye solution with pH 8.

4.3.5 Effect of H₂O₂ Concentration

H₂O₂ is a very strong oxidizing agent and the loading of hydrogen peroxide affects the overall efficiency of the sonocatalytic degradation process. To study the effects of H₂O₂ on the sonocatalytic activity, H₂O₂ was added into the process in concentrations ranging from 0.5 mmol/L to 2.5 mmol/L. As shown in Figure 4.9, increase in degradation efficiency of Rhodamine B was observed when H₂O₂ was added from 0.5 mmol/L to 1.5 mmol/L which are 45.59 % and 75.08 % respectively. As more H₂O₂ is added, the degradation efficiency of organic dyes was improved due to the ability of H₂O₂ to generate more •OH radicals by self-decomposition of under ultrasonic irradiation and reduction by •OH or H• radicals (Alwash, et al., 2013).

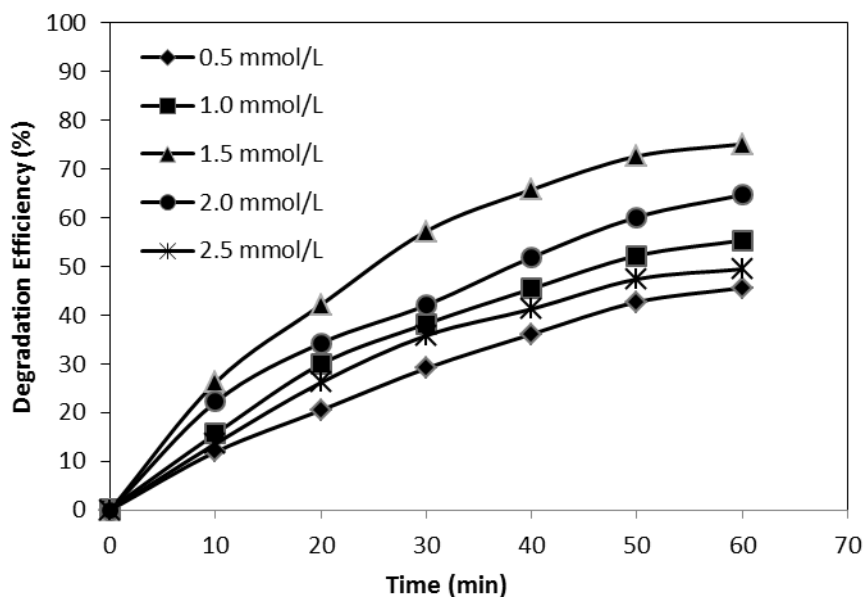


Figure 4.8: Effect of pH on the Sonocatalytic Degradation of Rhodamine B (Initial Dye Concentration = 7.5 mg/L, pH = 8, Catalyst Loading = 1 g/L, Reaction Time = 60 minutes)

A decrease in degradation efficiency, however, was observed when the concentration of H₂O₂ was further added from 1.5 mmol/L to 2.5 mmol/L. At 2.5 mmol/L H₂O₂ concentration, the degradation efficiency decreased to 49.45 %. This can be explained by the scavenging effect of H₂O₂ to produce less reactive HOO· radicals along with water and oxygen (Abbasi & Asl, 2008).

4.3.6 Reusability of TiO₂ catalyst

It is important to evaluate the reusability of TiO₂ catalysts to know the practicality of applying the catalyst in factories. To reduce waste production and saving cost, a good catalyst is expected to be reused or recycled by proper treatment after it is used for waste treatment.

Used TiO₂ catalyst powder was rinsed with distilled water for 3 times before being dried in an oven at 50 °C overnight. The reusability study was carried out

using initial dye concentration of 7.5 mg/L, catalyst loading of 1 g/L, pH 8 for 0 minutes. Figure 4.10 shows the comparison of degradation efficiency of a fresh TiO₂ catalyst, catalyst that was reused for the first time and catalyst that was reused for the second time. The degradation efficiency achieved by the three catalytic cycles were 75.08 %, 56.87 % and 35.72 % respectively. The drop in degradation efficiency might be caused partial disintegration of the catalyst surface caused by the strong mechanical force created from the movement of liquid on the catalyst surface (Abdullah & Pang, 2010). Partial disintegration of catalyst reduces the micro and mesopores at TiO₂ particles, which subsequently reduces the available surface area available for •OH generation.

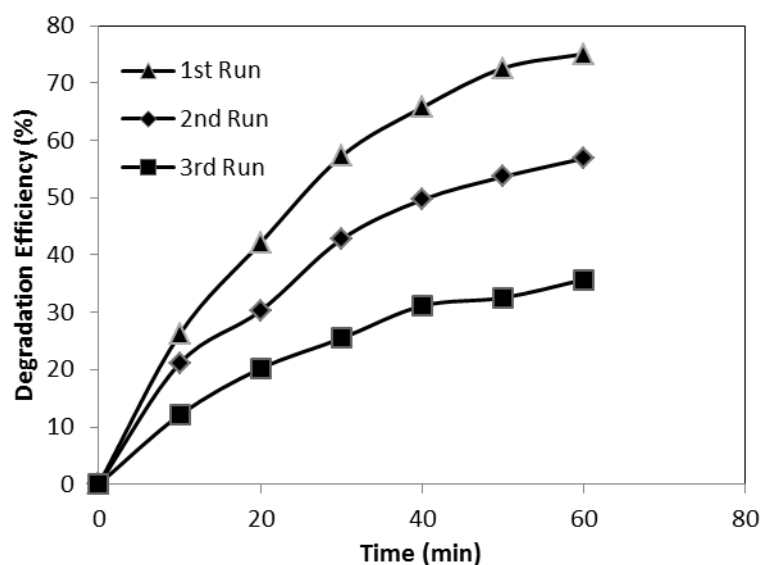


Figure 4.9: Degradation Efficiency of Fresh and Reused TiO₂ Catalysts (Initial Dye Concentration = 7.5 mg/L, pH = 8, Catalyst Loading = 1 g/L, H₂O₂ Loading = 1.5 mmol/L, Reaction Time = 60 minutes)

4.4 Kinetic Study

Kinetic study was carried out to determine the reaction order for sonocatalytic degradation of Rhodamine B. Several rate orders were tested with pseudo-first order kinetic rate. After evaluating, pseudo-first order kinetics fitted all the data the best, with regression coefficients of at least 0.965. The pseudo-first order rate expression

for the reaction rate ($-r$) of sonocatalytic degradation of Rhodamine B by $\bullet\text{OH}$ radical is given as below:

$$\ln C_0/C_t = k_{app}t \quad (4.1)$$

where

C_0 = initial dye concentration of Rhodamine B

C_t = concentration of dye at time t

The 5 cases that are studied were plotted using Eq. (4.41) and the results are shown in Figure 4.11. Since the regression coefficient, r^2 for all the cases are above 0.95, it shows that the degradation of Rhodamine B by sonocatalytic reaction using TiO_2 catalyst follows the pseudo-first order kinetics. The k_{app} values and r^2 values are presented in Table 4.3.

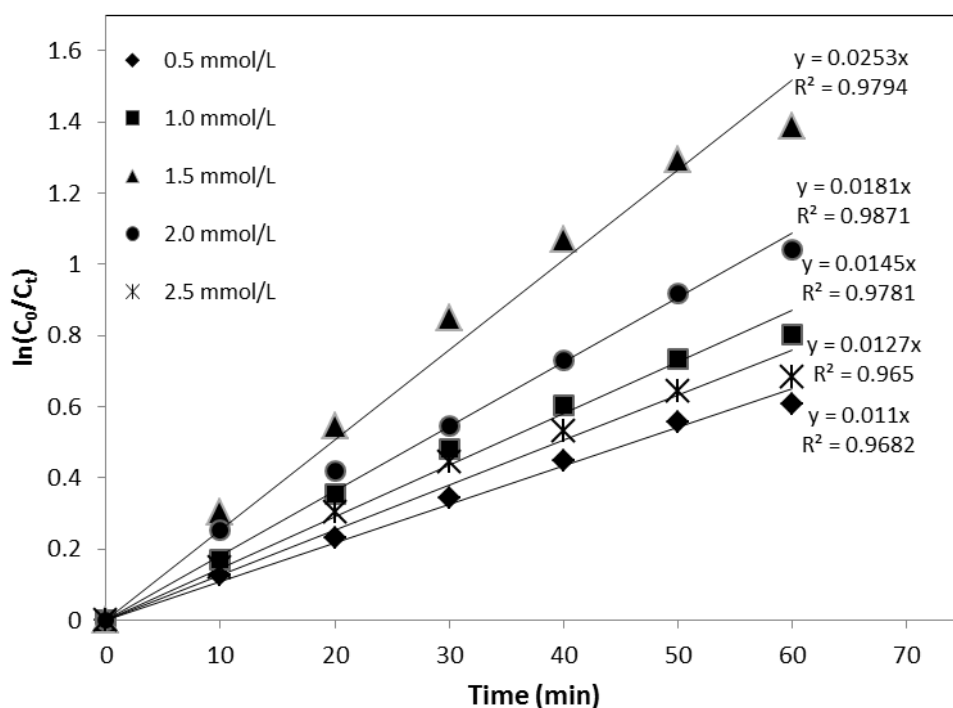


Figure 4.10: Reaction Kinetics Graph for Sonocatalytic Degradation of Rhodamine B (Initial Dye Concentration = 7.5 mg/L, pH = 8, Catalyst Loading = 1 g/L, Reaction Time = 60 minutes)

Table 4.3: Apparent Rate Coefficients and Regression Constants for the Sonocatalytic Degradation of Rhodamine B

H₂O₂ Loading (mmol/L)	Apparent Rate Coefficient, k_{app} (min⁻¹)	Regression Constant, r^2
0.5	0.011	0.9682
1.0	0.0145	0.9781
1.5	0.0253	0.9794
2.0	0.0181	0.9871
2.5	0.0127	0.9650

4.5 Possible Mechanisms for Sonocatalytic Degradation of Rhodamine B

One possible mechanisms of the sonocatalytic degradation of Rhodamine B using TiO₂ powder is by sonoluminescence. Ultrasonic irradiation can induce the formation of light with a very wide range of wavelength (Wang, et al., 2007c). Those wavelengths that are lower than 375 nm are able to excite TiO₂ catalyst, exciting electrons from the valence band to the conduction band, which leads to the formation of a hole-electron pair (Wang, et al., 2005). The electrons will react with O₂ to produce •O₂⁻ and the electron holes will react with H₂O to produce •OH radicals, and both product are very reactive species that will increase the degradation of Rhodamine B (Nosaka, et al., 2014; Wang, et al., 2007b; Eskandarloo, et al., 2015).

Another mechanism that contributes to the degradation of Rhodamine B would be the “hot spot” generated when the acoustic cavitation collapses. The high temperature generated creates a lot of cavities on TiO₂ surface to produce •OH radicals (Wang, et al., 2007c).

CHAPTER 5

CONCLUSION

5.1 Conclusion

Characterization of untreated and heat treated TiO_2 was carried out using XRD and SEM. It was found that transition of anatase to rutile TiO_2 started to occur at heat treatment temperature of $800\text{ }^\circ\text{C}$ for 2 hours. XRD analysis showed that the weight proportion of anatase phase decreased from 12.5 % in an untreated TiO_2 powder to 4.2 % in the TiO_2 powder that was treated at $800\text{ }^\circ\text{C}$. It was found out that rutile TiO_2 catalyst with more anatase phase performed better because the presence of anatase phase can restrain the recombination of electron and hole, thus improving the degradation efficiency. Agglomeration of TiO_2 particles was also observed under SEM for powders that were heated to $600\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$. This causes the surface area of the powder to be lost and results in a loss of sonocatalytic activity. Rhodamine B showed the highest degradation efficiency than Methylene Blue and Methyl Orange due to its larger molecular size. The parameter studies carried out were the initial concentration of organic dye, catalyst loading, solution pH and H_2O_2 concentration and the optimum conditions for the degradation of Rhodamine B were 7.5 mg/L dye concentration, , 1 g/L TiO_2 powder, pH 8 and 1.5 mmol/L H_2O_2 . A Rhodamine B degradation of 75.08 % in one hour was achieved under these optimum conditions. The sonocatalytic degradation followed a pseudo first order kinetics. The degradation efficiency of reused TiO_2 during the second and third time were 56.87 % and 35.72 %.

5.2 Recommendations

BET surface analysis can be carried out to understand the effect of heat treatment on the specific surface area of the TiO₂ powder. The extent of agglomeration of powder under different heat treatment temperatures can be studied. Besides that, it can also be used to study the mechanical effect of ultrasound on the surface area of the catalyst.

On top of that, the particle size distribution of the TiO₂ powder should be studied to understand the effect of heat treatment on the changes in particle size of TiO₂ powder as well as the effect of ultrasound on the size of the powder. Lastly, gas chromatography can be carried out on the liquid sample to determine the types of intermediate compounds formed when Rhodamine B is degraded.

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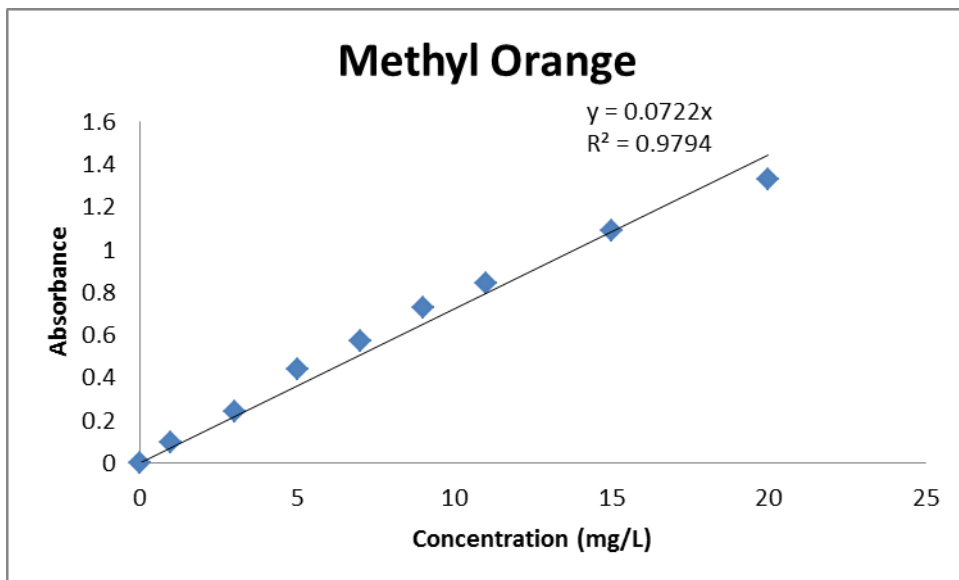
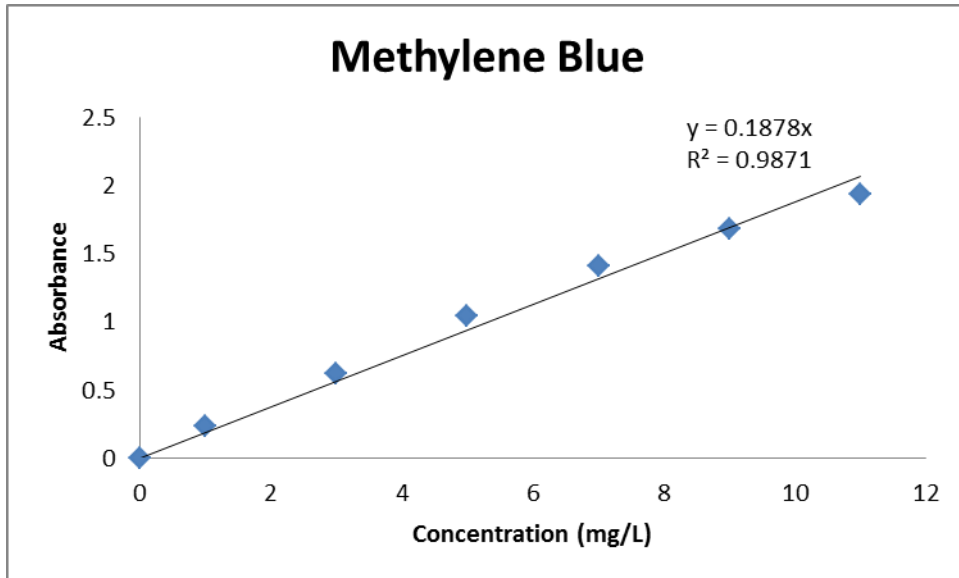
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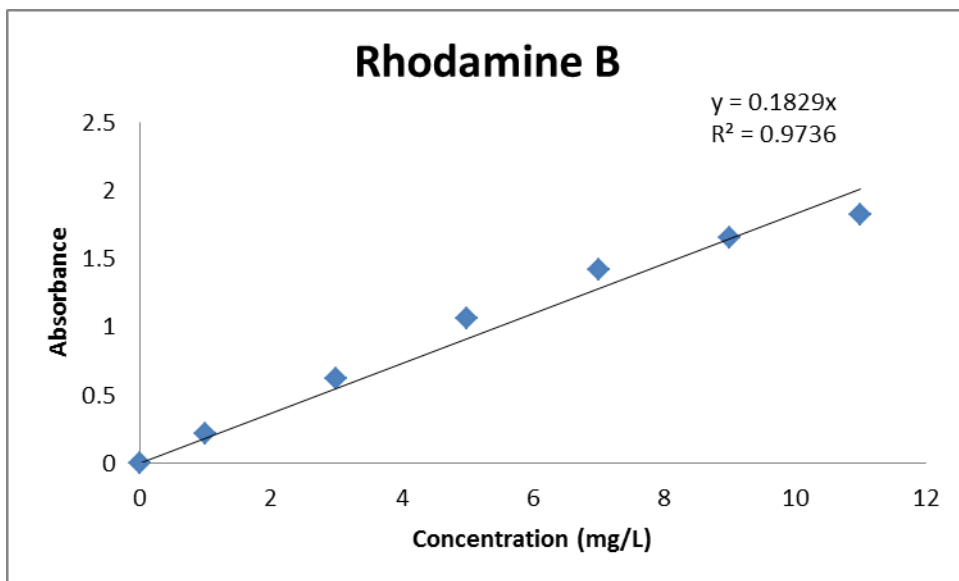
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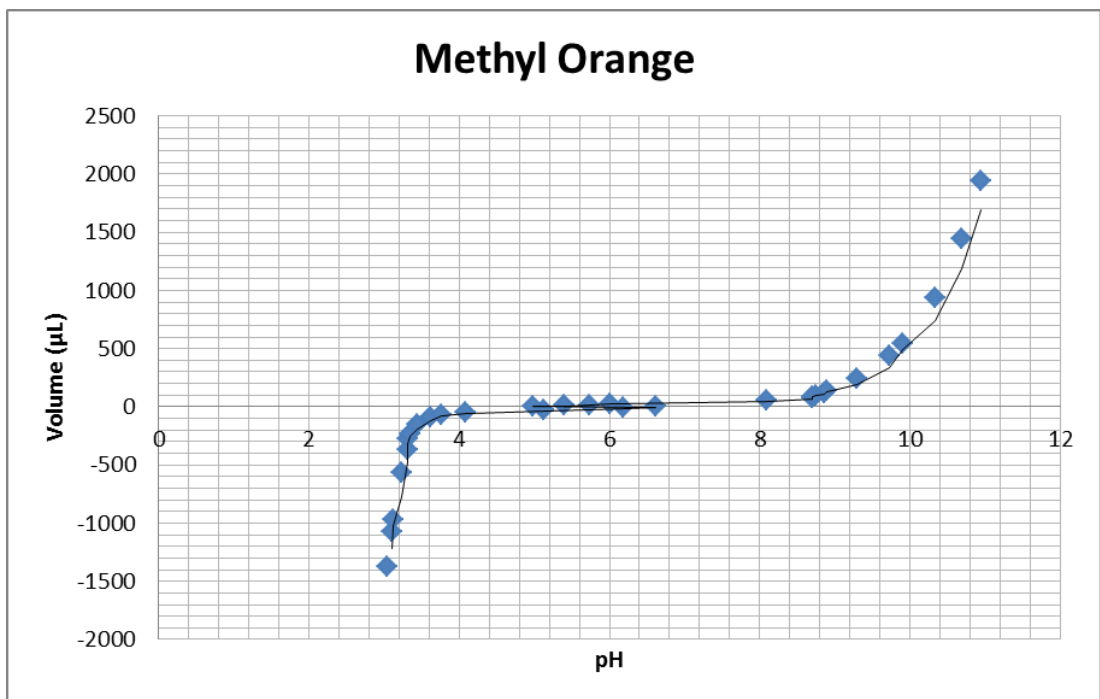
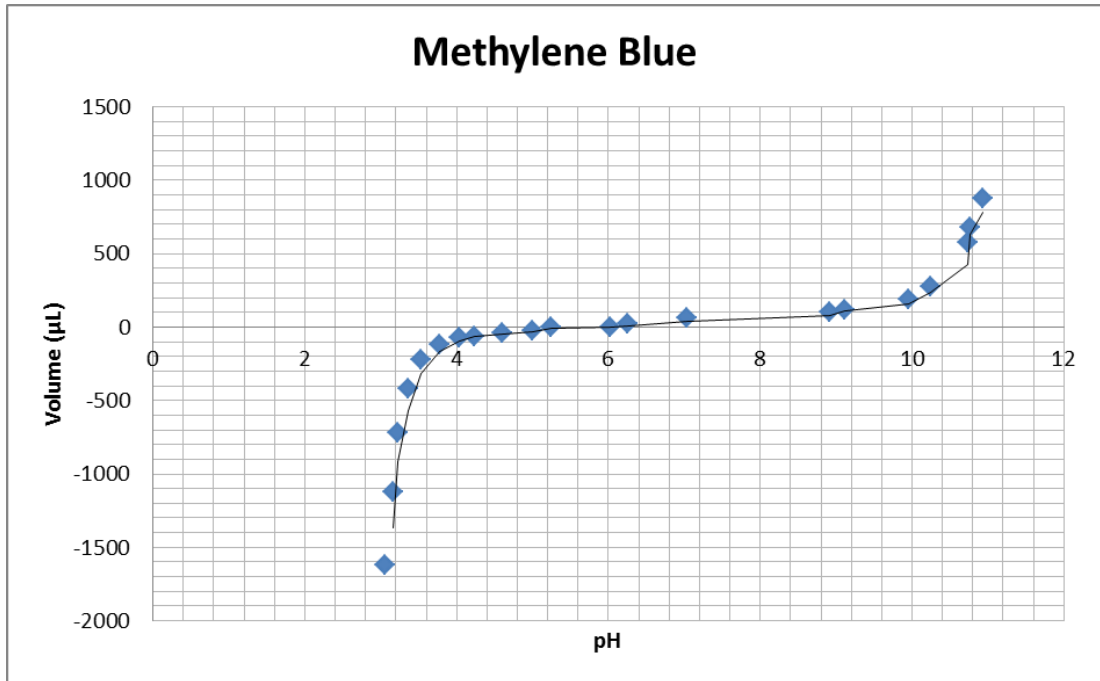
APPENDICES

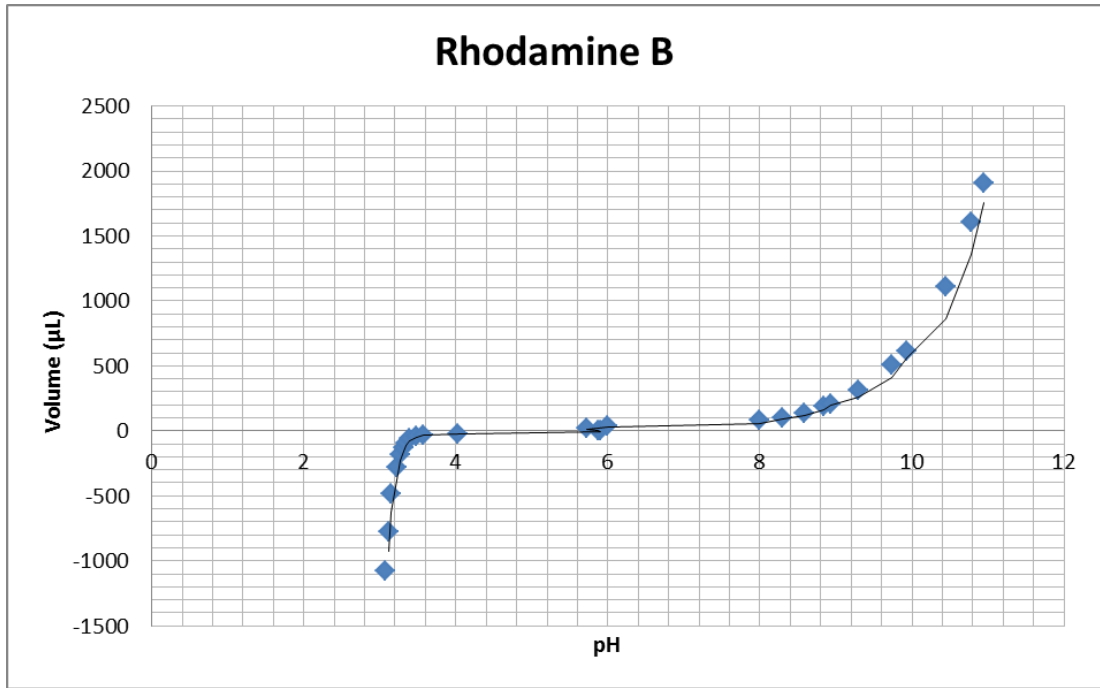
APPENDIX A: Calibration Curves for Methylene Blue, Methyl Orange and Rhodamine B





APPENDIX B: pH Adjustment Curve for Methylene Blue, Methyl Orange and
Rhodamine B





APPENDIX C: Sample Calculation for Preparation of Dye Solution

To prepare stock solution of 500 mg/L:

Rhodamine B (Purity 95%)

To obtain 100% pure 1 g/L dye, 0.5263 g dye powder was added to 1 L distilled water.

To prepare 100 mL of 10 mg/L of organic dye from 500 mg/L stock solution:

$$C_1V_1=C_2V_2$$

$$500V_1=10(1000)$$

$$V_1=20.0 \text{ mL}$$

Table A: Volume of Stock Solution to Prepare 1L of Different Concentration of Dye

Concentration of Dye (mg/L)	Volume of Stock Solution (mL)
2.5	5
5.0	10
7.5	15
10.0	20
12.5	25

APPENDIX D: MSDS