SYNTHESIS OF TiO$_2$/G-C$_3$N$_4$ COMPOSITE FOR
SONOCATALYTIC DEGRADATION OF ORGANIC DYE

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

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September 2018
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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ABSTRACT

The carcinogenic and mutagenic effects of organic pollutants have become the biggest concern due to the ineffectiveness of conventional wastewater treatment methods. Organic dyes released into water resources mainly due to the textile, dye and pharmaceutical industries. About 10-25 % of textile dyes will be released and 2-20 % of them are directly released to effluents during dyeing process. The ultrasonic irradiation will generate photon-induced electron–hole pairs in the presence of titanium dioxide (TiO$_2$) to produce hydroxyl radicals (•OH) which used as strong oxidising agent to degrade organic dyes. In this research, titanium dioxide/graphitic carbon nitride (TiO$_2$/g-C$_3$N$_4$) at different weight ratios were synthesised by using sol-gel followed by calcination method. As-synthesised pure TiO$_2$, pure g-C$_3$N$_4$ and TiO$_2$/g-C$_3$N$_4$ at various weight ratios were characterised by X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) and Fourier transform infrared spectroscopy (FTIR) analyses. As-synthesised pure TiO$_2$ possess spherical particles, while g-C$_3$N$_4$ displayed sheet-like morphology. The as-synthesised TiO$_2$/g-C$_3$N$_4$ appeared as spherical TiO$_2$ particles distributed on sheet-like g-C$_3$N$_4$.

Various parameters were studied during sonocatalytic degradation process, such as weight ratio of TiO$_2$ to g-C$_3$N$_4$, catalyst loading, initial malachite green (MG) concentration, initial solution pH and types of organic dyes. The optimum condition for the degradation of dyes was identified at 1.5 g/L of TiO$_2$/g-C$_3$N$_4$-0.5 in degradation of 10 mg/L of MG at solution of pH 5, which successfully removed 79.01 % of MG. The effectiveness of dye degradation was followed sequence from MG, congo red (CR), methylene blue (MB), reactive blue 4 (RB 4) and methyl orange (MO) in descending order. The sonocatalytic reaction followed the pseudo-first order rate kinetics in the kinetic study. About 50 % of the chemical oxygen demand (COD) was removed after 30 minutes by using TiO$_2$/g-C$_3$N$_4$-0.5 composite. TiO$_2$/g-C$_3$N$_4$ composite exhibited higher catalytic ability in degradation of dyes than pure TiO$_2$ and pure g-C$_3$N$_4$. 
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<td>hydroxyl radical</td>
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<td>organic radical</td>
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<tr>
<td>θ</td>
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</tr>
<tr>
<td>β</td>
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<tr>
<td>λ</td>
<td>wavelength of X-ray</td>
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<tr>
<td>ε_max</td>
<td>maximum tensile stress</td>
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<td>pi bond</td>
</tr>
<tr>
<td>π*</td>
<td>excited pi bond</td>
</tr>
<tr>
<td>AOP</td>
<td>advanced oxidation process</td>
</tr>
<tr>
<td>ATR</td>
<td>attenuated total reflectance</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>COD</td>
<td>chemical oxygen demand</td>
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<tr>
<td>CR</td>
<td>congo red</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<td>MB</td>
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<td>MG</td>
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<td>MO</td>
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<td>reactive blue 14</td>
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<tr>
<td>RhB</td>
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<td>SEM-EDX</td>
<td>scanning electron microscopy with energy dispersive X-ray spectroscopy</td>
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<td>ultraviolet-visible</td>
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<td>volatile organic compounds</td>
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CHAPTER 1

INTRODUCTION

1.1 Background of Water Pollution

It has long been known that the quality of river water or groundwater continues to deteriorate and being polluted due to agricultural, industrial and domestic activities. Water has been the richest resource on earth since its coverage is around 70% of the earth surface. Thus, South African National Water Act (Act number 36 of 1998) specified that the quality of water resource has to be continuously monitored as well as maintaining its sustainable use (Murray, Slabbert and Moloi, 2003). The pollutants which are released into the water resource is not only harmful to human health and aquatic ecosystems, it will also affect the use of amenities and other legitimate uses of water (Murray, Slabbert and Moloi, 2003).

The sources of water pollution can be differentiated into point source or nonpoint source. If the polluting substance is released directly into water system, it is called as point source. The most common example is the emission of sewage from the pipe directly into the water system. Nonpoint source pollution refers to the pollutants enter a water system through land runoff, atmospheric deposition and drainage system. The water pollutants are also different from aspect of physical such as odour and colour, biological such as pathogens, organic or inorganic compounds (Mahlambi, Ngila and Mamba, 2015).

Over the past decade, the carcinogenic and mutagenic effects of organic pollutants become the biggest concern due to the ineffectiveness of conventional water treatment methods to degrade these contaminants in aqueous media. Volatile organic compounds (VOCs) is one of the toxic and carcinogenic substances which contributes to stratospheric ozone layer depletion as well as global warming. VOCs are organic chemical compounds which are easily evaporated under normal atmospheric conditions. VOCs can be resent as indoor or outdoor air pollutants. It can adversely affect the people’s healthiness. For instance, short-term exposure to VOCs can irritate eye and respiratory system. Exposed people will suffer from dizziness and headaches. Environmental Protection Agency is responsible to control VOCs since photochemical smog created may contribute to serious pollution issues under certain conditions. The development of antibiotic resistance bacteria and genes
become the major concern due to mutagenic characteristic of these pollutants (Mahlambi, Ngila and Mamba, 2015).

Beside VOCs, persistent organic pollutants (POPs) is one of the organic pollutants which will highly influence human health and the environment throughout the world. Human are exposed to these chemicals mainly through the consumption of food and air in the outdoor and indoor workplace. POPs can be transferred by water and wind, affecting people and wildlife located in different places. The problem become serious since they can remain in environment for a long duration without breaking down in the environment and further pass over each species to the others through the food chain. The toxicity of POPs can bring serious diseases when they accumulated in fatty tissue and animal’s organ. For example, endocrine system and immune system will be destroyed. It will also initiate cancer and genetic-related diseases. The examples of POPs are organochlorine pesticides such as dichlorodiphenyltrichloroethane, industrial waste especially polychlorinate biphenyls, as well as unwanted by-products from industry, such as polychlorinated dibenzo-p-dioxins and dibenzofurans, which is commonly called as 'dioxins'.

Meanwhile, the pollution related to the organic dyes become a serious issue nowadays mainly due to the textile industries, dye industries, pharmaceutical industries, paper industries and tannery. Although natural and synthetic dye compounds contribute to wonderful colour to the world through coloured products, they are still considered as pollutant which is harmful to human lives and environment. During the dyeing process in textile industries, about 10 to 25 % of textile dyes will be released, while 2 to 20 % are directly released in effluent. The effluent that containing dyes which released into the water source will bring negative impacts not only due to their colour, but the properties of breakdown products which are carcinogenic, toxic and mutagenic. The example of carcinogens discharged into environment including benzidine, naphthalene and other aromatic compounds (Zaharia, et al., 2009; Suteu, et al., 2009).

1.2 Importance of the Study

Heterogeneous sonocatalytic oxidation has gained a lot of attention in recent years. There are studies showing that the application of heterogeneous sonocatalytic oxidation process can mineralize and decompose organic pollutants by accelerating the sonoreaction in the presence of semiconductor catalyst. Recent years, the focus
on semiconducting oxide sonocatalysts is gradually increasing since they have great potential especially in solar energy conversion and environmental purification. Sonocatalysis uses ultrasound to create cavitation phenomena. The phenomenon involves formation, growth and breakdown of cavities in small time intervals whereby large amount of energy was released simultaneously (Sangave and Pandit, 2004). The high localized temperatures and pressures will disengage the water molecules into radicals.

Semiconducting oxide catalysts can be used in treatment of organic contaminants either in air or water source while this process is commonly named as advanced oxidation process (AOP). AOP can generate active oxidising radicals such as •OH, hydrogen peroxide (H₂O₂) and superoxide anion radicals (O₂•⁻) in treatment of organic pollutants (Ribeiro, et al., 2015). There are a lot of metal semiconductors which regarded as good materials for sonocatalysts, including TiO₂, zinc oxide, iron (III) oxide, cadmium sulphide and zinc sulphide. These metal semiconductors are poor conductors under normal conditions, but they can be transformed into good conductors after they have been shined by a specific illuminant as well as acting as catalysts.

The application of catalysts will improve the performance of sonochemical degradation process since it will create more nucleation sites to the growth of microbubbles. It will result in enhancement of pyrolytic degradation efficiency and susceptible radical generation, making it more potential in decolourisation of textile dyeing wastewater (Khataee, et al., 2015). The catalytic process can break down the pollutants and destructive organic components into simple components such as carbon dioxide (CO₂) and water. TiO₂ has high catalytic activity due to the lifetime of electron-hole pairs and the appropriate band gap. Since it presents at stable state in harsh environment, TiO₂ is potentially in the making of gas sensors which required to be operated at temperature over 400 °C and above. It just requires an ultrasound source in order to activate the TiO₂ easily. Other than that, the hydroxide groups (OH) present on the surface of the TiO₂ is came from the hydroxylation of TiO₂ in water, while these OH groups might be the sources of the OH radicals.

The TiO₂ semiconductor catalyst is considered as low-cost, non-toxic, stable and appropriate to use the energy source generated from ultraviolet light or ultrasound. Its oxidation and reduction abilities under the light or sound irradiation are strong due to the production of electron-hole pairs. The series of reduction—
oxidation reaction initiated by electron-hole pairs can degrade most of the organic pollutants. However, using TiO$_2$ catalyst with the presence of lights to solve dye wastewater problem, its efficiency is highly reduced especially for high-concentrated dye wastewaters (Fu, et al., 2005). Thus, the shortcoming can be solved by utilising ultrasound irradiation since ultrasound has strong penetrating ability for any water medium (Suslick, et al., 1999). The competency of ultrasound and ultraviolet with visible light is approximately the same in catalysing those chemical reactions. Hence, there are a lot of researches related to the sonocatalytic degradation of different types of organic compounds by using ultrasound as source of irradiation beside using visible and ultraviolet light.

Other than that, g-C$_3$N$_4$ has been drawn researchers’ concern according to its applications in the generation of hydrogen and pollutants decomposition under irradiation of visible light. According to Zhang, et al. (2017), the band gap of pure g-C$_3$N$_4$ is considered as low which is 2.7 eV. Thus, it is effective in light capturing within the visible light region. Generally, g-C$_3$N$_4$ can be easily manufactured by pyrolysis of precursors which consist of nitrogen, such as melamine, dicyandiamide, trithiocyanuric acid, cyanamide and urea (Lan, Zhang and Wang, 2016). It is a promising material for some applications and theoretical predictions owning to its nitrogen-rich properties, large surface area and outstanding stability in structure. The presence of high nitrogen content in g-C$_3$N$_4$ increase the number of active sites, which will further improve the electron transport and wettability between the electrolytes and active material, enhancing the efficiency of mass transfer (Zhao, et al., 2017b). A lot of researchers successfully used g-C$_3$N$_4$ as a photocatalyst to produce hydrogen and other discoveries on organic pollutant degradation (Wang, et al., 2009; Dong, 2014; Zhang, et al., 2012). The excellent photocatalytic efficiency of pure g-C$_3$N$_4$ proved by the researchers increase the possibility of g-C$_3$N$_4$ to be used in enhancement of sonocatalytic efficiency.

The coupling of g-C$_3$N$_4$ will reduce the recombination rate of electron-hole pairs generated and induce a synergistic effect including efficient charge separation and upgrading of stability, leading to enhanced quantum yields (Cao, 2015). The deficiency of individual component is thereby being compensated. Thus, Li, et al. (2015) reported that it may be desirable to generate a heterojunction sonocatalyst with enhanced sonocatalytic activity under ultrasound irradiation. Both g-C$_3$N$_4$ and TiO$_2$ displayed suitable energy levels to construct the heterojunction, which will
slow down the recombination of excited charge carries and improve their catalytic performance (Zhang, et al., 2017). The use of TiO$_2$/g-C$_3$N$_4$ composites have been incorporated by using several approaches. For instance, the fabrication of TiO$_2$/g-C$_3$N$_4$ hybrids by hydrothermal method while hybrids showed promising photocatalytic activities in degradation of MO solution (Lu, 2017).

1.3 Problem Statement

With all the problems such as energy shortage and dangerous of human survival due to environment pollution, various water treatment technologies have been developed. However, the effective way of degradation of organic pollutants from water have still to be discovered. There are three common types of water treatment method which are biological, chemical and physical method.

For biological treatment such as aerobic and anaerobic water treatment, microorganisms are used to biodegrade the pollutants in the water (Mittal, 2011). However, the biodegradation is very time-consuming and incomplete while the efficiency of biological treatment is insufficient (Zangeneh, et al, 2015). Chemical water treatment was used to kill bacteria or viruses through the reactions between the pollutants and certain chemicals. Chlorination and ozonation are the examples of chemical water treatment. However, this method will produce hazardous chlorinated by-products and cause ozone’s toxicity and instability. Physical water treatment techniques can capture and separate the pollutants from water by using physical means such as ultrafiltration, reverse osmosis and carbon adsorption. However, the pollutants are not fully eliminated since the nature of the processes is non-destructive. It will possibly lead to unfavourable secondary pollutants when the condition is not prevented (Zangeneh, et al, 2015). Therefore, advanced technologies are highly required to increase removal efficiency of these pollutants from water.

Apart from the above, sonocatalytic technology is recognized as an effective mean to cope with the situation. The problem related to TiO$_2$ catalyst to achieve the best degradation rate is still present similar to the problem of photocatalytic degradation. Nowadays, a lot of TiO$_2$ composite are synthesised accompanied with the use of other materials to improve its catalysis efficiency. Those methods are possibly suitable to be used in fabrication of TiO$_2$ sonocatalyst, such as doping with transition metal and coupling with arrow band-gap semiconductor.
Therefore, fabrication of TiO$_2$/g-C$_3$N$_4$ composite with enhanced catalytic performance has become an emerging trend. It can be prepared through co-calcination, hydrothermal treatment and microwave-assisted synthesis. For now, it was reported that TiO$_2$/g-C$_3$N$_4$ heterojunctions was synthesised in the structure of mesoporous, core-shell, nanotube/nanosheet and nanoparticle/nanosheet. However, the investigations were more concentrated on modifying the composition rather than interaction type that defines a heterojunction interface. The detailed studies on fabrication of TiO$_2$/g-C$_3$N$_4$ composites have to be conducted in this research.

1.4 Aims and Objectives
The objectives of the study are:

i. To synthesise TiO$_2$/g-C$_3$N$_4$ composite sonocatalyst at various weight ratio using sol-gel and calcination process.

ii. To characterise the chemical and physical properties of as-synthesised TiO$_2$/g-C$_3$N$_4$ composite using various characterisation techniques.

iii. To demonstrate the process behavior for sonocatalytic degradation process of organic dyes.

1.5 Scope and Limitation of the Study
The study covers the synthesis, characterisation of as-synthesised TiO$_2$/g-C$_3$N$_4$ composite and process parameters study for sonocatalytic degradation process. Fabrication of TiO$_2$/g-C$_3$N$_4$ composite will be carried out using calcination method. After the synthesis process, the as-prepared TiO$_2$/g-C$_3$N$_4$ composite will be characterised by XRD, SEM-EDX and FTIR analyses. Simultaneous degradation of organic dye will be tested by using ultrasonic processor. The TiO$_2$/g-C$_3$N$_4$ with different ratios will be synthesised other than fabrication of pure g-C$_3$N$_4$ and TiO$_2$. The characterisation of catalyst fabricated will be carried out to determine their structure difference. The parameter studies will be conducted including amount of catalyst loading, initial dye concentration, initial solution pH and types of organic dyes used. The liquid samples from parameter studies were analysed using ultraviolet-visible (UV-Vis) spectrophotometer and COD analysis.
2.1 Dyes

Dye is a type of colourants that purposely adding a colour or changing the colour to textiles, paper and leather so that the colouring is not readily modified by washing, light and heat. They are widely used in the cosmetics, food, pharmaceutical, textile, paper, photographic, paint and plastics industries. The pigment is different from dye since the pigment is finely divided solid that blended with other materials or dissolved in a liquid (paint or ink). Dyes are organic compounds due to the presence of carbon, whereas pigments may be inorganic compounds or organic compounds due to the uncertainty in the presence of carbon. During the production process in factories, dye is soluble coloured substance which is able to flow into solution and convey colour by selective absorption of light. Pigments are not chemically influenced by medium in which they are integrated and appearance will change either by selective absorption or light scattering (Gürses, et al., 2016).

Dye can show its colour unlike most organic compounds due to its absorption of light in the range of 400 to 700 nm and presence of at least one chromophore which is a type of colour-bearing group. Besides, it has conjugated system which having an alternating single and double bonds structure. The electrons resonance in dye may contribute to its stabilization in organic compounds (Abrahart, 1977). The colour will disappear when any of these features is missing. The molecules will absorb the electromagnetic radiations in the visible and UV regions, exciting the electrons to move from lower to higher electronic energy level. Chromophore is a covalently unsaturated group which is important for absorption of light in the visible or UV region. Examples of chromophores are carbon triple bond (C≡C), azo (N=N), cyanate (C≡N), carbon double bond (C=C), carbonyl (C=O) and nitro group (Gürses, et al., 2016). Only the compounds which absorb light in the visible range can show the colour. For chromophores such as C≡C or C=C that having π electrons, π electrons will be excited to π* transitions. For those having both π and non-bonding electrons (C=O, C≡N or N=N), it will experience π → π*, n → σ* and n → π* transitions (Gürses, et al., 2016). The relationship between visible wavelength and
observed colour were shown as Table 2.1. Figure 2.1 shows several types of chromophoric groups present in organic dyes which contribute to appearance of colour.

Table 2.1: Wavelength Absorbed Versus Colour in Organic Dyes (IARC, 2010)

<table>
<thead>
<tr>
<th>Wavelength Absorbed (nm)</th>
<th>Colour Absorbed</th>
<th>Colour Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>435-480</td>
<td>Blue</td>
<td>Yellow</td>
</tr>
<tr>
<td>480-490</td>
<td>Green-Blue</td>
<td>Orange</td>
</tr>
<tr>
<td>490-500</td>
<td>Blue-Green</td>
<td>Red</td>
</tr>
<tr>
<td>500-560</td>
<td>Green</td>
<td>Purple</td>
</tr>
<tr>
<td>560-580</td>
<td>Yellow-Green</td>
<td>Violet</td>
</tr>
<tr>
<td>580-595</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
</tbody>
</table>

Figure 2.1: Common Chromophoric Groups Present in Organic Dyes (IARC, 2010)

Besides chromophores, dyes also consist of colour helpers which are called as auxochromes, for instance, carboxylic acid group, sulfonic acid group, amino group, and hydroxyl groups. Auxochromes can be characterised as colour enhancing groups as the value of maximum wavelength (\(\lambda_{\text{max}}\)) as well as maximum tensile stress (\(\varepsilon_{\text{max}}\)) will increase by lengthening the conjugation through resonance. In fact, there is no absorption when the wavelength exceeded 200 nm while the combination of auxochrome and chromophore will give to a new chromophore with different values of \(\lambda_{\text{max}}\) and \(\varepsilon_{\text{max}}\). For instance, the \(\lambda_{\text{max}}\) and \(\varepsilon_{\text{max}}\) of benzene are 256 nm and 200 respectively, while the \(\lambda_{\text{max}}\) and \(\varepsilon_{\text{max}}\) of phenol increase to 270 nm and 1450
respectively. It is obvious that the OH group can enhance the conjugation that involves the electron lone pair on the oxygen atom (O), causing the increment of $\varepsilon_{\text{max}}$ and $\lambda_{\text{max}}$.

Dyeing process can be done by dissolving colourant in a solution and make it interacts with the dyed material. Dyes can be classified into several types such as basic, acid, direct, mordant, reactive, sulphur, disperse, vat and azo as shown in Table 2.2.

Table 2.2: Characteristic of Different Classes of Dyes (Lam, et al., 2012)

<table>
<thead>
<tr>
<th>Types of Dyes</th>
<th>Descriptions</th>
<th>Examples of Dyes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>• Water-soluble anionic dye</td>
<td>• Acid yellow 36</td>
</tr>
<tr>
<td></td>
<td>• Reversible dyeing process</td>
<td></td>
</tr>
<tr>
<td>Azo</td>
<td>• Presence of an azo group (-N=N-) as the chromophore</td>
<td>• Disperse orange 1</td>
</tr>
<tr>
<td>Basic</td>
<td>• Cationic dye, water soluble</td>
<td>• Basic brown 1</td>
</tr>
<tr>
<td>Direct</td>
<td>• Do not require any form of ‘fixing’</td>
<td>• Direct orange 26</td>
</tr>
<tr>
<td></td>
<td>• Water soluble because of sulfonic acid groups</td>
<td></td>
</tr>
<tr>
<td>Disperse</td>
<td>• Insoluble in water</td>
<td>• Disperse red 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Disperse yellow 3,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Disperse blue 27</td>
</tr>
<tr>
<td>Reactive</td>
<td>• React with cellulosic fibre to form a covalent bond</td>
<td>• Reactive blue 5 dye</td>
</tr>
<tr>
<td>Vat</td>
<td>• Containing multi-ring systems</td>
<td>• Vat Blue 4</td>
</tr>
<tr>
<td></td>
<td>• Insoluble in water but become solubilised by alkali reduction</td>
<td>(Indanthrene)</td>
</tr>
</tbody>
</table>

During the dyeing and finishing operations in textile industry, around 200,000 tons of dyes are being released yearly (Ogugbue and Sawidis, 2011). This is because the dyeing process is not very efficient. Majority of the dyes are being released from common wastewater treatment process and then remained in environment due to the factors of high-water stability, light, temperature and
chemicals existed. In the manufacturing of textiles, the use of anti-microbial agent that is biological degradation resistance is quite popular especially for natural fibres (Couto, 2009). In fact, the most polluting sector from all industrial sectors is textile plants based on their effluent composition and volume of effluent generated (Şen and Demirer, 2003). It was estimated that the colourants that losing to the environment during dyeing process is about 10 % to 50 %. Some dyes are highly toxic which in turn reduce photosynthetic activity and penetration of light. This is further resulted in oxygen (O₂) deficiency and restricted downstream function such as irrigation and recreation (Drumond Chequer, et al., 2013).

2.2 Conventional Types of Wastewater Treatment

In order to maintain green environment, cost-effective treatments to destroy the pollutants to benign chemical or remove the pollutants are necessary. The examples of common treatment process including as electrochemical oxidation, biodegradation, membrane process and AOPs. Some conventional methods will be explained in this section.

2.2.1 Biological Treatment

Biological wastewater treatment is a secondary treatment process which is used to eliminate any components remained from primary treatment. Substances or sediments such as oil will be eliminated from the wastewater in the primary water treatment process. Due to the excellent reactivity of microorganisms with various organic and inorganic species, biological treatments were being used to remove the heavy metal in the 1990s (Rasalingam, Peng and Koodali, 2014). The microorganisms will alter the chemical and physical characteristic of the metals which in turns affect the mobility of metal. The wastewater treatment by biological processes that are used to degrade wastewater including subsurface methods, such as aerobic or septic tank disposal systems, activated sludge processes, anaerobic digestion and aeration system such as spray and surface aeration. Besides, biological treatment processes can be differentiated into anaerobic and aerobic processes. Aerobic processes involve the presence of O₂, while anaerobic process is a biological process that do not require the use of O₂ (Mittal, 2011).

The bioreactor will provide suitable bioenvironmental conditions for the reproduction of microorganisms. The dissolved organic matter is used by bioreactor
as energy especially O\textsubscript{2} and food. The purification of wastewater can be described as dissolved organic matter being converted into thick bacterial biomass. The microbial biomass is then being separated from treated wastewater through sedimentation. Microorganisms like heterotrophic bacteria and fungi will remove organic matter biologically from settled wastewater. The microorganisms use two different biological processes for the decomposition of organic matter, which are biosynthesis and biological oxidation. For biological oxidation, some end-products such as mineral will be formed, stayed in the solution and then released with the effluent as in equation (2.1). For the biosynthesis, the colloidal and dissolved organic matter is transformed into new cells to form a high-density biomass which can be eliminated by sedimentation in equation (2.2) (Samer, 2015).

Biological oxidation:
\[
\text{COHNS (Organic matter) + Bacteria + O}_2 \rightarrow \text{CO}_2 + \text{ammonia (NH}_3) + \text{Energy} + \text{Other end products}
\] (2.1)

Biosynthesis:
\[
\text{COHNS + Bacteria + O}_2 \rightarrow \text{C}_5\text{H}_7\text{NO}_2 \text{ (New cells)}
\] (2.2)

### 2.2.2 Physical Treatment

In physical methods, there are no involvement of chemical or biological changes in wastewater treatment but only the occurrence of physical phenomena. For instance, larger entrained substance can be removed by using coarse screening and sedimentation. Sedimentation refers to the settling of solids by gravity under calm conditions for a short period, waiting for the settling of solids and removal of “clarified effluent”. This method is commonly used at the end or the beginning of the wastewater treatment applications. Aeration is one of the physical treatment processes which involve physical addition of air (such as O\textsubscript{2}) into the wastewater. In filtration, filter medium is used to separate the solids from wastewater, while additional use of sand filters is responsible in the removal of entrained solids from treated wastewater.

Other than that, adsorption is one of the physical process that have been widely used since it has low cost, high flexibility, simple design and operation. The most important advantage of using this method is no harmful substances will be
produced. The absorbents that are commonly used to remove industrial waste including activated carbon, coal, fly ash and biomaterials. However, some materials mentioned above is not effective due to the weak interaction between absorbent and adsorbent (Rasalingam, Peng and Koodali, 2014). The disadvantage is it merely eliminate the pollutants from one phase (aqueous) to another (solid matrix). If the pollutants are strongly bounded to the absorbents, the cost will become expensive for the regeneration.

Membrane filtration also provides a physical barrier for the effective removal of viruses, solids, bacteria and other undesirable molecules. The materials that are allowed to pass through the membrane is only for a certain shape and size. The crossflow with pressure-driven membrane separation processes that are commonly applied in liquid/liquid separation and liquid/solid separation including reverse osmosis, nanofiltration, ultrafiltration and microfiltration (Cassano, 2018). Microfiltration can be used in removal of protozoa and bacteria, while ultrafiltration can remove virus. Since the membrane systems do not require substantial portion of buildings or land as conventional system, lower installation cost is needed.

2.2.3 Chemical Treatment

In chemical treatment, chlorination can be used to upgrade water quality by applying some chemical reaction. Chlorination use a strong oxidising chemical like chlorine to destroy bacteria and cause the increment of wastewater decomposition rate. There are some important criteria to choose an appropriate disinfectant for the treatment purpose, such as ability to destroy infectious agents under normal conditions, absence of toxic and carcinogenic compounds, handling convenience and safety of storage. Other than that, it is effective to oxidise various types of pathogenic organism, organic and inorganic compounds. High degree of disinfection can be done by changing the dose of chlorine and contact time. The dose that required is commonly ranged from 5 to 20 milligrams per litres (mg/L) (United States Environmental Protection Agency, 1999). However, the storage, handling and shipping of chlorine have a risk due to its highly corrosive and toxic characteristic. It is still dangerous since the long-term effect of discharging into environment is still unknown (United States Environmental Protection Agency, 1999).

Ozone is one type of strong oxidising agent that is functioned as oxidising disinfectant of wastewater. When the O atoms that dissociated by energy source from
O₂ molecules collides with another O₂ molecules, there will be formation of unstable gas and ozone. In most of the wastewater treatment operations, ozone is produced after applying a high voltage alternating current of around 6 to 20 kilovolts through a dielectric discharge gap when oxygen-bearing gas presents (United States Environmental Protection Agency, 1999). The free radical hydrogen peroxyl and hydroxyl are formed when the ozone is decomposed in water, while the radicals formed possesses great oxidising capacity and highly important in disinfection process. The bacteria will be destroyed due to the protoplastic oxidation, causing disintegration of cell wall (United States Environmental Protection Agency, 1999).

Furthermore, neutralization involves the addition of alkali or acid to modify pH levels until it becomes neutral. The examples of common acid and alkaline solutions are hydrofluoric acid, sulphuric acid, hydrochloric acid, nitric acid, potassium hydroxide and sodium hydroxide. Coagulation can eliminate the substances from wastewater by adding of chemical to form insoluble end product through chemical reaction. The coagulating chemicals used include polyvalent metals, aluminium sulphate, lime and some compounds such as ferric sulphate and ferric chloride. The negative charge of non-settleable solid is neutralised when coagulant chemical with charge opposite to suspended solid is added to water. The small suspended particles will stick together when the charge is neutralised (Prakash, Vimala and Jayakaran, 2014).

2.3 Advanced Oxidation Process (AOP)
In 1980s, AOPs were first proposed for treatment of portable water (Deng and Zhao, 2015). This process is an oxidation process involving the production of sufficient ⋅OH to purify organic pollutants wastewater generated from ozone, hydrogen peroxide, oxidants or photocatalysis with presence of ultraviolet radiation (Krishnan, et al., 2017). Beside ⋅OH, sulphate radicals can be produced to eliminate traceable organic compounds, refractory organic matters and inorganic pollutants. There are some studies related to AOP inactivation of pathogens and pathogenic indicators, but they are rarely utilised for disinfection since the half-life of these radicals are too short which is in microseconds (Cho, et. al., 2005). Thus, the required detention times for disinfection are restrained because the radical concentration is critically low (Tchobanoglous, et. al., 2003). The radicals can function as strong oxidising agent to
degrade wastewater pollutants adequately, disintegrating them to become smaller and converting to less non-toxic products.

There are several types of AOPs applied in wastewater treatment, such as ozone-based AOPs, Fenton-related AOPs, UV-based AOPs and sulphate radical-based AOPs (Deng and Zhao, 2015). •OH is the most reactive radical for the degradation of organic compounds. Its oxidation power is between 1.95 V (pH 14) and 2.8 V (pH 0) using saturated calomel electrode, which is always acted as reference electrode (Tchobanoglous, et. al., 2003). Table 2.3 shows the oxidation power of different oxidation species, showing that •OH having relatively high electronegative oxidation potential. The organic pollutant can be attacked by •OH through four basic pathways, such as radical combination, radical addition, electron transfer and hydrogen abstraction (Deng and Zhao, 2015). The •OH play an important role in AOPs to destroy organic compound due to its non-selective and electrophilic nature. The characteristic of •OH are shown in Figure 2.2.

Table 2.3: Relative Oxidation Power (Krishnan, et al., 2017)

<table>
<thead>
<tr>
<th>Oxidising Groups</th>
<th>Relative Oxidation Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>1.00</td>
</tr>
<tr>
<td>Hypochlorous Acid</td>
<td>1.10</td>
</tr>
<tr>
<td>Permanganate</td>
<td>1.24</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>1.31</td>
</tr>
<tr>
<td>Ozone</td>
<td>1.52</td>
</tr>
<tr>
<td>Atomic Oxygen</td>
<td>1.78</td>
</tr>
<tr>
<td>Hydroxyl Radical</td>
<td>2.05</td>
</tr>
<tr>
<td>TiO$^{2+}$</td>
<td>2.35</td>
</tr>
</tbody>
</table>

![Figure 2.2: •OH Characteristics (Anju, 2015)](image-url)
The equation (2.3) to (2.6) show the common degradation pathways of organic pollutants. Equation (2.3) shows a hydrogen atom is taken away from an organic compound (RH) by •OH to release an organic radical (•R). The •R will further react with H₂O₂ to form more •OH in equation (2.4) and mineralize the organic compound. The carbon-center radicals will react with O₂ and being converted into organic peroxyl radicals (ROO•) as shown in equation (2.5) (Deng and Zhao, 2015).

\[
\begin{align*}
\text{•OH} + \text{RH} & \rightarrow \text{H}_2\text{O} + \text{•R} \quad (2.3) \\
\text{•R} + \text{H}_2\text{O}_2 & \rightarrow \text{ROH} + \text{•OH} \quad (2.4) \\
\text{•R} + \text{O}_2 & \rightarrow \text{ROO•} \quad (2.5) \\
\text{ROO•} + \text{RH} & \rightarrow \text{ROOH} + \text{•R} \quad (2.6)
\end{align*}
\]

Since reactivity of •OH radical is high, AOP is widely applied to degrade different types of contaminants. Instead of transferring organic compounds into another phase, the organic compounds can be eliminated effectively by using AOPs. Thus, post treatment is not necessary since secondary pollutants are not generated like "spent carbon" from adsorption of activated carbon. In short, it is more beneficial compared to conventional wastewater treating processes which can generate massive quantities of chemical or biological sludge (Azbar, et al., 2004).

### 2.4 Theory of Ultrasound

Ultrasound is a sound wave that has frequency ranges from 18 kHz to 10 MHz with associated acoustic wavelengths at around 0.15 mm. The acoustic field within molecules is significantly higher than molecular dimensions of a chemical species. By applying short period of high temperatures and pressures, molecules will be decomposed while reactivity of chemical substances will increase. Ultrasonication can actually lead to heterogeneous and homogeneous catalysis in many ways.

Cavitation is the most important chemical effects of ultrasound that derived from non-linear acoustic phenomena. There are various forms of cavitation including particle, acoustic, optic and hydrodynamic cavitation. It highly depends on the
generation method and related experimental parameters, such as frequency, temperature, reactor shape, pressure and solvents (Kuna, et al., 2017). Acoustic and hydrodynamic cavitation will cause physically and chemically changes in solution which are highly different from optic and particle cavitation. The cavitation will generate large amount of “hot spots” due to the accumulation of energy, causing extensive pressures and temperatures (Agarwal, Ng and Liu, 2011). Hydrodynamic cavitation was induced by the pressure fluctuation after altering the flow system geometry. Fluctuation of pressure will generate acoustic cavitation in the sound waves passageway (Colmenares, 2014).

In acoustic cavitation, the bubbles in liquid will undergo formation, growth process and implosive collapse when irradiated with ultrasound. It always takes place on surface of bubbles (solution-phase chemistry), within collapsing bubbles (gas-phase chemistry) and at liquid-solid interface (physical modification). Expansion (negative pressure) and compression (positive pressure) waves will be produced when the sound passing over a liquid, causing bubbles to grow and recompress. However, acoustic cavitation under extreme conditions will induce implosive compression, causing intense local heating, high temperature and pressure of approximately 5000 °C and 1000 atm (Figure 2.3).

![Figure 2.3: Cavitation and Implosion Phenomena (Anju, 2015)](image)

Power ultrasound is popular to produce extremely fine emulsions and dispersions while these fine-size emulsions and dispersions will enhance chemical reactions. This is due to the increase in interfacial contact area between liquid and solid or between two or more immiscible liquids, leading to a better and faster course
of the reaction. Besides, it is useful in breaking up the bondages and creating free radicals. The physical and chemical consequence of ultrasound terminated from the cavitation circumstance, but not from interaction between ultrasonic waves and chemical species directly. The ultrasound will generate chemical effect such as implosive microbubbles collapse and responsible in production of free radicals. Figure 2.4 shows the physical effect of ultrasound to generate micro jet and shock waves during asymmetric and symmetric cavitation (Kuna, et al., 2017).

![Acoustic Cavitation Mechanism](image)

Figure 2.4: Acoustic Cavitation Mechanism (Kuna, et al., 2017)

### 2.4.1 Mechanism of Sonocatalysis

Hot spot theory and sonoluminescence can be used to explain sonocatalytic degradation of organic compounds. Sonoluminescence is a phenomenon in which the gas bubble is periodically suspended in a solution arising from nucleation, collapse of gas bubbles and light emission. The extreme conditions will result in the cleavage of water molecules and O\(_2\) to become radicals like ⋅H, ⋅OH and ⋅O. These radicals are then reacted with each other as well as H\(_2\)O and O\(_2\) in rapid cooling stage. Organic pollutants will be degraded, while inorganic pollutants will be reduced or oxidised in highly reactive nuclear environment. Water will undergo ultrasonic reaction to form reactive free radicals. In equation (2.7), ⋅OH and ⋅H which are being as highly reactive primary radicals are produced through acoustic cavitation. Equations (2.8) to (2.10) show the radicals recombination and other reactions occur inside the bubble (Anju, 2015).
H₂O + ultrasound $\rightarrow$ ⋅OH + ⋅H \hspace{1cm} (2.7)

⋅OH + ⋅H $\rightarrow$ H₂O \hspace{1cm} (2.8)

⋅OH + ⋅OH $\rightarrow$ H₂O₂ \hspace{1cm} (2.9)

2⋅OH $\rightarrow$ H₂ + O \hspace{1cm} (2.10)

Besides, the presence of O₂ in water will result in the generation of OH radicals as shown in equation (2.11) and (2.12).

O₂ + ultrasound $\rightarrow$ O + O \hspace{1cm} (2.11)

O + H₂O $\rightarrow$ 2⋅OH \hspace{1cm} (2.12)

⋅OH has a redox potential of approximately 2.8 eV which is responsible to initiate oxidation for most of the organic pollutants. The formation of light with wavelength of 200 to 500 nm can cause sonoluminescence during ultrasonic irradiation, while highly active OH radicals will be produced for those with wavelength below 375 nm (Anju, 2015). The electron-hole pairs formation and OH radical formation can be initiated by the hotspot formation upon bubbles breakdown on catalyst surface.

The formation of light triggered by sonoluminescence will undergo the mechanisms from equation (2.13) to (2.22). The involvement of semiconductor will definitely increase the efficiency of sonocatalytic reaction (Anju, 2015).

Semiconductor + hv $\rightarrow$ h⁺ + e⁻ \hspace{1cm} (2.13)

h⁺ + e⁻ $\rightarrow$ Heat \hspace{1cm} (2.14)

h⁺ + OH⁻ $\rightarrow$ ⋅OH \hspace{1cm} (2.15)

h⁺ + H₂O $\rightarrow$ ⋅OH + H⁺ \hspace{1cm} (2.16)
Conduction band electrons scavenging,

$$e^- + O_2 \rightarrow \bullet O_2$$ \hspace{1cm} (2.17)

Production of multiple peroxide species,

$$H^+ + \bullet O_2^- \rightarrow HO_2\bullet$$ \hspace{1cm} (2.18)

$$HO_2\bullet + e^- + H^+ \rightarrow H_2O_2$$ \hspace{1cm} (2.19)

When the $H_2O_2$ reached sufficient concentration, the semiconductor will help to decompose $H_2O_2$ to form more $\bullet OH$.

$$\text{Semiconductor (e$^-$)} + H_2O_2 \rightarrow \bullet OH + OH^-$$ \hspace{1cm} (2.20)

$$H_2O_2 + hv \rightarrow 2\bullet OH$$ \hspace{1cm} (2.21)

$$H_2O_2 + \bullet O_2^- \rightarrow 2\bullet OH + O_2$$ \hspace{1cm} (2.22)

### 2.4.2 TiO$_2$ as Sonocatalyst

Generally, the organic contaminants can be eliminated by ultrasonic process but large amount of energy are required with long duration of treatment (Pang, Abdullah and Bhatia, 2010). This is due to its low reaction rate which can reduce its performance. Semiconductive material is necessary to be used as catalyst in the sonocatalytic degradation to improve the efficiency of the process and solve this disadvantage. The purpose of using catalyst is to promote formation of microbubbles and provide more active sites for nucleation process, further generating more reactive radicals (Wang, et. al., 2009). Most of the research works in the field of sonocatalysis are concentrated on the use of TiO$_2$-based sonocatalysts and other sonocatalysts such as zinc oxide, copper oxide and cadmium sulphide for the purification of organic dyes in aqueous solution (Hassani, et al., 2017). These metal semiconductors are poor conductors under normal conditions, but they can be transformed into good...
conductors after they have been shined by a specific illuminant as well as acting as catalysts.

TiO$_2$ has been chosen as the catalyst since it has benefits such as low solubility, cheap, high surface area, nontoxic, reusable and biologically stable (Fox and Dulay, 1993). Thin films of TiO$_2$ can be fabricated by coating certain component with a TiO$_2$ solution by techniques such as chemical vapor deposition, chemical spray pyrolysis, sol-gel method and electrodeposition. Every method has its own benefits and drawbacks. It has high catalytic activity due to the lifetime of electron-hole pairs and the appropriate band gap.

TiO$_2$ is one of the n-type semiconductors which can be used to extract hydrogen from water. TiO$_2$ has three types of crystallization structures, which are rutile, brookite and anatase. Rutile is stable at elevated temperature since the atoms in such crystalline grain will accumulate closely. The conversion of anatase to rutile normally occurs at elevated temperature at around 600 °C. By comparing these three structures, rutile and anatase are most widely used in photocatalysis, but not for brookite (Anju, 2015). Anatase phase is believed to be the most appropriate sonocatalyst compared to others. Besides, it is expected the reaction concept of TiO$_2$ in photocatalysis can be explained based on sonocatalysis.

The structure of rutile and anatase are similar since there are formed with octahedral TiO$_2$. The only difference between them are the degrees of distortion of each octahedron and arrangement of the octahedral chains as shown in Figure 2.5. The octahedron of rutile is irregular and appeared as a superficial orthorhombic distortion, while the octahedron of anatase is somewhat distorted. This will make the anatase less symmetrical than rutile. For rutile, each octahedron of a rutile is surrounded by ten octahedrons. Two octahedrons are co-edge while the others are co-corner. For anatase, each octahedron of anatase is surrounded by eight octahedrons. Four octahedrons are co-edge, but others are co-corner. Thus, rutile and anatase are having different crystalline structures, densities, and energy band gap (Gribb and Banfield, 1997; Agrios and Pichat, 2005; Demeestere, Dewulf and Langenhove, 2007).
The catalytic ability of anatase is higher than rutile. The first reason is that the anatase has lower recombination ability of electron and hole since the band gap of anatase is wider than that of rutile, which is about 0.2 eV. Secondly, TiO$_2$ with anatase phase has hydration reaction since more OH functional group present on the surface which can catch the hole rapidly, enhancing catalysis process. Thirdly, the recombination probability of electron-hole is relatively low since transmission rate of electron for anatase is 89 times higher than rutile phase (Yamashita, et. al., 1994).

2.4.3 Mechanism of Sonocatalysis in TiO$_2$

The mechanism of sonocatalyst can be explained by using the principle of photocatalysis. The ability to inhibit the recombination of electron-hole pairs can highly affect the efficiency of the process. In both photocatalysis and sonocatalysis, formation is always the first step. The ability of the recombination of electron-hole pairs by electron transport throughout the composite can be inhibited by using TiO$_2$ as catalyst (Anju, 2015).

The band structure of TiO$_2$ particles composes of high-energy conductive band and low-energy valence band, while the vacant space between conductive band and valence band is called as band gap. The energy band gap of semi-conductive TiO$_2$ is not as large as that of an insulator and it does not overlap as in conductors. Thus, the holes will remain in valence band while the electrons can move to the
conductive band when the energy is larger than or equal to the band gap (Nosaka & Fox, 1988). The excitation of electron and hole by photons is shown in Figure 2.6.

Sonocatalytic oxidation occurs on the surface of TiO$_2$. The solar excitation will produce photon-induced electron–hole pairs. Once the created holes and electrons recombine again, the energy will be released and given up as light or heat. This reaction generally occurs on the inner and outer surface of a crystalline grain (Garcia and Takashima, 2003). The reaction occurred can be simplified as in equation (2.23) and (2.24):

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2 + h^+ + e^- \quad (2.23)
\]

\[
h^+ + e^- \rightarrow \text{recombination} + \text{energy} \quad (2.24)
\]

Figure 2.6: Chemical Photoexcitation and Deexcitation Events in a Solid (Nosaka & Fox, 1988)

The redox reaction proceeds on the sonocatalyst before recombination occurs. The electron in the conductive band is a good reducing agent, while the hole in the valence band is a good oxidising agent. Most of the catalytic oxidations will directly or indirectly use oxidative stress supported from hole. Since the hole has greater activation than electron in the photolysis, therefore it mainly carries the photons. Besides, there is reaction of hole with H$_2$O molecules or OH$^-$ ions adsorbed on the surface of photocatalyst to produce OH radicals which are considered as strong oxidisers.
2.5 Modification of TiO$_2$-based Catalysts

According to Wang, et al. (2009), g-C$_3$N$_4$ can function well in water splitting. It is stated that its layer structure become the most reliable carbon nitride allotrope. Since the photocatalytic activity as well as sonocatalytic activity of the pure g-C$_3$N$_4$ is always less efficient, the combination of TiO$_2$ with g-C$_3$N$_4$ will be a potential catalyst in organic degradation. Pure g-C$_3$N$_4$ is less efficient without addition of semiconductor because the electron-hole pairs recombination is rapid. The g-C$_3$N$_4$ has an appropriate band position at around -1.3 eV to +1.4 eV with a band gap of 2.7 eV. This represents that the heterostructure is effective in enhancing sonocatalytic activity (Li, et al., 2015).

Since g-C$_3$N$_4$ is a catalyst which is free from metal component, it will attract a lot of researchers’ interests due to the visible light response, solar energy conversion, removal of poisonous gas and environmental remediation (Wang, et al., 2018). It also acts like as a n-type semiconductor with special properties in the aspect of physiochemical, exclusive. electric, structural and optical properties. Thus, it has a wide application in multifunctional nanoplatforms for catalytic, electronic and energy applications (Wen, et al., 2017).

For the normal TiO$_2$/g-C$_3$N$_4$ catalysts, the electrons generated by photocatalyst in the g-C$_3$N$_4$ conduction band will move to the conduction band of TiO$_2$, while the holes in the TiO$_2$ valence band will move to the valence band of g-C$_3$N$_4$. In fact, a charge transfer between semiconductors can enhance the photogenerated electron-hole pairs separation (Tang, et al., 2014). The problem is the unconsumed photogenerated electrons or holes will remain inside the catalyst, inhibiting their separation. Besides, when the photogenerated electrons and holes cannot be transported, they will recombine again and cause the reduction of catalytic activity (Lin, et al., 2015). Most of the researchers used TiO$_2$/g-C$_3$N$_4$ combination to test for photocatalysis performance but seldom for sonocatalysis. Thus, the effectiveness of TiO$_2$/g-C$_3$N$_4$ in sonocatalytic activity have to be further investigated.

2.6 Characterisation of TiO$_2$/g-C$_3$N$_4$

2.6.1 XRD

XRD is a technique which is used to identify crystalline structure and atomic spacing. The structure of crystalline materials can be determined from dual wave nature of X-rays.
When target material interacts with an incident beam of monochromatic X-rays, the X-rays will scatter from atoms within the target material. Cathode ray tube will generate X-rays, while the monochromatic radiation will be generated after filtration. This radiation is concentrated and directed towards the sample. Before the analysis, the sample must be smeared uniformly on a sample holder until smooth surface is formed. A reflected beam of maximum intensity will be obtained if the waves 1 and 2 are in phase. According to Bragg law, the difference in path length between wave 1 to 2 and wave 2 to 2 should be an integral number of wavelengths.

\[ n\lambda = 2d \sin \theta \]  

(2.25)

where
\( n \) = integer
\( \lambda \) = wavelength of X-rays
\( d \) = d-spacing
\( \theta \) = half scattering angle, °

Besides, the crystallite size of materials (D) can be calculated from XRD patterns by using the Scherrer equation as shown in equation (2.26) (Abbasi, et al., 2015).

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

(2.26)

where
\( K \) = shape factor, 0.9
\( \lambda \) = wavelength of X-ray, 1.540562 Å
\( \beta \) = full width at half maximum (FWHM), °
\( \theta \) = Bragg angle for the studied peak, °

2.6.2 SEM-EDX

SEM is a type of electron microscope that scans a focused electron beam on a surface for picture creation. The production of various signals from the interaction of sample and electrons in the beam is used to receive certain information of the sample. The information that can be obtained including chemical composition, texture, orientation
and crystalline structure of materials. Before analysing, the samples were dehydrated and vacuumed to maintain its original structural details. After the surface was coated with gold, the sample was now ready for analysis. The element composition of the catalysts can be determined by using SEM. EDX is complementary to SEM. It is mainly used to determine the existence and relative abundance of elements on sample surface. When an energetic electron beams hits the sample surface, X-ray photon are generated and detected.

2.6.3 FTIR

FTIR is an important technique to obtain infrared spectrum of absorption or emission of liquid, solid or gas (Griffiths and Haseth, 1986). The functional groups present in a molecule can be identified by using FTIR. Besides, the identity of a compound can be confirmed and detection of specific impurities present can be done by using the unique collection of absorption bands. High-spectral-resolution data over a wide spectral range will be collected simultaneously by an FTIR spectrometer. This is the major benefit of FTIR compared to dispersive spectrometer, which covers the measurement of intensity for narrow range of wavelengths at a time (Griffiths and Haseth, 1986).

2.7 Effect of Operating Parameter

Sonocatalytic activity can be affected by factors such as catalyst loading, temperature of heat treatment, pH of the dye, TiO$_2$/g-C$_3$N$_4$ catalyst ratio, catalyst dosage and types of organic dyes (Khataee, et al., 2016; Senthil, et al., 2017). In this study, the parameters that are going to study including TiO$_2$/g-C$_3$N$_4$ weight ratio, amount of catalyst loading, initial dye concentration, initial solution pH and types of organic dyes.

2.7.1 Effect of TiO$_2$ to g-C$_3$N$_4$ Weight Ratio

The TiO$_2$/g-C$_3$N$_4$ catalyst showed outstanding photocatalytic performance in the decomposition of organic compound. The extended available wavelength range and enhanced charge separation efficiency are the most key points to increase efficiency of photocatalytic activity. However, it is still unconfirmed about the dominant mechanism in overall sonocatalytic reaction rate. Ogi, et al. (2002) reported that significant phenol decomposition would occur by using single-bubble
sonoluminescence produced from endless sinusoidal signal of the resonance frequency at 50 kHz to activate TiO$_2$. The enhancement was mainly because of the electron-hole pairs formation activated by the ultraviolet light of sonoluminescence. According to Nakajima, et al. (2007), they agreed that the thermal excitation of TiO$_2$ was the main reason for better sonocatalytic performance of TiO$_2$ compared to SiO$_2$ in the purpose of degrading 1,4-dioxane.

The catalytic activity of g-C$_3$N$_4$/TiO$_2$ is highly depended on g-C$_3$N$_4$ and TiO$_2$ weight ratio. According to Zhao, et al. (2012), the photocatalytic ability for g-C$_3$N$_4$/TiO$_2$ catalysts were tested at different weight ratios of 0.2, 1, 2 and 5. The removal efficiencies of phenol for the g-C$_3$N$_4$/TiO$_2$-0.2, g-C$_3$N$_4$/TiO$_2$-1, g-C$_3$N$_4$/TiO$_2$-2 and g-C$_3$N$_4$/TiO$_2$-5 were 69.1 %, 82.7 %, 96.6 % and 82.8 %, respectively. It can be concluded that the increase of weight ratios would improve the photocatalytic ability of g-C$_3$N$_4$/TiO$_2$. It was due to the enhanced charge separation contributed by electric field at the g-C$_3$N$_4$ and TiO$_2$ interface as well as the visible light response from g-C$_3$N$_4$. However, the concept become reversed when the weight ratio is more than 2. It was possibly due to the blocking of UV light irradiated on TiO$_2$ by excess amount of g-C$_3$N$_4$ (Zhao, et al., 2012).

2.7.2 Effect of Catalyst Loading

The amount of catalyst used may highly affect the effectiveness of wastewater treatment. According to Tayeb and Hussein (2015), the effectiveness of pollutant degradation increased from 94.56 % to 97.58 % when the TiO$_2$ catalyst loading used increased from 0.10 g to 0.20 g at a constant dye concentration of 5 ppm. One of the possible reasons was due to the increment of dye attachment on the catalyst when the catalyst dosage increased. In other words, more dye molecules would adsorb on the sonocatalyst since more active sites present for cavity formation to take place. The existence of catalyst as nanosized particles contribute to greater surface energy and large surface to volume ratio result in high tendency of aggregation.

However, the degradation rate of dye decreased when the catalyst loading reached certain concentration. The degradation rate of iron (II, III) oxide and TiO$_2$ nanocomposite drop when the dosage exceeded 0.3 g/L (Paramarta, et al., 2017). When the catalyst dosage gradually increased, the active sites of TiO$_2$ was insufficient to be filled by dye molecules since it had reached saturation condition (Siddique, et al., 2014). Although additional catalyst was added, it did not improve
the degradation rate. Another possible reason was related to the surplus of catalyst may restrict the energy obtained from ultrasound wave.

2.7.3 Effect of Initial Dye Concentration

Another parameter that will influence the degradation rate is the initial concentration of organic dye. When the initial dye concentration increased, the sonocatalytic activity increased, leading the increment of degradation rate of dye (Hashemian, 2013). One of the possible reasons is due to the increment of frequency of collision between dye molecules and \( \bullet \text{OH} \) produced from reactant. Thus, the effective collisions will highly increase for the reactions between catalyst and dye particles to occur. Since the lifetime of \( \bullet \text{OH} \) is very short up to a few nanoseconds, it can only react where they are formed. Hence, the probability of collision will be improved when the amount of dye molecules increases.

Wang, et al. (2005) reported that the sonocatalytic activity decreased when the dye concentration reached a certain level. The drop of degradation efficiency was due to the screening effect between high amount of \( \bullet \text{OH} \) radicals and high concentration of organic dye. According to Abdullah and Pang (2010), the adsorption of high concentration of organic dye molecules on the surface of catalyst inhibited the reaction between them. Thus, the degradation efficiency was highly reduced.

2.7.4 Effect of Initial Solution pH

Different types of dye required different pH condition to achieve the highest degradation rate. According to Siddique, et al. (2014), reactive blue 19 (RB 19) dye was used to determine the optimum pH condition by using TiO\(_2\) catalyst. The higher pH solution (alkaline condition) was not favourable compared to lower pH solution (acidic solution). In acidic condition, the adsorption performance between dye molecules and catalyst surface was improved due to the existence of negatively charged sulfonic group. The negatively-charged present on TiO\(_2\) surface would repel the adsorption of dye in alkaline conditions, but the TiO\(_2\) surface with positively-charge in low pH will enhance the adsorption of RB 19 dye.

CR is one type of dye which can easily dissociated into CR anion in acidic condition due to the presence of two sulfonic groups. Zhang, et al. (2007) reported that the characteristic of CR in degradation performance was similar to RB 19. Higher degradation rate of CR could be observed before pH 8 since congo anion was
being repelled from negatively-charge catalyst surface in alkaline conditions. Besides that, the degradation ratio showed a slight increase at around pH 12. This might be due to the partial radical oxidation degradation occurred. The use of rhodamine (RhB) was reported by Qiu, et al. (2016) with TiO$_2$ catalyst deposited on nickel under ultrasonic power in the degradation experiment. The best removal effectiveness was shown in solution condition of pH 2 to pH 3, while the removal rate was highly decreased when reached pH 4. The acidic condition allowed RhB to travel into cavitation bubble and then interact with the radicals generated by cavitation. Since the free radical reaction was being quenched in high pH value, the degradation rate reduced in alkaline condition. Thus, this can be concluded that different types of dyes might have different optimum operating pH values.

2.7.5 Effect of Types of Organic Dyes

The molecular structure and molecular size of various types of organic dyes might influence their degradation behaviour. Based on the research conducted by Abdullah and Pang (2010), three different types of dye were used in the experiment and degradation efficiency follow from CR, MB and then MO in descending order. The presence of azo labile bonds in CR making it unstable and more easily to be attacked by the free radicals. Although the molecular sizes of MO and MB are approximately the same, MB is still more unstable because the ring only has one charged site. For MO, the charged sites were located outside the ring. Besides that, the reactivity coefficient of dye molecules to •OH radical also influences the degradation efficiency. This can be proved by greater degradation rate in CR with azo bonds to that of MO in the existence of dimethylamine group.

2.8 Kinetic Study

Fundamental understanding of kinetic study is vital for up-scale of catalytic chemical processes. The study of chemical kinetics consists of analysis and determination of amount of substance as a function of time. In order to determine the rate of degradation of organic dye in a sonocatalytic reaction, kinetic model was studied. According to Abbasi and Asl (2008), the kinetic of dye degradation using sonocatalysis could be explained by pseudo-first order kinetic model. The rate constant $k'$ can be determined by equation (2.27).
\[ -r = \frac{d[\text{organic dye}]}{dt} = k'[\text{organic dye}][\cdot\text{OH}] \]  \hspace{1cm} (2.27)

The concentration of \(\cdot\text{OH}\) radicals was assumed to be constant since it is very reactive. Thus, equation (2.27) was simplified into a pseudo-first order equation and \(k'[\cdot\text{OH}]\) becomes apparent pseudo-first order constant \(k_{app}\).

\[ -r = \frac{d[\text{organic dye}]}{dt} = k_{app}[\text{organic dye}] \]  \hspace{1cm} (2.28)

where
\[ k_{app} = k'[\cdot\text{OH}] \]

The integration of equation (2.28) will generate an equation that relate the dye concentration and the duration of reaction. Equation (2.29) is formed and used to describe the sonocatalytic degradation of organic dye.

\[ \ln \frac{C_0}{C_t} = k_{app}t \]  \hspace{1cm} (2.29)

where
\[ C_0 = \text{initial dye concentration (mg/L)} \]
\[ C_t = \text{concentration of dye at time } t \text{ (mg/L)} \]
\[ k_{app} = \text{apparent rate constant (min}^{-1}) \]
\[ t = \text{time (min)} \]
CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Overall Research Field

The experimental procedures, equipment, materials and chemicals used in this study was discussed in this section. The flow chart of work plan is listed in Figure 3.1. Based on the Figure 3.1, the TiO$_2$ and g-C$_3$N$_4$ were synthesised as well as TiO$_2$/g-C$_3$N$_4$ catalysts. Three types of catalyst powder were characterised by using XRD, SEM-EDX and FTIR analyses. The catalysts were then used in dye degradation under application of ultrasound. Operating parameter studies were carried out to determine the optimum dye degradation condition. Lastly, the liquid samples from parameter studies were analysed using ultraviolet-visible (UV-Vis) spectrophotometer and COD analysis.

![Flowchart](image-url)

Figure 3.1: Experimental Plan in Overall Research Field
3.2 Materials and Chemicals
The chemicals used in the experiment are shown in Table 3.1. Titanium (IV) isopropoxide and melamine were used to synthesise TiO$_2$/g-C$_3$N$_4$ catalyst for the degradation of dyes whereas hydrogen peroxide will be used as the oxidising agent. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to alter the solution pH. The dyes which act as model pollutants were CR, MG, RB 4, MB and MO.

Table 3.1: List of Type and Purpose of Chemical Reagents Used

<table>
<thead>
<tr>
<th>Chemical Reagents</th>
<th>Brand</th>
<th>Purity</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium (IV) isopropoxide</td>
<td>Sigma Aldrich</td>
<td>≤ 100 %</td>
<td>Catalyst synthesis</td>
</tr>
<tr>
<td>Melamine</td>
<td>Merck</td>
<td>≤ 100 %</td>
<td>Catalyst synthesis</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Chem Sol</td>
<td>99.9 %</td>
<td>Catalyst synthesis</td>
</tr>
<tr>
<td>HCl</td>
<td>Merck</td>
<td>50 %</td>
<td>pH adjustment</td>
</tr>
<tr>
<td>NaOH</td>
<td>Merck</td>
<td>37 %</td>
<td>pH adjustment</td>
</tr>
<tr>
<td>CR</td>
<td>R&amp;M Chemical</td>
<td>≤ 100 %</td>
<td>Model pollutant</td>
</tr>
<tr>
<td>MG</td>
<td>Riendemann Chmldt</td>
<td>≤ 100 %</td>
<td>Model pollutant</td>
</tr>
<tr>
<td>RB 4</td>
<td>Sigma-Aldrich</td>
<td>35 %</td>
<td>Model pollutant</td>
</tr>
<tr>
<td>MO</td>
<td>R&amp;M Chemical</td>
<td>≤ 100 %</td>
<td>Model pollutant</td>
</tr>
<tr>
<td>MB</td>
<td>R&amp;M Chemical</td>
<td>≤ 100 %</td>
<td>Model pollutant</td>
</tr>
</tbody>
</table>

3.3 Equipment
The types and function of equipment needed are tabulated in Table 3.2. Firstly, the heat treatment by furnace was used in the synthesis of pure g-C$_3$N$_4$, pure TiO$_2$ and combination of both which is TiO$_2$/g-C$_3$N$_4$ composite. The furnace was used to calcine TiO$_2$/g-C$_3$N$_4$ catalyst at temperature of 500 °C. Next, the sample with the highest catalytic activity was selected through the degradation testing under sonocatalysis process. The degradation rate of organic dyes was measured using a UV-vis spectrophotometer. A pH meter was used to measure the pH when adjusting the pH of the dye solution. XRD was used to determine their phase composition and crystallite size, while SEM-EDX was used to study the surface morphology respectively. FTIR are needed for analysing the functional group. COD analysis was conducted by using COD reactor and COD spectrophotometry.
### Table 3.2: Model and Function of Instrument

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Brand</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace</td>
<td>Carbolite RHF 1500</td>
<td>To calcine TiO$_2$/g-C$_3$N$_4$ at 500 °C.</td>
</tr>
<tr>
<td>pH meter</td>
<td>Eutech PC-300</td>
<td>To measure pH of solutions.</td>
</tr>
<tr>
<td>SEM-EDX</td>
<td>Hitachi Model S-3400N</td>
<td>To examine morphology of TiO$_2$/g-C$_3$N$_4$ powder.</td>
</tr>
<tr>
<td>XRD</td>
<td>LabX XRD-6000</td>
<td>To perform phase identification of crystalline.</td>
</tr>
<tr>
<td>Ultrasonic processor</td>
<td>Hielscher UP400S</td>
<td>Source of ultrasound and water bath.</td>
</tr>
<tr>
<td>UV-vis spectrophotometer</td>
<td>Jenway 6320D</td>
<td>To measure concentration of dye.</td>
</tr>
<tr>
<td>FTIR</td>
<td>Nicolet IS10</td>
<td>To determine the presence of functional group.</td>
</tr>
<tr>
<td>Ultrasonic bath</td>
<td>WiseClean WUC-A03H</td>
<td>Source of ultrasound and water bath.</td>
</tr>
<tr>
<td>COD reactor</td>
<td>DRB 200</td>
<td>Allows reaction of oxidant and sample under controlled condition.</td>
</tr>
<tr>
<td>COD spectrophotometry</td>
<td>DR 3800</td>
<td>To determine COD value of sample.</td>
</tr>
</tbody>
</table>

### 3.4 Experimental Setup for Liquid Sample Analysis

Figure 3.2 shows the experimental setup for sonocatalytic degradation of organic dye together with the addition of 1.5 g/L of catalyst. The ultrasonic irradiation source was obtained from an ultrasonic processor with model of Hielscher UP400S. The equipment was operated at ultrasonic frequency of 24 kHz and ultrasonic power of 200 W. The amplitude of the oscillatory system can be altered between 20% and 100%. 100 ml of dye solution was filled in a beaker and placed under ultrasonic probe. The probe was immersed in the dye solution so that the dye solution can absorb most of the ultrasonic irradiation.
3.5 Experimental Procedure

3.5.1 Preparation of g-C₃N₄ Powders
Thermal polycondensation of melamine was used to fabricate g-C₃N₄ powders according to Li, et al. (2017). In this method, melamine (5 g) was placed into a crucible with cover. It was then heated in a muffle furnace with heating rate of 10 °C/min at 550 °C for 2 hours. After heat treatment, it was cooled down to room temperature to form yellow colour which can be ground into powder.

3.5.2 Preparation of TiO₂/g-C₃N₄ Catalyst
Synthesis of TiO₂/g-C₃N₄ composite was conducted according to Zhao, et al. (2017b). It was started with spreading g-C₃N₄ powder to 30 mL of water and 35 mL of ethanol solution together under 30 minutes of ultrasonic dispersion. The ultrasonic dispersion was carried out by placing the beaker filled with solution in the ultrasonic bath. Next, 8 mL of titanium (IV) isopropoxide was poured into the solution under continuous stirring. Ultrasonic dispersion was then carried out again for 1 hour. The resulted products were then rinsed with ethanol and deionized water for several times. The mixture was then heated at 80 °C in an oven for overnight. In the last step, the annealing of products obtained were carried out at 500 °C for 4 hours. Fabrication of pure TiO₂ particles were conducted using the same method by excluding the addition of g-C₃N₄ powder.
3.5.3 Characterisation of Catalyst

3.5.3.1 XRD
XRD was used to carry out the crystallization phase analysis to determine the crystalline structure of TiO$_2$/g-C$_3$N$_4$. The Cu-Kα (λ = 1.540562 Å) radiation source was manipulated at 40 kV/30 mA. The intensity of diffracted X-rays was recorded continuously by monitoring the diffraction pattern emerging in the 2θ ranging from 10° to 80° with a scan rate of 2°/min and a scan step of 0.02° (Li et al., 2016). The powder sample was placed and pressed into a sample holder by using a glass slide. It is important to make sure that the surface of the powder is smooth without any scratches. After that, the sample holder will be installed into the sample stage of XRD instrument.

3.5.3.2 SEM-EDX
The pure TiO$_2$, pure g-C$_3$N$_4$ and TiO$_2$/g-C$_3$N$_4$ catalyst were attached on specimen holder by using the double-d-sided adhesive tape. Gloves must be worn during the sample preparation step to eliminate the possibility of SEM system contamination. The sample holder was then inserted into SEM system for observation. The acceleration voltage used to take scanning electron images was 15.0 kV with magnification of 4 k, 8 k and 10 k. The EDX coupled to SEM was used to determine element composition of the catalysts.

3.5.3.3 FTIR
Before the sample analysis, the attenuated total reflectance (ATR) plate was wiped with ethanol solution to remove contaminants. A background scan was obtained to eliminate the interfering bands produced by carbon dioxide and water vapour in the air from the spectrum. After obtaining background spectrum, catalyst sample was placed on the ATR plate. The press of the ATR was lower down by turning the dial until a click sound was heard.

3.5.4 Preparation of Organic Dyes
Before performing the degradation of organic dye, organic dye solutions are first prepared by addition of 0.5 g dye powder into a 1 litre of deionised water to obtain a
stock dye solution with concentration of 500 mg/L. The stock solutions will then be diluted based on the concentration needed during parameter studies.

3.5.5 Operating Parameter Study Optimization

3.5.5.1 Effect of TiO\textsubscript{2} to g-C\textsubscript{3}N\textsubscript{4} Weight Ratio

The TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} composites were synthesised by using the similar method as in Section 3.5. The composition of TiO\textsubscript{2} to g-C\textsubscript{3}N\textsubscript{4} was adjusted based on the weight ratio. TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} composite samples at various TiO\textsubscript{2} to g-C\textsubscript{3}N\textsubscript{4} weight ratios (0.5, 1.0 and 2.0) were prepared through a physical mixing process. The corresponding prepared samples were denoted as TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-0.5, TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-1 and TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-2 (Senthil, et al., 2017). Firstly, 100 ml of MG dye solution with concentration of 10 mg/L was filled into a beaker. The solution pH was adjusted at pH 5 by using 0.1 M HCl or 0.1 M NaOH solution. Next, 1 g/L of TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-0.5 catalyst was added into MG solution and then placed under ultrasonic processor for 30 minutes of ultrasonic irradiation.

3.5.5.2 Effect of Catalyst Loading

The degradation efficiency of dye is different due to different catalyst loading. The amount of catalyst used in this study were 0.5 g/L, 1.0 g/L, 1.5 g/L, 2.0 g/L and 2.5 g/L (Senthil, et al., 2017). The catalyst was added into MG solution with concentration of 10 mg/L, while the initial pH value was adjusted at pH 5. The ultrasonic irradiation was carried out in 30 minutes. During the ultrasonic irradiation, 5 ml of MG solution was collected in 5-minutes interval for UV-vis spectrophotometry analysis. Degradation efficiency for different catalyst loading were determined. The optimum catalyst loading with best degradation performance was carried forward to be used in the following experiments.

3.5.5.3 Effect of Initial Dye Concentration

The effect of initial dye concentrations on the dye degradation efficiency under ultrasonic irradiation was studied. The initial MG concentrations used were 10 mg/L, 15 mg/L, 20 mg/L, 25 mg/L and 30 mg/L at solution pH of 5. The optimum catalyst loading determined in the previous experiment was used to carry out 30 minutes of
ultrasonic irradiation. The initial concentration that performed the best removal rate was carried forward to the following experiments.

3.5.5.4 Effect of Initial Solution pH
The optimum pH for degradation of organic dye under ultrasonic irradiation was determined by altering the pH value to pH 1, pH 3, pH 5, pH 7 and pH 9. The pH values were adjusted by adding of 0.1 M HCl or 0.1 M NaOH solution depend on initial pH. The optimum catalyst loading and initial dye concentration obtained from previous parameter studies were used. The optimum solution pH was carried forward to the following parameter study.

3.5.5.5 Effect of Types of Organic Dyes
The effect of different organic dyes on sonocatalytic degradation in the presence of TiO$_2$/g-C$_3$N$_4$ powder was determined by changing MG to CR, RB 4, MO and MB. The experiment was carried out under optimum condition determined from previous parameter studies.

3.5.6 Kinetic Study
The kinetic study on the degradation of the organic dye was investigated using the mathematical kinetic models as shown in equation (2.29).

3.5.7 Liquid Sample Analysis

3.5.7.1 UV-Vis Spectrophotometry
UV-vis spectrophotometry was used to determine the remaining dye concentration in the sample after sonocatalytic process. Before the determination, calibration curves for different dyes were constructed. Firstly, the dyes with known concentration were prepared and its respective absorbance were determined by using UV-vis spectrophotometer. A calibration curve of absorbance versus concentration was plotted (Beer, 1852). The absorbance of solution is directly proportional to the concentration of solution according to Beer-Lambert Law. From the equation of the calibration curve, the final concentration of dye solution can be calculated.

In this experiment, amplitude of 60 % with cycle of 0.6 was used. Before the operation begins, the beaker filled with 100 ml of 10 mg/L dye solution in the
presence of 1.5 g/L of TiO$_2$/g-C$_3$N$_4$ catalyst was placed directly under ultrasonic transducer so that the dye solution can absorb most of the ultrasonic irradiation. The reaction was being conducted for 30 minutes at room temperature and ambient pressure. During the operation of sonocatalytic process, the liquid sample was collected with time interval of 5 minutes. The catalyst was then being separated from dye solution by using syringe filter. UV-visible spectrophotometer was used determine the remaining dye concentrations. The dye conversion can be calculated as equation (3.1), where $C_t$ is the concentration of the dye at time interval and $C_o$ is the concentration of the dye before irradiation.

$$\text{Dye degradation efficiency} = \frac{(C_o - C_t)}{C_o} \times 100\%$$ (3.1)

3.5.7.2 COD Analysis

The application of COD is used to identify the quantity of organic compounds in the solution. It is always used as measurement indicator of water quality. In order to study the extent of mineralization, COD degradation of sample was determined by Colorimetric Determination Method 8000. The MG degradation was carried out at optimum condition obtained from previous parameter studies for 30 minutes. The sample solutions were collected in 5-minutes time interval. The sample solution was then separated from the catalyst by using syringe filter. Next, 2 ml filtered dye solutions were mixed with COD digestion reagent vials and heated for 2 hours. The COD values of the sample solutions were determined by using COD spectrophotometer.
CHAPTER 4

RESULTS AND DISCUSSION

This chapter presents the results obtained in the present work. In the first section, the characterisation studies of pure TiO₂, pure g-\(\text{C}_3\text{N}_4\) and TiO₂/g-\(\text{C}_3\text{N}_4\) powder are conducted by using XRD, SEM-EDX and FTIR analyses. The second section of the chapter presents the sonocatalytic degradation of MG using TiO₂/g-\(\text{C}_3\text{N}_4\) powder. The process behaviour of sonocatalytic degradation are studied such as TiO₂ to g-\(\text{C}_3\text{N}_4\) catalyst ratio, catalyst loading, initial dye concentration, initial solution pH and type of dyes. The third section presents the kinetic study of TiO₂/g-\(\text{C}_3\text{N}_4\) catalyst. Lastly, the COD analysis is conducted by degradation of MG dye under ultrasound irradiation.

4.1 Characterisation of TiO₂/g-\(\text{C}_3\text{N}_4\) powder

4.1.1 XRD Results

The XRD characterisation was carried out to justify the difference between the crystalline structure of the pure TiO₂, pure g-\(\text{C}_3\text{N}_4\) and TiO₂/g-\(\text{C}_3\text{N}_4\) particles. Figure 4.1 shows the XRD patterns of pure TiO₂, pure g-\(\text{C}_3\text{N}_4\) and TiO₂/g-\(\text{C}_3\text{N}_4\) particles. Based on Figure 4.1 (a), pure TiO₂ consists of all typical peaks of anatase phase stated by Senthil, et al. (2017), while no rutile phase was exhibited. This implied that the addition of g-\(\text{C}_3\text{N}_4\) on TiO₂ did not initiate anatase to rutile transformation. TiO₂ synthesised from titanium (IV) isopropoxide precursor was calcined at temperature of 500 °C which is below phase transformation temperature, so the crystalline structure of TiO₂ only existed in anatase phase. According to Senthil, et al. (2017), the pure TiO₂ will show its diffraction peaks at \(2θ = 25.3°, 37.8°, 48.1°, 54.0°, 55.1°, 62.8°, 68.9°, 70.1°, 75.3°\) and 83.2°. These diffraction peaks are indexed to lattice planes of anatase TiO₂ at (101), (004), (200), (105), (211), (204), (116), (220), (215) and (303), respectively. For rutile phase of TiO₂, the diffraction peaks at 27.47° and 40.05° correlated to diffraction planes of (110) and (111), respectively.

Figure 4.1 (e) shows that pure g-\(\text{C}_3\text{N}_4\) appeared two peaks at \(2θ = 13.08°\) and 27.31°. According to Zhao, et al. (2017a), pure g-\(\text{C}_3\text{N}_4\) had diffraction planes of (100) and (002) at \(2θ = 13.14°\) and 27.57°, respectively. The presence of plane (100) was
due to the in-planar packing of 3-s-triazine structure unit. Pure g-C₃N₄ in Figure 4.1 (e) displayed extra two peaks at 64.62° and 77.79° while it was absent in typical peak of g-C₃N₄. The possible reason is due to the impurities present during the calcination process of melamine.

Figure 4.1: XRD patterns of (a) TiO₂, (b) TiO₂/g-C₃N₄-2, (c) TiO₂/g-C₃N₄-1, (d) TiO₂/g-C₃N₄-0.5, (e) g-C₃N₄.

Figure 4.1 (a) to (d) shows that the peak intensities of anatase TiO₂ were getting weaker. Pure TiO₂ had the strongest peaks among other composite samples. This was due to the reduction of weight percent ratio for TiO₂ to g-C₃N₄. According to Zhao, et al. (2017a), composite samples with good crystallinity showed sharp and narrow peaks. When the weight ratio of TiO₂/g-C₃N₄ decreased, the diffraction peaks were getting wider and less sharp. This indicated that the samples crystallinity was decreased as increasing weight ratio of TiO₂/g-C₃N₄.

Based on the XRD patterns of TiO₂/g-C₃N₄ composite in Figure 4.1 (b) and (c), the absence of typical peaks of g-C₃N₄ might be due to the low amount of g-C₃N₄ utilised. The g-C₃N₄ content did not show significant peaks even the TiO₂ to g-C₃N₄ weight ratio was larger or equal to 1. Boonprakob, et al. (2014) also found that no g-
Diffraction peaks of TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-0.5 showed the presence of diffraction plane (002) at 2\(\theta\) = 27.57\(^{\circ}\). This represented that only TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-0.5 composite had obvious characteristic of g-C\textsubscript{3}N\textsubscript{4}. The peak at 27.57\(^{\circ}\) belonged to stacking of conjugated aromatic system (Zhao, et al., 2017a). The overall results did not seem any obvious changes in typical peaks. This indicated that the composite samples were mostly composed of TiO\textsubscript{2} and g-C\textsubscript{3}N\textsubscript{4}.

By using the results obtained by XRD, the crystallite sizes of the samples were calculated by using the Scherrer equation as shown in equation (2.26) (Abbasi, et al., 2015). The calculated crystallite sizes were tabulated in Table 4.1. When the TiO\textsubscript{2} content in the sample decreased, the size of crystal TiO\textsubscript{2} reduced. The possibility of the reduction was due to the tendency of TiO\textsubscript{2} agglomeration was reduced. As the weight percentage of TiO\textsubscript{2} increased, the TiO\textsubscript{2} particles possessed more chances for accumulation and resulted the larger crystallite size of particles.

**Table 4.1: Crystallite Size of TiO\textsubscript{2} and TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} Composite at Different Weight Ratio**

<table>
<thead>
<tr>
<th>Sample</th>
<th>2(\theta), (^{\circ})</th>
<th>FWHM, (^{\circ})</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO\textsubscript{2}</td>
<td>25.4106</td>
<td>0.40000</td>
<td>3.553</td>
</tr>
<tr>
<td>TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-2</td>
<td>25.3198</td>
<td>0.45110</td>
<td>3.150</td>
</tr>
<tr>
<td>TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-1</td>
<td>25.3607</td>
<td>0.78360</td>
<td>1.814</td>
</tr>
<tr>
<td>TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-0.5</td>
<td>25.3500</td>
<td>1.06000</td>
<td>1.341</td>
</tr>
</tbody>
</table>

### 4.1.2 SEM-EDX Results

Based on Figure 4.2 (a), it can be observed the TiO\textsubscript{2} particles appeared as spherical shape. Most of the spherical particles were agglomerated together irregularly. Senthil, et al. (2017) found that the structure of g-C\textsubscript{3}N\textsubscript{4} appeared as sheet form. This is consistent with the present study where Figure 4.2 (e) displays the sheet-like structure but aggregate together. According to Zhao, et al. (2017a), the sheet-like g-C\textsubscript{3}N\textsubscript{4} could be formed after heating of dicyandiamide. In this study, melamine was used instead of dicyandiamide. However, the g-C\textsubscript{3}N\textsubscript{4} formed showed similar morphology as stated by Zhao, et al. (2017a).
After incorporating TiO$_2$ on the g-C$_3$N$_4$ sheets, the amorphous TiO$_2$ would turn to crystalline TiO$_2$ after calcination. This justified the results shown in the SEM images of TiO$_2$/g-C$_3$N$_4$ composites. Figure 4.2 (b) to (d), the spherical TiO$_2$ particles was distributed on the g-C$_3$N$_4$ sheets. Figure 4.2 (b) shows that high amount of TiO$_2$ deposition on the g-C$_3$N$_4$ sheet without aggregation of g-C$_3$N$_4$. This was due to the
involvement of highest amount of TiO$_2$ (Wang, et al., 2018), most of the g-C$_3$N$_4$ sheet-like surface was being covered by spherical TiO$_2$ particles. As the amount of g-C$_3$N$_4$ increased, the aggregation of g-C$_3$N$_4$ was obviously observed as shown in Figure 4.2 (c) and (d). The amount of TiO$_2$ seems to be reduced in TiO$_2$/g-C$_3$N$_4$-0.5 compared to TiO$_2$/g-C$_3$N$_4$-1 composite.

The composition of pure TiO$_2$, pure g-C$_3$N$_4$ and TiO$_2$/g-C$_3$N$_4$ with different weight ratios were determined by EDX analysis. Figure 4.3 (a) shows that pure TiO$_2$ only consists of titanium (Ti) and O elements, while pure g-C$_3$N$_4$ contains carbon (C) and nitrogen (N) elements in Figure 4.3 (e). The elemental compositions of TiO$_2$/g-C$_3$N$_4$ show the existence of Ti, O, C and N elements as shown in Figure 4.3 (b) to (d). As the TiO$_2$ to g-C$_3$N$_4$ ratio decreased, it is obvious that the weight percentage of Ti and O element were reduced while the weight percentage of C and N elements were increased. The increment of TiO$_2$ and reduction of g-C$_3$N$_4$ in weight percent are shown in Table 4.2 to further justify the composition difference.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight percentage (wt. %)</th>
<th>Ti</th>
<th>O</th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td></td>
<td>55.55</td>
<td>44.45</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TiO$_2$/g-C$_3$N$_4$-2</td>
<td></td>
<td>52.84</td>
<td>35.39</td>
<td>5.78</td>
<td>6.99</td>
</tr>
<tr>
<td>TiO$_2$/g-C$_3$N$_4$-1</td>
<td></td>
<td>22.70</td>
<td>24.51</td>
<td>24.86</td>
<td>27.92</td>
</tr>
<tr>
<td>TiO$_2$/g-C$_3$N$_4$-0.5</td>
<td></td>
<td>14.03</td>
<td>18.06</td>
<td>35.68</td>
<td>32.23</td>
</tr>
<tr>
<td>g-C$_3$N$_4$</td>
<td></td>
<td>0</td>
<td>0</td>
<td>34.28</td>
<td>65.72</td>
</tr>
</tbody>
</table>

### 4.1.3 FTIR Results

Figure 4.4 shows the FTIR spectra of TiO$_2$, g-C$_3$N$_4$ and TiO$_2$/g-C$_3$N$_4$ at different weight ratios. The most significant peak to identify the presence of TiO$_2$ was the broad absorption peak appeared between 400 to 700 cm$^{-1}$. This broad peak attributed to the Ti-O-Ti bridging stretching modes as well as the Ti-O stretching modes (Sabri, Nawi and Nawawi, 2015). The existence of stretching vibrations and bending of O-H group was proven by the peaks appeared at 1630 and 3500 cm$^{-1}$, respectively. There are two peaks appeared at bending of O-H group which could justify the existence of O-H groups.
Figure 4.3: EDX Spectra of (a) TiO$_2$, (b) TiO$_2$/g-C$_3$N$_4$-2, (c) TiO$_2$/g-C$_3$N$_4$-1, (d) TiO$_2$/g-C$_3$N$_4$-0.5, (e) g-C$_3$N$_4$. 
Based on Figure 4.4 (e), several strong peaks appeared at 795, 1204, 1311, 1395, 1541 and 1623 cm$^{-1}$. These peaks between 1200 to 1600 cm$^{-1}$ indicated the presence of C-N hetero cycles. Senthil, et al. (2017) and Boonprakob, et al. (2014) reported that pure g-C$_3$N$_4$ might show peaks at 1253, 1325, 1403, 1571 and 1640 cm$^{-1}$ due to the stretching modes of C-N hetero cycles. Other than that, the breathing mode of triazine units contributed to a strong peak at 806 cm$^{-1}$. The main contributor of the wide peak between 3100 to 3300 cm$^{-1}$ was the stretching of N-H bonds of amine, which were amine bonds and imine group (Yuan, Yang and Li, 2015; Yan and Yang, 2011). This broad peak could be observed in Figure 4.4 (e), proving the presence of N-H bonds. Since all the typical peaks stated by Senthil, et al. (2017) are shown in FTIR pattern of pure g-C$_3$N$_4$, indicating that the absence of other impurities.

Figure 4.4 (b) shows that TiO$_2$/g-C$_3$N$_4$-2 displayed similar FTIR spectrum as TiO$_2$. There were no absorption peaks to prove the presence of g-C$_3$N$_4$ since the weight percentage of g-C$_3$N$_4$ was significantly low. Both TiO$_2$/g-C$_3$N$_4$-1 and TiO$_2$/g-C$_3$N$_4$-0.5 composite samples portrayed typical peaks of g-C$_3$N$_4$ as shown in Figure 4.4 (c) and (d) although the transmittance is lower than pure g-C$_3$N$_4$. It was observed...
that the increment of transmittance for g-C₃N₄ when g-C₃N₄ content in the sample increased. Beside g-C₃N₄, typical TiO₂ wide peak between 500 cm⁻¹ to 700 cm⁻¹ could be observed in TiO₂/g-C₃N₄-1 and TiO₂/g-C₃N₄-0.5 composite samples. However, the transmittance of broad peak reduced due to the reduction of TiO₂ content.

4.2 Parameter Studies in Sonocatalytic Process

4.2.1 Effect of TiO₂ to g-C₃N₄ Weight Ratio
To investigate the optimum weight ratio of TiO₂/g-C₃N₄ composite that possessed the greatest performance in sonocatalytic degradation of dye, TiO₂/g-C₃N₄ catalyst with different weight ratio were synthesised. Figure 4.5 shows the degradation efficiency of pure TiO₂, pure g-C₃N₄ and TiO₂/g-C₃N₄ composite of various weight ratios.

![Figure 4.5: Effect of TiO₂ to g-C₃N₄ Weight Ratio on the Sonocatalytic Degradation of MG (pH = 5, Catalyst Loading = 1.0 g/L, Initial MG Concentration = 10 mg/L, Reaction Time = 30 minutes)](image_url)

Based on Figure 4.5, blank test without catalyst shows degradation percentage of 3.54 %. Pure TiO₂ shows degradation efficiency of 7.80 % whereas pure g-C₃N₄ shows the lowest MG degradation percentage of 5.97 %. The catalytic
activity of pure TiO$_2$ was not promising without the support of deposition material. The absence of g-C$_3$N$_4$ reduced the surface area for adsorption of dye molecules. Besides, pure g-C$_3$N$_4$ was unable to exhibit sonocatalytic activity, so it could only act as deposition material.

It could be observed that TiO$_2$/g-C$_3$N$_4$ composite samples showed better performance in degradation efficiency. The combination of TiO$_2$ and g-C$_3$N$_4$ would extend the light absorption in visible region triggered by sonoluminescence, this further increased the tendency of charge carrier separation. These charge carriers would diffuse to the catalyst's surface (Jiang, et al., 2015 and Zhao, et al., 2016). The MG decolourisation efficiency of TiO$_2$/g-C$_3$N$_4$-2, TiO$_2$/g-C$_3$N$_4$-1 and TiO$_2$/g-C$_3$N$_4$-0.5 were 10.55 %, 20.17 % and 37.63 %, respectively. The degradation efficiency of MG increased as decreasing the weight ratio of TiO$_2$ to g-C$_3$N$_4$. TiO$_2$/g-C$_3$N$_4$-0.5 achieved the highest degradation performance (37.63 %) in decolourisation of MG solution under ultrasound irradiation among all the as-prepared sonocatalysts. It was mainly due to the generation of direct Z-scheme heterojunction for TiO$_2$/g-C$_3$N$_4$ composite at appropriate amount (Senthil, et al., 2017; Luo, et al., 2016). Besides, it could also be explained by the red-shift of light absorption range between TiO$_2$/g-C$_3$N$_4$ composite. Since the structure of TiO$_2$/g-C$_3$N$_4$ exists in two phase interfaces, it highly encouraged the movement of electrons between both surfaces. The high charge separation efficiency of electron-hole pairs was enhanced due to the close interfacial connection between TiO$_2$ and g-C$_3$N$_4$ in the composite. Besides, the matching of valence and conduction bands also contributed to the high charge separation efficiency of electron-hole pairs (Boonprakob, et al., 2014).

The studies conducted by Zhao, et al. (2012) reported that the degradation efficiency was decreased when the weight ratio of g-C$_3$N$_4$ to TiO$_2$ was more than 2. They stated that the presence of large surface area of the g-C$_3$N$_4$ hybrids would contribute to deposition of TiO$_2$. Suitable addition amount of g-C$_3$N$_4$ would provide a well dispersion of particles on sheets and further reduced the TiO$_2$ agglomeration. When the TiO$_2$ content was two times to the g-C$_3$N$_4$ content in weight percent (TiO$_2$/g-C$_3$N$_4$-2), the sonocatalytic activity was dropped significantly from 37.63 % to 10.55 %. Same result was obtained by Senthil, et al. (2017) that the degradation efficiency reduced when the TiO$_2$ content increased to 40.36 wt. %. This was due to the insufficient amount of g-C$_3$N$_4$ to be deposited by TiO$_2$ to form heterojunction
structure. Thus, TiO$_2$/g-C$_3$N$_4$-0.5 was chosen as preferable catalyst to be used in the following parameter studies.

### 4.2.2 Effect of Catalyst Loading

The effect of catalyst loading on the sonocatalytic degradation of MG was investigated under the same conditions. It is crucial to achieve the maximum degradation efficiency while not utilising excess amount of catalyst. The amount of catalyst used were 0.5, 1.0, 1.5, 2.0 and 2.5 g/L and the results are shown in Figure 4.6. The results showed a positive rising trend when increasing the irradiation time within 30 minutes. When the catalyst loading increased from 0.5 g/L to 2.0 g/L, the sonocatalytic activity increased. The degradation efficiencies of MG in the presence of 0.5, 1.0, 1.5 and 2.0 g/L TiO$_2$/g-C$_3$N$_4$-0.5 catalyst were 32.77, 36.93, 79.01 and 84.43 %, respectively. However, the degradation efficiency was slightly dropped when the catalyst dosage reached 2.5 g/L, which was 82.64 %.

![Figure 4.6: Effect of Catalyst Loading on the Sonocatalytic Degradation of MG (pH = 5, Initial MG Concentration = 10 mg/L, Reaction Time = 30 minutes)](image)

The increment in MG degradation could be explained by the increment in the surface area of catalyst exposed to ultrasound irradiation. This would further increase the amount of nucleation sites for the formation of bubble cavities to improve the water dissociation reaction and produce more •OH. The increment of catalyst active
sites was essential desirable for the attachment of dye molecules to generate more electron-hole pairs and enhance sonocatalytic degradation (Theerthagiri, et al., 2014).

However, excess catalyst dosage would cause increment of turbidity of the dye solution, which in turns generate antagonistic interaction by blocking the penetration of ultrasound to catalyst surface. The mutual screening effects will block the dye molecules to receive ultrasound wave energy (Wang, et al., 2007). Other than that, scavenging of OH radicals on the catalyst surface would reduce sonocatalytic activity. Same result was obtained by Wang, et al. (2010) for photocatalytic degradation of MB, CR, azo fuchsine, RhB and MO by using composite of TiO$_2$ and ZnO.

By considering the economic factors, the dosage of 1.5 g/L was selected as the optimum catalyst loading for MG degradation. This was due to the increment of efficiency in dosage of 1.5 g/L and 2.0 g/L was not significant.

4.2.3 Effect of Initial Dye Concentration

The effect of initial MG concentration towards the sonocatalytic degradation of MG was studied. The initial MG concentration tested in the study was in the range of 10 to 30 mg/L. As shown in Figure 4.7, the degradation efficiencies of 10, 15, 20, 25 and 30 mg/L were 79.01, 74.24, 72.49, 57.19 and 28.65 %, respectively.

![Figure 4.7: Effect of Initial Dye Concentration on the Sonocatalytic Degradation of MG (pH = 5, Catalyst Loading = 1.5 g/L, Reaction Time = 30 minutes)](image-url)
It could be observed that decolourisation of MG was highly influenced by initial MG concentration. The higher the initial MG concentration, the lower the sonocatalytic activity. The reduction in efficiency of initial MG concentration in the range of 10 to 20 mg/L was not significant, but 30 mg/L of MG showed steeply drop in degradation efficiency.

When excess amount of dye molecules presents in the solution, dye molecules would be attached on the surface of catalyst until it reached saturation point. Thus, the availability for surface area of catalyst would reduce (Abdullah and Pang, 2010). Beside the high degree of saturation on catalyst surface, there was also the interception of photons when the dye molecules reached the catalyst surface. The saturation problem might further inhibit the adsorption of hydroxyl ions on the catalyst active sites, while the interception of photon would prevent photons adsorption by TiO$_2$/g-C$_3$N$_4$-0.5 catalyst (Shafeeyan, Wan Daud and Shamiri, 2014).

Based on the studies conducted by Khataee, et al. (2016), the removal rate of dye would reach a maximum point at certain level of initial MG concentration. After this maximum point, the generated ⋅OH were insufficient to decolourise the dye molecules since it became the limiting factor for the degradation process.

Based on Figure 4.7, initial dye concentration of 10 mg/L showed the highest degradation efficiency of MG among others. This would be the optimum dye concentration to be used for the subsequent parameter studies.

### 4.2.4 Effect of Initial Solution pH

In this parameter study, solution pH in the range of pH 1 to 9 were investigated. Figure 4.8 displays the degradation efficiency of 10 mg/L MG in 30 minutes. Degradation efficiency of MG in acidic conditions such as pH 1 and pH 3 were 23.57 % and 7.58 %, respectively. Based on the results, the highest degradation efficiency was occurred at pH 5, which was 79.01 %. When the solution pH was set at pH 7 and pH 9, the degradation efficiency was decreased to 67.50 % and 62.97 %, respectively.

The surface of catalyst possessed the surface charge which was vital for sonocatalysis reactions. The surface charge could be defined as the difference in electrical potential between outer and inner surface of dispersed phase in a colloid. The electrical potential was related to the existence of hydroxyl group on catalyst
surface. This indicated that the acidity or basicity of the dye solution would directly affect the surface charge properties as well as the catalysis reaction.

![Graph](image)

Figure 4.8: Effect of Initial Solution pH on the Sonocatalytic Degradation of MG (Catalyst Loading = 1.5 g/L, Initial MG Concentration = 10 mg/L, Reaction Time = 30 minutes)

MG is a type of cationic dye. Its affinity to TiO₂ surface with positive charge was very weak. The high degradation of MG was observed at high solution pH conditions. The increment in pH will definitely change the charge of the TiO₂. The TiO₂ surface became negatively-charged in alkaline condition whereas positively-charged TiO₂ surface formed at low pH condition. According to Garg, et al. (2003), the carboxylic groups of MG experienced protonation with high density of positive charge in acidic condition. Both positively-charged MG molecules and catalyst surface would create electrostatic repulsion. The positively-charged hydrogen ions would compete with the cationic dye molecules for TiO₂ adsorption. Thus, the adsorption tendency of MG to TiO₂ surface was reduced and further reduced the degradation efficiency. On the contrary in alkaline condition, the surface of TiO₂ with negatively charged was more susceptible to be adsorbed by positively-charged MG molecules (Baek, et al., 2010; Sartape, et al., 2017).

However, the MG degradation decreased after the solution pH was above pH 7 based on the results. This was due to columbic repulsion between the hydroxide
ions and catalyst surface with negatively charged. The formation of \( \cdot \text{OH} \) was highly restricted (Bibak, and Aliabadi, 2014). As shown in Figure 4.8, the degradation efficiency was the highest for the pH value of 5. Neutral condition was the desired environment for degradation of MG. In practical, it is undesirable to add alkali to increase the solution pH in order to degrade the dye molecules. In short, dye solution with pH of 5 was selected as the optimum condition.

### 4.2.5 Effect of Types of Organic Dyes

Other than MG, several types of dyes were used to investigate the effect of different dyes on sonocatalytic degradation efficiency. In this study, CR, MB, RB 4 and MO were tested under optimum conditions. Based on the result shown in Figure 4.9, the increasing degradation efficiency followed the order from MO, RB 4, MB, CR and MG which were 11.98, 34.43, 55.41, 63.90 and 79.01 %, respectively.

![Figure 4.9: Effect of Types of Organic Dye on the Sonocatalytic Degradation of Dyes (pH = 5, Catalyst Loading = 1.5 g/L, Initial Dye Concentration = 10 mg/L, Reaction Time = 30 minutes)](image)

The main factor affected the sonocatalytic activity was the molecular structure of organic dyes. The type of bond present and molecular weight of dye would highly influence the stability of the dyes. The properties of catalyst might also
affect the removal rate in a small extent (Abdullah and Pang, 2010). Both MG and MB are basic dyes and consist of cationic charges. The reason of high MG degradation efficiency was due to the presence of triphenyl methane structure that was easily activated by oxidation process (Rao and Venkatarangaiah, 2014). The structure of MG is the simplest among others, so this simple structure is favourable in the decolourisation of dye (Lavanya, et al., 2014). High degradation efficiency of MG might also relate to its high adsorption capacity. Small molecular size of MG allowed more interactions between active adsorption sites and dye molecules.

Meanwhile, CR molecules with a larger molecular size had limited adsorption capacity on catalyst surface. CR appeared as an anionic form in aqueous solution. By comparing CR with MB and MO, the structure of CR consists of azobenzene orazo bonds which might contribute greater reactivity coefficient with hydroxide radicals. According to Bhagwat, et al. (2017), CR exhibited a higher degradation rate in low pH condition. This was due to the ionisation of two sulphonic groups allocated in CR molecules, making the generation of soluble CR anions became easier.

MB is a type of cationic dye, while MO is anionic dye. Cationic MB possessed tendency to interact with negatively-charged catalyst. On the other hand, anionic MO would attract to cationic element easily by sulphonic group. According to Delsouz Khaki, et al. (2018), MO showed good degradation performance in acidic condition, while MB showed the opposite result. This was related to negatively-charged catalyst in alkaline solution would adsorb more MB molecules through electrostatic attraction. Delsouz Khaki, et al. (2018) stated that the best degradation process of MB and MO were in the pH range of 7-10 and 4-6, respectively. Meanwhile, the presence of dimethylamine group in MB and MO might inhibit its degradation rate (Adbdullah and Pang, 2010). The stability of MO and MB under ultrasonic irradiation could be differentiated by the presence of bonds since they were having similar molecular weight. MB was less stable under application of ultrasound due to the presence of charged sites in the aromatic ring structures while the charge site of MO located outside of the aromatic ring (Rao and Venkatarangaiah, 2014). Thus, MB was more susceptible to degradation than MO.

Epolito, et al. (2005) reported that RB 4 consisted of sulfonate group in 2-position, while 1,4-α-positions contained two amino groups. The presence of electron-donating group contributed to the elimination substitution or nucleophilic addition mechanism. The electron-donating group might adsorb on positively-
charged catalyst surface. However, the degradation efficiency of RB 4 was lower than MG since RB 4 had large molecular size. Montagudo, et al. (2014) reported that the degradation of RB 4 was less efficient without the presence of oxidant such as hydrogen peroxide. Without oxidant in the solution, the oxidative species such as hydrogen radicals were unable to be produced under ultrasonic irradiation. In short, MG showed the greatest degradation efficiency among others.

4.3 Kinetic Study

Kinetic study was carried out to determine the reaction kinetic order for sonocatalytic degradation of MG. Several rate orders were tested to determine the suitable reaction kinetic order. After evaluating, pseudo-first order kinetics was fitted well for all data, with regression coefficients of at least 0.88. It justified that the degradation of MG by sonocatalytic reaction using pure TiO₂, pure g-C₃N₄ and TiO₂/g-C₃N₄ at different weight ratios followed the pseudo-first order kinetics. The results are shown in Figure 4.10.

![Figure 4.10: Reaction Kinetics Graph for Sonocatalytic Degradation of MG with Different Types of Catalysts (Initial Dye Concentration = 10 mg/L, pH = 5, Catalyst Loading = 1 g/L, Reaction Time = 60 minutes)](attachment:image)

According to Abbasi, et al. (2008), the photocatalytic degradation reaction of organic pollutants was obeyed the pseudo-first-order. The \( k_{app} \) values and \( r^2 \) values are presented in Table 4.3. As shown in Table 4.3, TiO₂/g-C₃N₄-0.5 showed the highest \( k_{app} \) among other catalysts. This was due to the similar reason discussed in
section 4.2.1 where appropriate amount of TiO$_2$ well distributed on sheets-like g-C$_3$N$_4$ and further reduced the TiO$_2$ agglomeration.

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

<table>
<thead>
<tr>
<th>Catalyst Samples</th>
<th>Apparent Rate Coefficient, $k_{app}$ (min$^{-1}$)</th>
<th>Regression constant, $r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.0030</td>
<td>0.8836</td>
</tr>
<tr>
<td>g-C$_3$N$_4$</td>
<td>0.0022</td>
<td>0.9772</td>
</tr>
<tr>
<td>TiO$_2$/g-C$_3$N$_4$-2</td>
<td>0.0043</td>
<td>0.8808</td>
</tr>
<tr>
<td>TiO$_2$/g-C$_3$N$_4$-1</td>
<td>0.0078</td>
<td>0.9093</td>
</tr>
<tr>
<td>TiO$_2$/g-C$_3$N$_4$-0.5</td>
<td>0.0184</td>
<td>0.8936</td>
</tr>
</tbody>
</table>

4.4 COD Results

The COD removal by sonocatalytic process was investigated. The COD study of the dye solution was carried out with the optimum conditions. Based on Figure 4.11, about 50% of the COD had been removed after 30 minutes. Since the structure of the dye molecules was complicated, it was difficult to be degraded into small organic fragments. It was believed that the intermediate products of MG were too difficult to be oxidised by AOP and the complete oxidation might continue in a longer duration.

![Figure 4.11: COD Study on the Sonocatalytic Degradation of MG (pH = 5, Catalyst Loading = 1.5 g/L, Initial Dye Concentration = 10 mg/L, Reaction Time = 30 minutes, Wavelength = 620 nm)](image-url)
According to the study by Tripathi and Narayanan (2018), 75.1% of the COD removal could be achieved by using TiO$_2$/g-C$_3$N$_4$ photocatalyst at solution pH of 5 after 3 hours. They found that the adding of oxidant, hydrogen peroxide would highly increase the efficiency to 85.62%. Since the experiment was conducted in 30 minutes in this study, the removal percentage was lower compared to the result obtained by Tripathi and Narayanan (2018). It was believed that the removal efficiency would be higher if the experiment duration increased.
CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this study, the catalyst characteristic of pure TiO$_2$, pure g-$\text{C}_3\text{N}_4$ and TiO$_2$/g-$\text{C}_3\text{N}_4$ at different weight ratio were investigated. The ratio of TiO$_2$ to g-$\text{C}_3\text{N}_4$ used were 0.5, 1 and 2 in terms of weight percent. All the samples were characterised by XRD, SEM-EDX and FTIR analyses. The result of XRD patterns showed the presence of TiO$_2$ and g-$\text{C}_3\text{N}_4$ typical peaks in TiO$_2$/g-$\text{C}_3\text{N}_4$ composite samples. The typical peaks of g-$\text{C}_3\text{N}_4$ only appears in TiO$_2$/g-$\text{C}_3\text{N}_4$-0.5 composite and the diffraction peaks of TiO$_2$ was not sharp. This was due to the reduction of TiO$_2$ crystallinity. The crystallite size of TiO$_2$ particles were calculated by Scherrer equation and the results showed that the crystallite size of particles decreased when decreasing the weight ratio of TiO$_2$/g-$\text{C}_3\text{N}_4$ in the composite samples. SEM results showed that the TiO$_2$/g-$\text{C}_3\text{N}_4$ appeared as spherical TiO$_2$ particles distributed on the film-like g-$\text{C}_3\text{N}_4$ sheets. For FTIR results, both TiO$_2$/g-$\text{C}_3\text{N}_4$-1 and TiO$_2$/g-$\text{C}_3\text{N}_4$-0.5 composites portrayed the typical peaks of TiO$_2$ and g-$\text{C}_3\text{N}_4$. Meanwhile, TiO$_2$/g-$\text{C}_3\text{N}_4$-2 did not show characteristic of g-$\text{C}_3\text{N}_4$ particles due to the low amount of g-$\text{C}_3\text{N}_4$.

During sonocatalytic degradation process, various parameters were studied such as weight ratio of TiO$_2$ to g-$\text{C}_3\text{N}_4$, catalyst loading, initial MG concentration, initial solution pH and types of organic dyes. The optimum conditions for the degradation of dyes was identified at 1.5 g/L of TiO$_2$/g-$\text{C}_3\text{N}_4$-0.5 in degradation of 10 mg/L of MG at solution pH of 5. The highest degradation efficiency could reach about 79.01 %. The effectiveness of dye degradation was arranged from MG, CR, MB, RB 4 and MO in descending order. MG with triphenyl methane structure was the most susceptible to chemical oxidation among others due to its small molecular size, leading to higher adsorption capacity. The sonocatalytic reaction in this study followed the pseudo-first order rate kinetics. It was found that 50 % of the COD was removed after 30 minutes. Longer duration was required to increase the degradation of COD due to the formation of intermediate particles which would be difficult to be removed.
5.2 **Recommendations**

Thermogravimetric analysis should be carried out to study the physical and chemical changes of catalyst at different temperatures. It is crucial to ensure there is no weight loss due to the oxidation and decomposition when the catalyst is being introduced into commercial use. Besides, Brunauer–Emmett–Teller (BET) surface analysis is required to investigate the effect weight percent of TiO$_2$ and g-C$_3$N$_4$ in a composite sample on the specific surface area of the TiO$_2$/g-C$_3$N$_4$ particles. BET analysis can provide the extent of agglomeration of the sample since a larger surface area can increase the number of active sites for dye degradation. Lastly, gas chromatography can be carried out on the liquid sample to determine the types of intermediate compounds formed when dye is being degraded.
REFERENCES


APPENDIX A: Calibration Curves for MG, CR, RB 4, MO and MB

GraphA-1: Calibration Curve for MG

GraphA-2: Calibration Curve for CR
GraphA-3: Calibration Curve for RB 4

\[ y = 0.017x \]
\[ R^2 = 0.9923 \]

GraphA-4: Calibration Curve for MO

\[ y = 0.0788x \]
\[ R^2 = 0.9986 \]
GraphA-5: Calibration Curve for MB

MB

$y = 0.203x$

$R^2 = 0.9993$