EVALUATION AND PERFORMANCE OF GRAPHITIC CARBON NITRIDE (g-C_3N_4) AND COCONUT SHELL HUSK DERIVED-CARBON COMPOSITE FOR SONOCATALYTIC DEGRADATION OF ORGANIC DYE

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ABSTRAK

Air sisa ialah air terpakai yang telah dicemari oleh penggunaan rumah, industri dan komersial. Komposisi air buangan ialah 99.9% air dengan baki 0.1% adalah apa yang dikeluarkan. Air sisa pewarna adalah salah satu isu alam sekitar. Rawatan air sisa pewarna adalah perkara penting untuk kelestarian alam sekitar dan sosial. Walau bagaimanapun, kaedah ini mempunyai kelemahannya sendiri seperti, kos operasi dan kos pelaburan yang tinggi, masa pemprosesan yang lama, dan kebolehlaksanaan operasi berskala besar. Oleh itu, objektif kajian ini adalah untuk menentukan keadaan proses optimum untuk degradasi sonokatalitik pewarna dengan menggunakan komposit karbon terbitan tempurung kelapa g-C_3N_4 dan tempurung kelapa serta untuk menjelaskan mekanisme degradasi sonokatalitik pewarna ke atas g-C_3N_4 dan tempurung kelapa komposit karbon terbitan sekam. Berdasarkan keputusannya, adalah boleh dilakukan untuk mensintesis karbon, (C) yang diperoleh daripada tempurung kelapa yang boleh digunakan sebagai fotomangkin semata-mata dalam degradasi fotomangkin Methyl Orange (MO). Dalam keputusan, didapati bahawa g-C_3N_4, (CN) dengan pemuatan mangkin 0.1 g/L pada 5 ppm (20 min) mempunyai aktiviti fotomangkin tertinggi dengan 88.07% penyingkiran MO berbanding C. Selain itu, keadaan alkali adalah lebih kondusif untuk degradasi MO. Kajian ini mencadangkan bahawa kepekatan MO boleh dikurangkan dengan menggunakan Karbon yang diperolehi daripada tempurung kelapa. Pelaksanaan bahan mentah mesra alam memperkenalkan pemangkin yang lebih mampan untuk proses rawatan air sisa kos efektif yang menjadikan penggunaan sampel yang dikaji lebih praktikal. Menurut Matlamat Pembangunan Lestari 6: Air Bersih dan Sanitasi, kita boleh meningkatkan kualiti air dengan mengurangkan pencemaran, menghapuskan lambakan, dan meminimumkan pembebasan bahan kimia dan bahan berbahaya, mengurangkan separuh bahagian air sisa yang tidak dirawat dan meningkatkan kitar semula dan penggunaan semula yang selamat dengan ketara secara global.

ABSTRACT

Wastewater is used water that has been polluted by home, industrial, and commercial use. The composition of wastewater is 99.9% water with the remaining 0.1% is what is removed. Dye wastewater is one of the huge environmental issues. The treatment of dye wastewater is an important matter for environmental and social sustainability. Conventional treatments are commonly used in Malaysia. However, this method has their own drawbacks such as, high operating cost and investment costs, long processing times, and large-scale operation feasibility. Thus, this research objective is to determine the optimum process condition for the sonocatalytic degradation of dye by using g-C_3N_4 and coconut shell husk (CSH) derived carbon composite and to elucidate the mechanism of sonocatalytic degradation of dye over g-C_3N_4 and coconut shell husk (CSH) derived carbon composite. Based on the results, it is feasible to synthesize carbon, (C) derived from CSH which can be used as solely photocatalyst in photocatalytic degradation of Methyl Orange (MO). In the results, it is found that g-C_3N_4, (CN) with 0.1 g/L catalyst loading at 5 ppm (20 min) has the highest photocatalytic activity with 88.07% of MO removal compared to C. In addition, alkaline conditions are more conducive for MO degradation. This study suggested that the concentration of MO can be reduced by utilizing Carbon derived from CSH. The implementation of eco-friendly raw materials introduces a more sustainable catalyst for the wastewater treatment process cost-effective which makes the utilization of the studied samples to have more practicality. According to Sustainable Developing Goal 6: Clean Water and Sanitation, we can improve water quality by reducing pollution, eliminating dumping, and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally.

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LIST OF SYMBOLS

TiO_2	Titanium Dioxide
g-C_3N_4	Graphatic Carbon Nitrate
℃	degree Celsius
ml	millilitre
%	Percentage
rpm	Revolution per minute
CO^2	Carbon Dioxide
g	gram
min	minutes
cm	centimeter
W	Watt
nm	nanometer

LIST OF ABBREVIATIONS

DO	Dissolved Oxygen
UV	Ultraviolet
VB	Valence Band
CB	Conduction Band
AOP	Advanced Oxidation Process
US	Ultrasonic
NPs	Nanoparticles
CHS	Coconut Shell Husk
MO	Methyl Orange
COD	Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
NH3-N	Ammoniacal Nitrogen
SS	Suspended Solid
C	Carbon

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Malaysia aspires to be a developed nation by 2025 (Afiq et al., n.d.). Furthermore, Malaysia is a developing country in the midst of a fast transition to an urbanized and industrialized society. This development has resulted in a slew of environmental issues. In conjunction, wastewater discharge from industries constitutes one of the main environmental issues. Water pollution affects the welfare of all living things, including humans, the economy of the country and it contributes greatly on sustainability of water resource (Singh et al.2020). This indicates that untreated wastewater discharge will have serious environmental consequences and will have to be closely monitored. Two different sources for water pollution, which are namely point source and non-point source. Point-source pollution is easy to identify. As the name suggests, it comes from a single place. For example, sewage treatment plant and industrial discharges. Nonpoint-source pollution is more difficult to identify and address. This pollution comes from a variety of sources at once. Urban and agricultural runoff are examples of non-point sources.

Wastewater has recently been reported as a result of dye emissions from numerous businesses, including papermaking, textile dyeing, cosmetics, paints, and food processing. Discharging dye contaminants into water is a major concern due to their toxicity to human health and aquatic life. The dye contaminants in water are toxic, carcinogenic, and xenobiotic (Ravindra et al., 2019). Adsorption, coagulation/ flocculation, and precipitation are common wastewater treatment technologies method that takes a long time to operate and create secondary sludge, which is expensive to dispose. Quality of water is determined by a few parameters which are dissolved oxygen (DO), chemical oxygen demand (COD), biochemical oxygen demand (BOD), ammoniacal nitrogen (NH_3-N), and suspended solids (SS) present

in the water (Camara et al., 2020). Initially, the primary abatement technique used in treatment facilities was screens to remove big debris. Treatment facilities began allowing wastewater to settle before discharging as technology improved in the twentieth century, then began employing biological treatments (e.g., bacteria) to reduce pollutants, and eventually began using more complex chemical treatments. Raw, primary, secondary, and tertiary treatment are the terms used to describe these abatement technologies. By 1977, the Clean Water Act mandated that all municipal treatment plants undergo secondary treatment (Keiser et al., 2019).

Besides, this wastewater treatment investment was not cost effective. The treatment of dye wastewater is an important matter for environmental and social sustainability. Wastewater treatment have two main functions. The main function of wastewater treatment is to ensure that the discharge will not have such a great impact on the water quality and aquatic life. The second function of wastewater treatment is to reuse the wastewater that is treated. This function is focused on combating water scarcity in the world (A.J. Englande et al., 2015). Wastewaters differ significantly from drinking water sources, usually from rivers, lakes or reservoirs. The contaminant levels in most drinking water sources are quite low as compared with contaminant levels in wastewaters derived from industrial-type activities. In general, the challenges encountered during wastewater treatment are quite complicated, since the effluent contains a variety of contaminants, depending on where it originated from. So, there are different types of effluents to treat, each with its own characteristics requiring specific treatment processes.

Photocatalytic degradation has gained popularity as a strategy for treating dye-contaminated water among a number of treatment options. A photocatalyst is a material which absorbs light to bring it to higher energy level and provides such energy to a reacting substance to make a chemical reaction occur (Oshida, 2013). The photocatalytic performances will systematically be evaluated by decomposing dye wastewater. Photocatalytic activities in the presence of titanium dioxide (TiO_2) provide an exciting method for destroying harmful organic pollutants, as they operate in the UV-A range and can potentially utilize sun light. Heterogeneous photocatalysis on a semiconductor surface using

UV or solar light is an appealing advanced oxidation technology for water treatment applications. Photocatalytic techniques for the decomposition of the organic contaminants can make optimal use of abundant solar radiation. The primary mechanism of photocatalysis is to evict an electron from the valence band (VB) of the TiO_2 semiconductor to the conduction band (CB), resulting in a h+ hole in the valence band. This is caused by UV irradiation of TiO_2 at energies equivalent to or greater than the band gap. Figure 1.1 shows the general mechanism of photocatalysis (Ghaly et al., 2011).

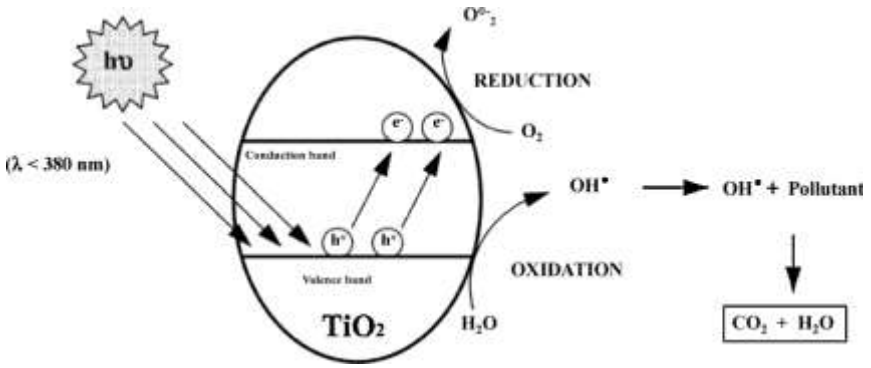


Figure 1.1: The General Mechanism of Photocatalysis
Source: Ghaly et al., 2011

Recently, several photocatalysts such as titanium dioxide (TiO_2), zinc oxide (ZnO), copper oxide (CuO) has been studied to facilitate carbon dioxide, CO_2 reduction by hydrogen, H_2O under light irradiation. Titanium dioxide is a solid semiconductor that generates electrons in the conduction band and holes in the valence band when exposed to light. However, there are still some challenges and drawbacks such as low-usage of light, rapid recombination rate of photo-generated carriers, low CO_2 conversion efficiency need to be overcome in order to become an efficient and effective platform to reduce concentration of CO_2 (Li et al., 2018). Many parameters, including size, specific surface area, pore volume, pore structure, crystalline phase, and exposed surface facets, are have a considerable impact on photocatalytic activity. As a result, photocatalysis research continues to focus on developing performance enhancements by changing these elements. Structural

dimensionality is another feature that can affect photocatalytic activity and has a big impact on TiO_2 materials' characteristics (Nakata & Fujishima, 2012). Due to its quick electron-hole recombination, TiO_2 has a low photoconversion efficiency for practical applications of photocatalytic CO_2 reduction. Aside from that, due to its wide band gap value, only 5% of incoming solar radiation can be absorbed because it can only be activated by light, bare TiO_2 is used for photocatalytic reactions UV (ultraviolet) light (Ismael, 2020).

The development of a nontoxic metal-free graphitic carbon nitride (g-C_3N_4) has received a lot of interest. However, they still have some fatal defects restricting their practical applications, such as low quantum efficiency, high electron-hole recombination rate, low charge migration rate, high electron-hole recombination rate, the usage of noble metals as cocatalysts or reagents (such as Pt and Pd, which leads to high cost), and small surface area (Li et al., 2019). Recently, carbon source has been successfully deposited on the g-C_3N_4 backbone to enhance its photocatalytic activity through increasing the electron transfer and reservoir properties. Therefore, in order to enhance the application potential of g-C_3N_4, many strategies were developed, such as coupling with other different materials and morphology control (Zhang et al., 2019).

With the implementations of the 17 Sustainable Development Goals, clean water and sanitation has increased in importance to raise the quality of living and reduce the environmental impact. The treated wastewater in Malaysia must achieve the minimum standard that is implemented by the Department of Environment. The public demand for pollutant-free waste discharge to receiving waters has made decontamination of industrial wastewaters a top priority. However, among the numerous and various treatment processes currently cited for wastewater treatment, only a few are commonly used by the industrial sector for economic and technological reasons.

1.2 Problem Statement

Wastewater is going to be a major problem in Malaysia for upcoming years. With the increasing number of polluted rivers in Malaysia, fresh water supply for domestic purposes

will be limited. Therefore, the water demand will rise along with the discharge of municipal wastewater. Furthermore, humanistic activities in Malaysia involve significant consideration as they discharged tonnes of harmful materials into the aquatic environment, containing toxic substances. Dye is widely utilized in the textile industry to colorize items at every stage of the manufacturing process (Kishor et al., 2021). Eutrophication of this brightly colored textile effluent has a significant impact on photosynthetic performance in plants and aquatic life.

Dye wastewaters are carcinogenic and toxic which will impose health and environmental problems (Bhardwaj & Bharadvaja, 2021). Humans that consume the water from these rivers will have increased risk of cancer and the toxic property of dyes will poison humans and even aquatic species. The disadvantage of textile materials is the significant environmental effect of wastewater discharged during the production process. The effluents contain nonbiodegradable dyes and other chemicals which are toxic and pose a serious threat to fresh water. Due to the presence of dye and additives used during the textile production process, there is metal contamination in textile effluent. The most frequent metals identified in dye chromophores in textile effluents are cobalt, copper, and chromium (Velusamy et al., 2021). The principal metals that create environmental concerns include chromium, zinc, iron, mercury, and lead. So, this textile wastewater must be treated before its discharge. Organic or synthetic dyes display significantly noticeable color in the effluent even at low concentration. By blocking the light, aquatic plants cannot undergo photosynthesis which causes the DO level in the river to decrease and harm the ecosystem (Y. J. Zhang et al., 2019).

In response to dye as an increasing pollutant, many dye treatment procedures have been developed in recent years. Although some may use a mix of two or more processes, these techniques can be classified as physical, chemical, or biological processes. The distinct qualities of each treatment method may be beneficial in one way but limited in another. Dye treatment efficiency, operation and investment costs, large-scale operation feasibility, and human and environmental friendliness are all factors that are commonly considered. Treatment procedures with high installation and operating costs, long processing times, low

efficiency, and harmful by-product output are frequently overlooked in industrial applications. Physical therapy is one of the most widely utilized therapies due to its ease of use, adaptability, and effectiveness. Adsorption, ion exchange, coagulation-flocculation, and membrane filtration are examples of dye treatment procedures in this category. Adsorption is the most extensively used physical technique for treating dye wastewater because it can efficiently remove many types of water contaminants. As a result, it generates a lot of sludge and has a higher recharge cost. Chemicals with a lower stability produce undesirable products and generate secondary contamination, both of which are harmful to the environment. Biological dye treatment is considered as one of the simplest and inexpensive ways to treat dye wastewater with its removal efficiency highly dependent on the growth of microorganism. Despite the simplicity of the processes, it might be difficult to integrate such systems into small-scale businesses due to the need for particular bioreactors or stabilization ponds, which come at a high initial cost. Because dye wastewaters generally contain a variety of colors, biological dye treatment methods may be ineffective (Wong et al., 2019).

Wastewater generated from textile industries are harmful to the environment because it contains contaminants such as organic matter, sulphide, oil, detergents, grease, soap and sodas. These pollutants need to be eliminated from the wastewater by going through wastewater treatment method that utilizes chemical, physical or biological treatment methods (Wong et al., 2019). However, organic dyes are harder to treat due to their chemical stability and biological resistance. There are some limitations in photocatalyst, inefficient utilization of visible light, low adsorption of organic pollutants, difficulty in distributing particles uniformly, aggregation of nanosized particles and difficulty in recovery of nanosized particles. Since the main focus of treating the wastewater is to overcome water scarcity and pollution, a metal-free semiconductor is chosen for this research. The common semiconductor will be used for these treatment methods are (TiO_2). TiO_2 has disadvantages of a wide band gap energy that results in unsatisfactory performance.

With the globe moving toward more sustainable technologies, sonocatalytic wastewater treatment technology is gaining popularity because of its environmentally beneficial and green wastewater treatment process (Wastewater Treatment: Molecular Tools,

Techniques, and Applications - Google Books, n.d.). TiO_2 is a typical semiconductor utilized in these treatment procedures. TiO_2 has the problem of having a large band gap energy, which leads in poor performance. Because the primary goal of dye wastewater treatment is to reduce water shortages and pollution, a metal-free semiconductor was chosen for this study. Graphitic carbon nitride (g-C_3N_4) is a recently found metal-free sonocatalyst. Due to the quantity and renewability of raw materials, this semiconductor will be less expensive than TiO_2 because it is metal-free.

1.3 Research Objectives

The objectives of our project

i. To determine the optimum process condition for the sonocatalytic degradation of dye by using g-C_3N_4 and coconut shell husk derived carbon composite.
ii. To elucidate the mechanism of sonocatalytic degradation of dye over g-C_3N_4 and coconut shell husk derived carbon composite.

1.4 Scope of Study

Due to the obvious presence of organic matter in wastewater, conventional wastewater treatment techniques are becoming more difficult to implement. To cope with this extremely concentrated and hazardous non-biodegradable organic materials, a new method is required. Advanced oxidation process (AOP) has arisen in recent decades to remediate wastewater discharged by industry. Recently expressed interest in using ultrasonic (US) in photocatalysis, such as sono-photocatalysis, to increase the dye wastewater treatment process effectiveness in the destruction of organic and inorganic pollutants in aqueous streams. Ultraviolet (UV) and ultrasonic (US) are used together in sono-photocatalysis (Zewde et al., 2019). Reactive oxygen species (ROS) such as superoxide radical anion, hydroxyl radical (OH %), hydrogen peroxide (H_2O_2), and singlet oxygen (O_2 %) are produced by AOPs and can quickly oxidize dye molecules in industrial effluents. The existence of solid particles (sonocatalysts) in solution allows for the utilization of low

ultrasonic (US) power intensities while also providing extra nucleation sites, increasing the number of cavitation events. Thus, improving degrading performance. Furthermore, the usage of semiconductor materials in sonocatalysis may result in the formation of electron/hole pairs, resulting in the generation of even more oxygen radicals.

Photocatalysis and sonocatalysis using metal oxide nanoparticles (NPs) have received more attention as effective approaches for the degradation of harmful organic pollutants among a variety of AOPs. (g-C_3N_4) has extensively attracted much suit in various research works concerning pollutants degradation under light irradiation due to their good photocatalytic activity, low cost, non-toxicity. Moreover, the synthesis of g-C_3N_4 micro- and nanostructures with a variety of morphologies is inexpensive, accessible, and simple to regulate for large-scale manufacturing. g-C_3N_4 nanoparticles coated with carbon nanotubes were utilized in a sono-photocatalytic method to degrade Methyl using sunlight. Sonocatalysis alone for the oxidation of colors in industrial effluents consumes a lot of energy and takes a long time to degrade, therefore it is difficult to use on a big scale. To address these issues, sonophotocatalysis (sonocatalysis + photocatalysis) may be a potential technique for water purification, though its cost-effectiveness should even be demonstrated in the field. Because of the favorable synergic effect of combining these two advanced oxidation processes, the increased treatment cost associated with an increase in energy consumption can be mitigated by the shortened treatment time required (Lops et al., 2019).

Dye molecules absorb light in the visible range, thus once adsorbed on the photocatalyst surface, they can transform received photons into electrons and inject them into the semiconductor photocatalyst's conduction band. This will allow for the separation of electrons and holes, as well as the creation of ROS, within the photocatalyst. As a result, the dye degradation at the catalyst surface will be enhanced by this photo-sensitization process. We believe that utilizing sunlight to efficiently breakdown dyes via a sono-photocatalytic process would be an added benefit. Batch test carried out at room temperature to assess the catalytic (photocatalytic and sonocatalytic) activity of g-C_3N_4 NPs and to better understand the degradation mechanisms of both dyes. The suspensions (dye+NPs) were held in the dark for 10 minutes before being exposed to ultrasonic waves or UV-visible light to achieve the

dye's adsorption-desorption equilibrium on the g-C_3N_4. As a result, the adsorption impact during sonocatalysis or photocatalysis could be correctly determined (Chauhan et al.,2020). In addition, the degradation mechanisms and the effects of operating conditions, such as dye concentration, presence of salts typical of industrial wastewater also investigated on the MO sonophoto-degradation. Finally, the best catalyst's stability and reusability will be investigated in order to pave the road for a commercial use of g-C_3N_4 for effective dye pollutant sonophotocatalytic degradation. Figure 1.2 shows the mechanism of sono-photocatalytic dye degradation (Theerthagiri et al., 2016).

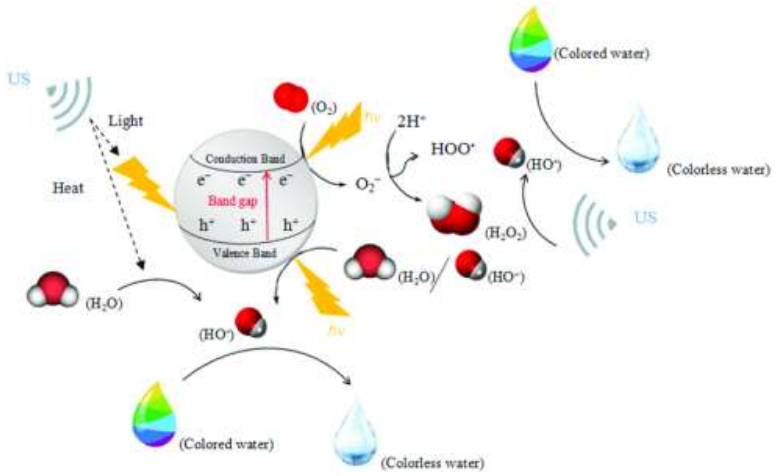


Figure 1.2: Mechanism of sono-photocatalytic dye degradation
Source: Theerthagiri et al., 2016

1.5 Significant of Study

Traditionally, products such as coconut mats and brushes are made from the husk, the hard, hairy shell. Because the husk contains a lot of lignin which acts as a natural adhesive, the department of Biobased Products at Wageningen UR discovered that sustainable production of board material from the husk is also possible. This study focuses on the preparation and sonocatalytic degradation performance of pure g-C_3N_4, and pure

carbon, The process is both ecologically beneficial and long-lasting. The residual material of the coconut is used in its entirety.

The implementation of eco-friendly raw materials introduces a more sustainable catalyst for the wastewater treatment process cost-effective which makes the utilization of the studied samples to have more practicality. If the sample is found to be reusable, it will be more cost-effective which is favorable for industrial application. The reusability of the sample with the best degradation performance will also be conducted. The use of environmentally friendly raw materials creates a better long-term catalyst for wastewater treatment. The raw materials employed in this research are also cost-effective, enabling for more practical use of the investigated samples. The developed g-C_3N_4 and coconut shell husk will be used as potential catalyst for photocatalytic dye wastewater treatment to solve the water security problem and provides alternative energy in order to reduce water contaminant.

According to Sustainable Developing Goal: Clean Water and Sanitation, we can achieve access to adequate and equitable sanitation and hygiene for all and end open defecation, paying special attention to the needs of women and girls and those in vulnerable situations. Improve water quality by reducing pollution, eliminating dumping, and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally. Substantially increase water-use efficiency across all sectors and ensure sustainable withdrawals and supply of freshwater to address water scarcity and substantially reduce the number of people suffering from water scarcity. Support and strengthen the participation of local communities in improving water and sanitation management.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Water pollution is one of the world's most critical environmental problems. Industrial effluent is a major cause of it. Because of its complicated composition, limited biodegradability, and high toxicity, industrial effluent may have a huge influence on ecosystems. In textile industry, dye is extensively used in every stage of the production process to colorize the products. Textile wastewater have become examples of industrial wastewater that are difficult to degrade because of its prodigious output and highly stable contained organic compounds (Liu et al., 2021). Textile industry wastewater contains toxins such as organic debris, sulphide, oil, detergents, grease, soap, and sodas, which are hazardous to the environment. Dissolved solids, color, noxious metals (chromium), printing gums (pentachlorophenol, detergents), sequestering agents (trisodium polyphosphate and sodium hexametaphosphate, chlorine, azo dyes), and stain removers (CCl_4, residual chlorine, fixing agents like formaldehyde and benzidine) are all present in the water released after fabric preparation. The majority of the compounds listed above are hazardous to the environment. Most textile companies employ 60–70% azo group dyes in the dyeing process, and roughly 15–20% of the whole dye is released into the environment throughout the process, causing terrible environmental impact (Donkadokula et al., 2020). As a result, wastewater must be thoroughly treated before being released into the environment or utilized for other reasons.

2.2 Classification of Dye

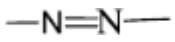
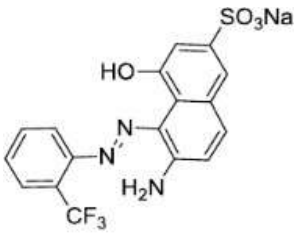
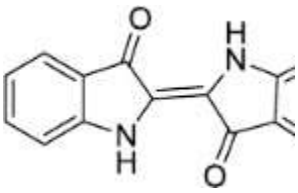
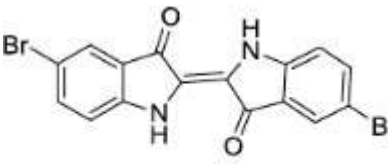
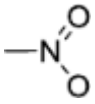
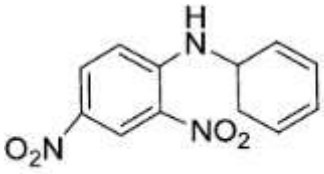
A dye is a colored material that binds to the substrate it is applied on chemically. Dyes are categorized according to their source, chemical structure, and mode of application. Dyes are compounds that generate color by modifying the crystal structure of the color substances, at least at some point, when applied to a substrate. The dyes may adhere to appropriate surfaces by establishing covalent bonds or complexes with salts or metals, physical adsorption, or mechanical retention (Vishnu et al., 2020)Dyes are made up of chromophores, which are responsible for the dye's color, and are classified depending on its application and chemical structure.

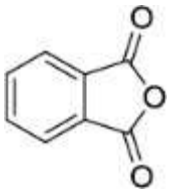
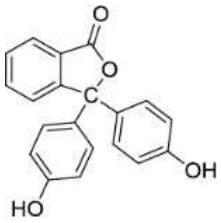
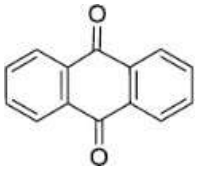
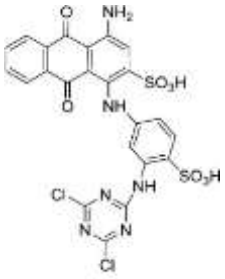
There are two main sources for dyes which are natural and synthetic. Natural dyes are derived from animals, plants, and minerals(Adeel et al., 2019). Natural colors' basic components originate from natural. Mordants will be needed if natural colors are to be used on textiles. The source for synthetic dyes is obtained from petroleum compounds. Synthetic dyes are substances considered recalcitrant xenobiotics. The different between natural dyes and synthetic dyes is largely that synthetic dyes are chemically manufactured whereas natural dyes are purely developed from nature. Natural dyes, although pure from chemicals, are often times more expensive than chemical dyes. Synthetic dyes are inexpensive to create, but they can cause skin allergies and the manufacturing process produces dangerous by-products. Synthetic dyes will affect both individuals and the environment as a result of this. This is why, for the most part, artificial dyes have replaced natural colors in the textile industry. Natural dyes, on the other hand, are still prized for their purity and are utilized in food, pharmaceuticals, and cosmetics intended for human consumption.

Different organic dyes are in use in textile for coloring the different products. Their chemical structures are diverse, including for example azo and nitro dyes, phthalocyanine and diarylmethane dyes with very different chemical and physical properties. Furthermore, a dye is a material that absorbs a portion of the visual spectrum (chromophore). The color is determined by the percentage of light that is reflective rather than absorbed by the dye. The

conjugated double bonds provide a chemical structure that is conducive to light absorption. As a result, aromatic amines are frequently found in colorants (Benkhaya et al., 2020).

Table 2.1: Classification of textile dyes according to the chromophore

Dye Class	Chromophore	Example
Azo Dyes		 Acid Red 337
Indigoid Dyes		 C.I. Vat Blue 35
Nitro Dyes		 Disperse yellow 14

Phthalein Dyes		 Phenolphtaleine
Anthraquinone Dyes		 Reactive Blue 4

Source: Benkhaya et al., (2020)

Table 2.2: Method of Applications Based on Dyes Class

Class	Principal Substrates	Method of Application
Reactive	Silk, wool, cotton and nylon	Reactive site on dye reacts with functional group on fibre for dye to be bounded under pH and heat influence.
Disperse	Polyamide, acetate, acrylic, polyester and plastic	Fine aqueous dispersions that can be padded on cloth and baked.
Direct	Paper, cotton, rayon, leather and nylon	Applied from slightly alkaline or neutral baths which containing additional electrolyte.

Vat	Rayon, cotton and wool	Water-insoluble dyes solubilized byreducing with sodium hydrogen sulfide, then exhausted onfiber and deoxidized.
Basic	Modified nylon, polyester, inks, paper and polyacrylonitrile	Applied in acidic dyebaths
Acid	Wool, silk, paper, inks, leather and nylon	Usually applied from neutral to acidic dyebaths
Solvent	Gasoline, plastics, varnishes, stains, inks, fats, oils, lacquers and waxes	Dissolution in the substrate

Source: Benkhaya (2020)

2.3 Textile Wastewater Treatment Method

Textile wastewater is responsible for a lot of environmental damage as well as human sickness. If contaminants in textile wastewater are removed without sufficient treatment, they might create decreased oxygen dissolved in receiving bodies, resulting in septic conditions that threaten aquatic life's existence. The high TDS in the wastewater raises the salinity of the receiving water bodies, whereas the high alkalinity raises the pH. The dyes' color is visually unappealing, especially in recreational waterways. Furthermore, some dyeing support chemicals, such as phenol, can impart flavor and odor (Islam et al., n.d.). Various physical, chemical, and biological treatment technologies have been developed to eliminate the toxicity of these wastewaters in the environment. The most extensively utilized conventional therapy procedures are coagulation and biological treatment. Despite their benefits, these technologies are unable to entirely degrade organic contaminants in industrial

wastewater, necessitating the exploration and development of new methods to treat refractory industrial wastewater (Liu et al., 2021).

Table 2.3 Summary of Treatment Methods for Wastewater Treatment

Mechanism	**Factors influencing treatment**	**Advantages**	**Limitations**
Physical treatment method			
Adsorption	Dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time	Cost-effective can be regenerated for the next use	Larger quantities required, and longer contact time required
Radiation treatment			
Radiation	Dye's reactivity and photosensitivity, and availability of dissolved oxygen	Cost-effective can be regenerated for the next use	Larger quantities required, and longer contact time required
Chemical treatment methods			
Oxidation	Oxidizing agents, oxidizing conditions, and pH	Efficient for all classes of dyes, short detention time, and less capital cost	Problems with process pH maintenance, removal of water, and sludge handling
Electrochemical oxidation	Nature of electrolyte, electrolyte concentration, and electrolysis time		
Precipitation	Precipitant and pH		
Biological treatment methods			
Aerobic	Specificity towards substrate	Specificity, effective and possibility of immobilization	Cost-intensive, and more extended detention periods

Source: Marimuthu, (2020)

2.3.1 Physical - Chemical Treatment

Physical principles such as adsorption and radiation are used in the therapy. Activated charcoal, zeolite, chitosan, and low-cost industrial wastes are some of the most often used adsorbents in water treatment facilities. UV, gamma, and X-rays are used in the radiation treatment of municipal wastewater. The oxidation and reduction processes, as well as the utilization of a variety of chemical substances, are among the chemical treatment options. Both organic and inorganic pollutants present in the wastewater are removed by a set of chemical treatment methods. Major chemical pollutants like pesticides, dyes, solvents, heavy metals, etc. are considered hazardous materials and major threats to the purity of water (Donkadokula et al., 2020).

Physical Chemical Wastewater Treatment refers to a number of treatment methods for removing contaminants from wastewater or influent. Generally, this unit operation consists of pH adjustment, coagulation, flocculation and sedimentation or floatation processes. Depending on the overall process, this procedure will remove certain contaminants and create treated water appropriate for disposal or the next process step (such as biological treatment). Sludge can then generally be treated and dewatered for subsequent disposal. Inorganic coagulants such as poly aluminium chloride are used in traditional coagulation systems to remove fluoride from wastewater (PAC). Organo (Asia) has developed the ORSREC system to reduce the use of inorganic coagulants by recycling and reusing the sludge created. ORSREC follows the three-tiered waste management method of REDUCE, REUSE, and RECYCLE. Fluoride content in treated water is around 3 ppm when using ORSREC. Furthermore, our proven ORSREC can limit sludge production and achieve optimal water quality using only a little number of coagulants (Services - wastewater / effluent treatment system - physical chemical treatment systems).

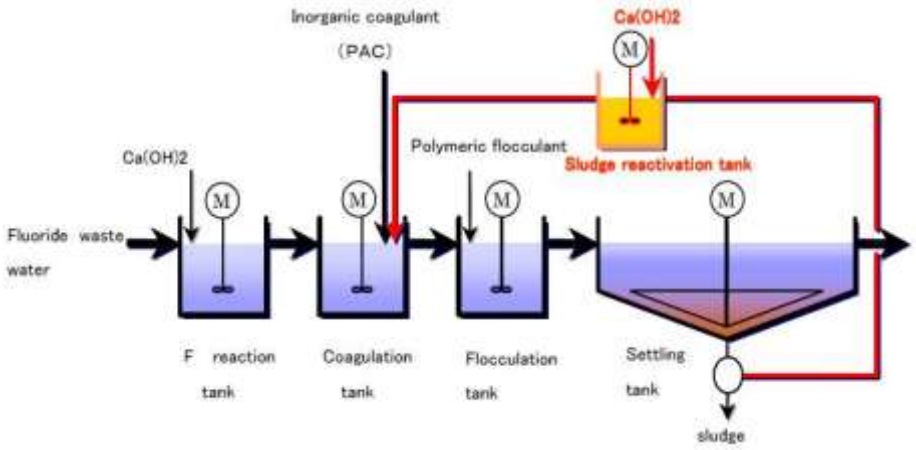


Figure 2.1: Organo Sludge Recycle System (Orsrec)

Source: (*Physical Chemical Treatment Systems – Organo Asia Sdn Bhd*, n.d.)

2.3.1.1 The Adsorption Treatment

The adsorption treatment technique eliminates dyes by contacting the target pollutants with the adsorbent's surface (Hu et al., 2021). This is the most often used tertiary treatment procedure in the textile industry. The adsorbents are usually porous solids, indicating that they have a large surface area that allows the organic dyes to adsorb on the surface of the adsorbents and be removed. Surface area, dye size, solution, temperature, pH of solution, contact duration, and dye-surface interaction are all important elements that might impact an adsorbent's effectiveness (Maleki et al. 2020). The fundamental disadvantage of the adsorption process is the adsorbent's short lifetime. Depending on how dirty the wastewater is, it must be regenerated or replaced on a regular basis.

2.3.1.2 Membrane separation

Membrane separation can purify and improve the quality of the final product. Nano-filtration, ultrafiltration, reverse osmosis, and micro-filtration are the four types of membrane separation. Membrane separation has a high separation efficiency, resulting in clean liquid effluent and raw material recovery. The biggest downside of this approach is membrane fouling, which reduces the membrane's effectiveness significantly. In comparison to adsorption and membrane separation, coagulation and flocculation are the most cost-

effective methods for removing organic contaminants. This approach is typically used in conjunction with a sedimentation tank, in which the flocs are allowed to settle to the bottom of the tank and then removed from the water by gravity (Donkadokula et al.,2020).

2.3.1.3 Coagulants

Coagulants are used to attract contaminants in the water to one another, forming a bigger clump of molecules. This will raise the weight of the molecules, causing gravity to remove them. The contaminants that are eliminated will remain in the same state as when they were released. The major disadvantage of physical treatment is the production of sludge when contaminants are removed. Because the sludge will be highly concentrated with the contaminant, it will need to be treated again before disposal.

2.3.1.4 Chemical dye

Chemical dye particularly the use of chemicals as well as the use of techniques in order for the reaction to take place. Chemical oxidation, electrochemistry, and Fenton reactions are among the procedures used. The chemical composition of a dye molecule is altered during an oxidation process in the presence of an oxidizing agent such as ozone, hydrogen peroxide, or permanganate. To speed up the oxidation process, catalysts like as iron, manganese, and titanium dioxide can be used. The Fenton method uses hydrogen peroxide and ferrous iron as catalysts to oxidize organic pollutants in effluent water in a quick and low-cost manner. However, because the iron salts are non-recyclable, the Fenton reaction produces a substantial quantity of iron oxide sludge at the end. Because the Fenton method requires an acidic environment for the reaction to take place, more acidic substances are used. Chemicals with a lower stability create undesirable products and cause secondary contamination, both of which are harmful to the environment. Chemical dye treatment methods have a greater operating cost than other treatments, with the exception of the electrochemical dye degradation process. In recent years, electrochemical dye degradation has shown to be a more successful and quick method than other traditional methods, since

hazardous colors have been degraded into smaller colorless molecules without the use of a coagulant (Wong et al. 2019).

2.3.2 Biological Treatment

Biological dye treatment is considered as one of the simplest and inexpensive ways to treat dye wastewater with its removal efficiency highly dependent on the growth of microorganisms. Bioremediation is a word that refers to a variety of strategies for detoxifying polluted water that involve either live or dead organisms. Natural attenuation, bioaugmentation, biostimulation, bioleaching, and rhizoremediation are examples of these approaches. Biosorption, a well-known bioremediation technique, uses ligands and functional groups to generate heavy metal ion complexes from biological materials or biomass. Due to the higher affinity of the sorbent for the ionic species, the dissolved species are attracted and bound to the solid biomass. Both the type of the biomass and the application have a significant impact on biosorption performance. The type of application is determined by surrounding growth factors such as pH, temperature, presence of cations and anions, metal speciation, and pollutant solubility and form, whereas the biomass responsible for this phenomenon usually involves changes in the cell wall of fungi, bacteria, or algae in terms of structure, size, or chemical composition. Biosorption by microbial biomass are also used to treat dye wastewater as microorganisms like bacteria, algae and yeast can remove various classes of dyes effectively (Wong et al., 2019).

Microorganisms perform aerobic and anaerobic processes in the biological dye treatment route. Aerobic treatment occurs in the presence of free oxygen and microorganisms in stabilization ponds, packed bed reactors, and aerated lagoon systems, whereas anaerobic treatment transforms organic dyes into methane and carbon dioxide in the absence of free oxygen. As a result, combining aerobic and anaerobic procedures in dye wastewater treatment provides another viable option for high color removal and aromatic amine oxidation. Despite the simplicity of the processes, it might be difficult to integrate such systems into small-scale businesses due to the need for specialized bioreactors or stabilization ponds, which come at a high initial cost. Because dye wastewaters generally

contain a variety of colors, biological methods for dye treatment may be ineffectual. Above all, due to the complexity of dye effluents from industrial discharge, no one technique can efficiently treat all kinds of dyes without restrictions. As a result, it's critical to assess each dye treatment technique's benefits and drawbacks (Wong et al., 2019).

2.4 Advanced Oxidation Process

For the past two decades, advanced oxidation processes (AOPs) have gotten a lot of attention when it comes to the progress of wastewater treatment technology. At the pilot scale, several of the approaches, such as Fenton, cavitation, ozonation, and photocatalytic oxidation, have proved successful in breaking down stubborn organic pollutants. Advanced oxidation processes (AOPs) are technologies that were developed in the 1980s to detoxify harmful contaminants. Through a series of complicated physical and chemical processes, AOPs can create oxidation active radicals such as hydroxyl radicals (OH). Because of its significant oxidation power, OH can efficiently degrade organic pollutants and totally transform refractory organic pollutants into harmless inorganic compounds like carbon dioxide and water. The rate of a reaction constant can reach 10^9 L/(mols) in extreme cases. Sulfate radicals (SO^{-4}) and superoxide radicals (O^{-2}) have recently been shown to have significant oxidation abilities and the capacity to destroy organic contaminants (Garrido-Cardenas et al., 2019).

They are also crucial elements of AOPs. The addition process, hydrogen abstraction reaction, and electron transfer are the three main types of reactions involved in the breakdown of organic molecules by free radicals. The addition and hydrogen abstraction processes are prone to OH, while the electron transfer reaction is prone to SO^{-4}. AOPs have a higher oxidation capacity, a faster reaction speed, less secondary pollutants, softer reaction conditions, and more applications in the field of water treatment than standard treatment methods. The improvement of the AOPs degradation effect and its degradation mechanism with different catalysts are systemically analyzed (Liu et al. 2021).

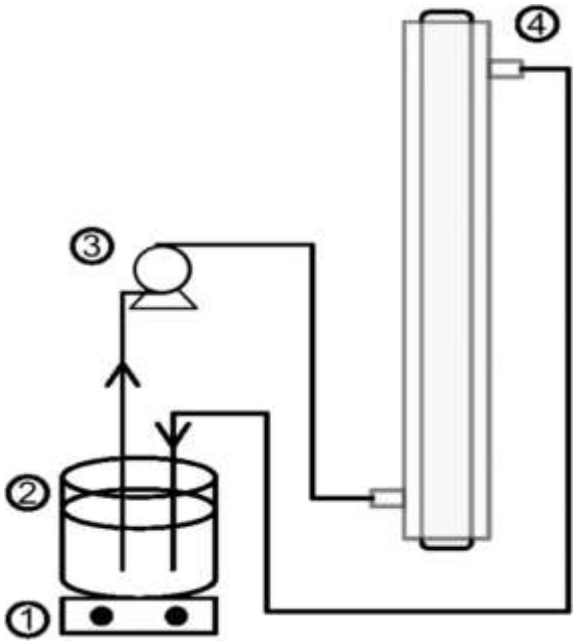


Figure 2.2: System set-up for Reactive Blue 19 dye degradation by advanced oxidation processes, in which (1) a magnetic stirrer; (2) a reservoir of 9 L capacity; (3) a flow pump, and (4) a photoreactor

Source: Donkadokula (2020)

2.4.1 Ozonation

Ozonation, a refractory wastewater treatment technology that uses ozone as an oxidant, is a promising degradation approach because it may convert refractory organics into intermediate, improving wastewater biodegradability. However, ozonation is incapable of achieving total mineralization, which has become an inescapable limitation in its use. The inclusion of a catalyst can stimulates ozone breakdown to create OH on the catalyst's surface, overcoming the flaw that ozone cannot be totally mineralized and improving degrading efficiency. Several studies have demonstrated that using H_2O_2 as a catalyst and including UV into the ozonation process improved the degradation of textile effluent (Bilińska & Gmurek, 2021).

Current AOPs still have drawbacks, such as a poor energy consumption rate, the potential for secondary pollutants, high catalyst and electrode material needs, and high prices. The use of AOPs, as well as the use of AOPs in conjunction with existing technologies, has improved numerous elements, including economic efficiency, environmental friendliness, and operability. They not only transcend the limitations of a single AOP, but they also vastly increase the field of their use. They offer a lot of potential in real-world industrial applications. However, before using AOPs on a big scale, the following issues must be addressed.

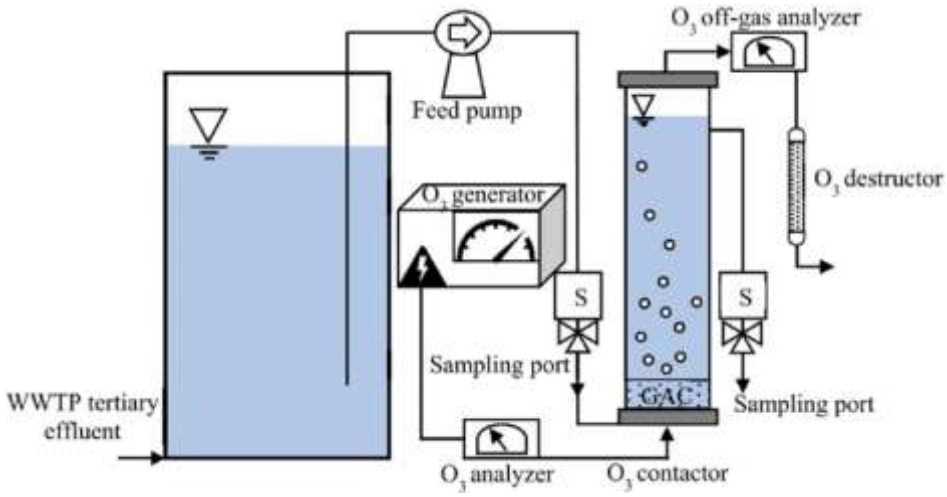


Figure 2.3: Water treatment by ozo-nation process
Source: (Uddin et al., 2021)

2.4.2 Reverse Osmosis

Reverse osmosis technology was initially used for the desalination of seawater and brackish water to produce drinking water. However, because to its fast expansion in a variety of applications, it has become a financially feasible alternative for treating and eliminating industrial effluents from wastewater. Due to its potential to produce low levels of pollutant concentration in the permeate and so recover good-quality water for still additional uses, advanced membrane technology with reverse osmosis is today recognized as the most promising technology for water recycling and reuse. Several factors influence the performance of membrane technology, including feed concentration, operating pressure,

particle size, and pH. Membrane permeability is determined by the membrane's pore size (*Wastewater Treatment by Reverse Osmosis Process - Mudhar Al-Obaidi, Chakib Kara-Zaitri, I. M. Mujtaba - Google Books*, n.d.). A large portion of the feed stream can be reused directly in the printing and dyeing process after treatment, whereas the residual reverse osmosis concentrate (ROC) of printing and dyeing wastewater, which is characterized by recalcitrant organics, high hardness, and high salinity, cannot be discharged directly and displays serious environmental risks (Wang et al., 2018). For most types of ionic substances, reverse osmosis membranes have a retention rate of 90% or higher. By using reverse osmosis, dye wastewater may be discolored, and chemical auxiliaries can be removed in a single process. All mineral salts hydrolyzed reactive dyes, and chemical auxiliaries can be removed. It should be emphasized that the higher the dissolved salt content, the more important the osmotic pressure becomes, and hence the more energy required for the separation process (Foisal et al.,2016).

How Does Reverse Osmosis Work?

RO is the process of pushing a solvent across a semipermeable membrane to a zone of low soluble concentration from a region of high soluble concentration.

A typical single-pass seawater RO system has the following components:

1. **Intake:** To set up RO system you need an intake pump at the source of the water to be purified.
2. **Pre-treatment:** This step includes removal of solids, sediments, carbonic acid from the water to protect the membrane. This step also includes dosing of oxidizing biocides like chlorine to kill bacteria.
3. **High-pressure pump:** The high-pressure pump is required to let the water pass through the membrane. Pressure for brackish water typically ranges from 225 to 376 psi and in the case of seawater it ranges from 800-1180 psi.
4. **Membrane:** In membrane assembly there is a pressure vessel with a membrane, allowing feed water to be pressed against the membrane. RO system membranes are made in a range

of configurations, but the two most common configurations are spiral-wound and hollow-fiber.

5. **Energy recovery:** Energy recovery is used to reduce the energy consumption. Much amount of energy input of the high-pressure pump can be recovered by the concentrate flow and efficient energy recovery device.
6. **Remineralization and pH adjustment:** Stabilization of desalinated water is done to protect downstream pipelines and storage, generally by adding lime or caustic soda to prevent corrosion. Liming material is used to maintain pH between 6.8 to 8.1 so that meets the potable water specifications.
7. **Disinfection:** Reverse osmosis is an effective blockade of pathogens, but post-treatment assures secondary protection against downstream and membranes problems. To sterilize pathogen which has bypassed the RO process, disinfection by means of UV lamps can be employed.

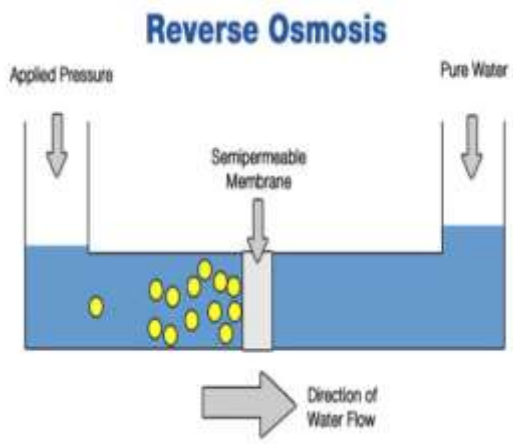


Figure 2.4: A Water Purification Process

Source: (Reverse Osmosis: Water Treatment Process)

2.4.3 Photocatalysis

Photocatalytic degradation is also one of the AOPs. Photocatalytic degradation necessitates the use of an ultraviolet (UV) light source and the addition of photocatalysts to produce oxidizing agents. A number of factors influence photocatalytic degradation

effectiveness, including solution pH, dye kinds, UV radiation intensity, and starting dye concentration (Rafiq et al.,2021). Photocatalytic decomposition is preferred because it produces no hazardous compounds that must be treated again. Moreover, photocatalysis is a key process in dye effluent treatment, in which irradiated electrons are stimulated from the valence band to the conduction band, resulting in the production of electron-hole pairs. The produced hydroxyl radical is a powerful oxidizing agent that totally destroys the dye into non-hazardous compounds (CO_2, H_2O, etc). Several organizations have studied the semiconductor titanium dioxide (TiO_2) for its photocatalytic activity and numerous uses. Despite the high photocatalytic efficiency of titanium dioxide (TiO_2), the greater energy bandgap (>3.2 eV) between the valence and conduction bands demands UV irradiation for the excitation of electrons from the valence band. Recombination of electron–hole pairs reduce photocatalytic performance. In addition, photocatalytic degradation is characterized by cheap operating costs and a technique that can achieve complete mineralization for dyes while operating at ambient pressure and temperature (Joshi & Gururani, 2022).

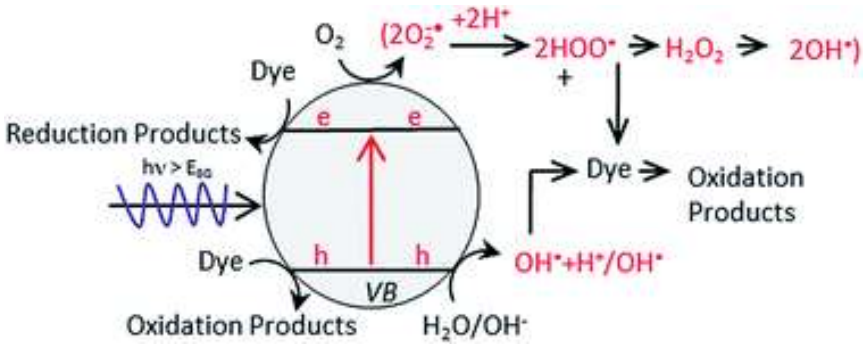


Figure 2.5: Principles and mechanisms of photocatalytic dye degradation on TiO_2 based photocatalysts: a comparative overview.

Source: (Ajmal, 2019)

2.5 Sonophotocatalytic

Nowadays the use of conventional wastewater treatment methods is becoming increasingly challenging mainly due to the presence of organic matter in wastewater. To cope with these extremely concentrated and hazardous non-biodegradable organic materials, a new method is required. Advanced oxidation process (AOP) has arisen in recent decades to remediate wastewater discharged by industry. Researchers have recently expressed interest in using ultrasonic (US) in photocatalysis, i.e. sonophotocatalysis, to increase the performance of the treatment process in the degradation of organic and inorganic contaminants in aqueous streams. Ultraviolet (UV) and ultrasonic (US) are used together in sonophotocatalysis (Zewdw et al., 2019). Apart from the benefits derived from the simultaneous application of US and UV radiation, the combined process has several other advantages, including causing more uniform catalyst dispersion, providing a regenerated catalyst surface, enhancing mass transfer, and increasing surface area by collapsing the catalyst into smaller particles (Asgari et al., 2020). Sono-photodegradation of azo dyes were demonstrated in presence of TiO_2 catalyst under UV light irradiation. Furthermore, sonocatalysis alone for the oxidation of dyes in industrial effluents requires high consumption of energy and high degradation time, then its direct application on large scale is difficult. To address these issues, sonophotocatalysis (sonocatalysis + photocatalysis) might be a viable technique for water purification, although cost effectiveness has to be proven in the field. Because of the favourable synergic impact of these two advanced oxidation processes, the increase in treatment costs associated with an increase in energy consumption can be mitigated by the shortened treatment time required. Moreover, the substitution of UV irradiation with sunlight may result in considerable cost savings. Dye sensitization has been found to initiate the photo-response to visible light of semiconductor materials having a large band gap energy, such as ZnO. As dyes, they can absorb light in the visible range, and hence, once adsorbed on the photocatalyst surface, they may transform received photons into electrons and inject them into the semiconductor photocatalyst's conduction band. Within the photocatalyst, this will allow for electron-hole separation and the generation of reactive oxygen species ROS. As a result, the dye degradation at the catalyst surface will be aided by this photo-sensitization process (Lops et al., 2019).

2.5.1 Mechanism of Sonophotocatalysis

Over the past few decades, the indiscriminate use of a large variety of synthetic dyes and their continuous input into aquatic environments has constituted a serious risk to human health and ecological systems. Sonophotocatalysis has recently attracted a lot of attention due to its green and environmentally friendly qualities among a number of treatment options for dye removal from the aqueous environment. The synergistic impact of sonolysis and photocatalysis is largely responsible for the reaction mechanism of sonophotocatalysis for dye removal. As a result of the pyrolysis of water molecules within the cavitation bubbles, sonolysis of the aqueous solution resulted in the production of H and OH radicals. During the sonochemical decolorization of dyes in aqueous solution, oxidative degradation happens most commonly as a result of free radical assault. The principal degradation mechanism of dyes in photocatalysis includes hydroxyl radicals and their direct oxidation by photogenerated holes. Hence, by increasing the generation of free radicals, the combination of photocatalysis with sonolysis (i.e. sonophotocatalysis) appears to boost the decolorization rate. In addition, sonophotocatalysis can overcome the limitations associated with each individual process. The primary drawback of photocatalysis is that it reduces catalytic activity owing to impurities molecules blocking active sites on the catalyst surface. The use of ultrasound in a photocatalytic system increases turbulence in the solution, lowering mass transport constraints and allowing for the regeneration of the catalyst surface due to particle fragmentation and deagglomeration. Moreover, the presence of a heterogeneous catalyst adds to the increased rate of cavitation bubble development by supplying extra nuclei, which promotes water molecule breakage and hydroxyl radical production. The synergistic impact of sonolysis and photocatalysis boosts reactive radical production, promotes bubble cavity formation, speeds up dye molecule mass transfer to the catalyst surface, and removes any contaminants from its surface. The adsorbed dye molecule on the catalyst surface interacts with the free radicals generated during photocatalysis during sonophotocatalysis. The dye molecules are then desorbed off the catalyst surface by the shock waves caused by cavitation bubbles. The reactive radicals formed by the implosion of cavities in the vicinity of the photocatalyst particles, on the other hand, can degrade the dye molecules. Nanoparticles with

smaller diameters and bigger surface areas often have more active sites, which are better for sonophotocatalysis (Pirsaheb & Moradi, 2021).

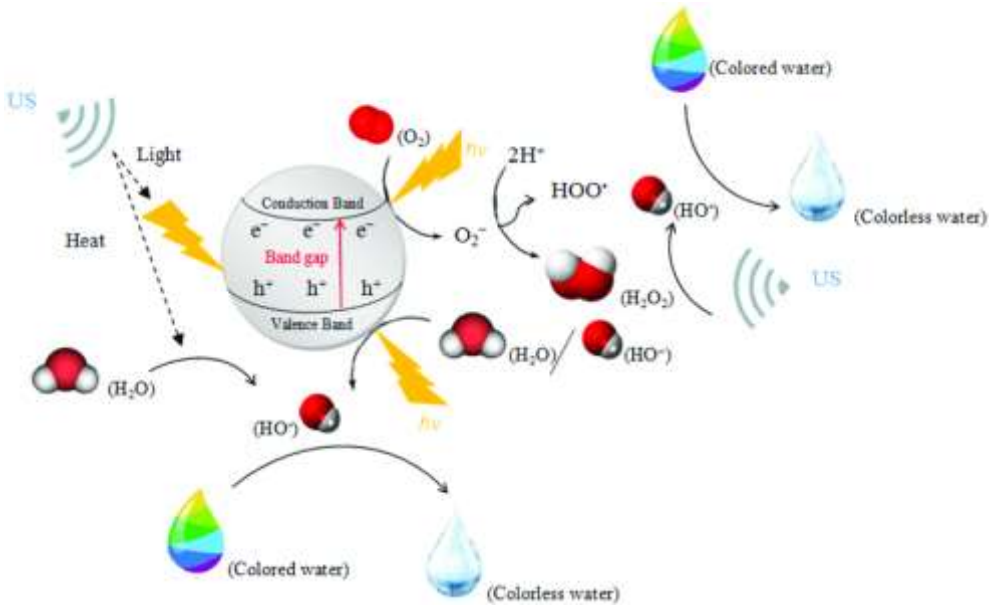
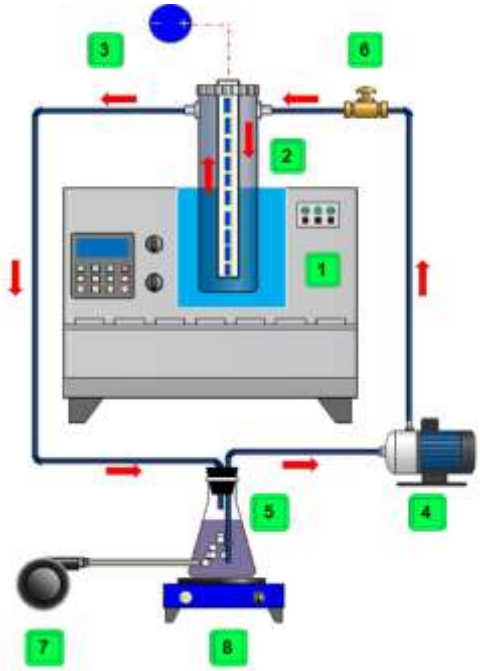


Figure 2.6: Mechanism of sonophotocatalytic dye degradation
Source: Pirsaheb & Moradi, (2021).

2.6 Sonophotocatalytic Reactor

The common optimum operating conditions for sonochemical and photocatalytic oxidation coupled with the similarity in the mechanism of destruction leading to a possible synergism and the possible elimination of some of disadvantages observed for individual processing techniques due to the effects of the other technique has prompted the development of sonophotocatalytic reactors in recent years.



1: Ultrasonic bath 2: Reactor vessel 3: LED source 4: Peristaltic pump 5: Reservoir 6: Sampling valve 7: Aeration pump 8: Magnet stirrer

Figure 2.7: Sonophotocatalytic Reactor

Source: (Meghdad Pirsaheb, Negin Moradi, 2021)

2.6.1 Uv-Visible Light Enhanced Reactor

Ultraviolet (UV) irradiation enhances the efficiency of semiconductor-mediated degradation of aqueous pollutants synergistically. It is important to find an appropriate light source for the enhanced photocatalytic performance of the catalyst. Heterogeneous photocatalysis with TiO_2 still has a number of difficulties that limit its use and commercialization in the environmental sphere. The primary technological obstacles are the ineffective use of visible light and the post-treatment recovery of TiO_2 particles. Due to its large band gap (3.2 eV), TiO_2 can only be stimulated by UV light with a wavelength less than 380 nm. Because of the band gap, it can only be used in the UV section of the spectrum, where most of the solar energy is wasted. Another technique to expand the absorption spectrum of light and improve TiO_2's photocatalytic activity is to combine it with other

narrow band gap semiconductors. Researchers discovered that a physical combination of sulphur and TiO_2 boosted photocatalytic activity of TiO_2 when illuminated with UV light, but that same physical mixture did not improve photocatalytic activity when illuminated with visible light. Grinding TiO_2 under varied circumstances, such as atmospheres (grinding in gaseous NH^3), solvents (grinding in ethanol, hexane, water, etc.) or temperatures, increased its photocatalytic activity under visible light irradiation. In addition, grinding TiO_2 with other semiconductors (co-grinding method), such as the hybrid organic or inorganic compound that employs suitable materials to integrate in TiO_2 matrix, is another technique to increase photocatalytic activity of TiO_2. Honda-Fujishima disclosed a photocatalytic water splitting procedure for H_2 production in 1972, which led to the use of a variety of semiconductor photocatalysts for photocatalysis. However, most semiconductor photocatalysts, including the commonly used TiO_2, have a large band gap and can only employ UV irradiation, as well as cause charge carrier recombination and have delayed surface reactions. As a result, effective photocatalytic systems are required to increase the efficiency of clean H_2 generation (Tasleem & Tahir, 2021).

2.7 Parameter Studies for Sonocatalytic Degradation Of Dye

There are two parameters that can affect sonocatalytic activity. The catalyst dosage and solution pH.

2.7.1 Catalyst Dosage

The dosage of sonocatalyst in the treated solution may affect the degradation rate of organic dyes. The accelerated rate when increasing catalyst dosage is caused by the increased OH radical's production. This is due to an increase in active reaction sites. The additional sonocatalyst in the solution will provide more surface for the nucleation of cavitation bubbles (Nie et al., 2021). The efficiency increased as the g-C_3N_4 dosage raised. The generation of OH radicals will increase with the increased amount of sonocatalyst in the solution. This concludes that the efficiency will increase as more sonocatalyst is present in the wastewater solution. This linear relation applies until a certain limit is reached. At higher catalyst dosage,

the sonocatalysts will aggregate and decrease the efficiency in degradation. The aggregation causes effective surface area to be reduced which leads to a decrease in number of active sites to produce OH radicals. Other than that, the excessive amount of sonocatalyst in the solution will reduce the amount of cavitation bubbles formed because they will hinder the circulation of ultrasonic waves(Nie et al., 2021) Thus, the optimum catalyst dosage shall be the one where the degradation efficiency is the highest at the lowest catalyst dosage.

2.7.2 pH of Solution

The pH parameter has a very important synergistic effect on organic dye degradation in sonocatalytic processes for organic dye degradation. Because the pH parameter affects the surface load amount of the nanocatalyst particle used in sonocatalytic processes. This change in surface charge affects the interaction of the dye molecule with the nanocatalyst particle. Solution pH of the textile wastewater can contribute greatly to the degradation efficiency of the organic dyes present (Nas, 2021). Stated that solution pH would affect the surface binding-sites of the catalyst and also the chemical form of reactants in the sample. Also, the pH function has an important effect on organic dye degradation due to the formation of oxidizing species in the process carried out sonocatalytic.

He, et al. (2018) reported that OH radicals would transformed back into water at solution pH 2. At acidic condition, hydrogen ions (H+) will scavenge OH radicals and convert them back into water, causing a decrease in oxidation of the organic pollutants as shown in Equation 2.7.2

$$H^+ + \bullet OH + e^- \rightarrow H_2O \qquad (2.7.2)$$

Heymann, et al. (2018) had reported the effects of solution pH on g-C_3N_4 and Methylene Blue. The adsorption of Methylene Blue was found to be lower at low solution pH values while it was higher at a high solution pH level. This implied that the adsorption of the targeted pollutants will be better at a more alkaline solution. It was also reported that the rate constant for the degradation of organic pollutants in increased at alkaline condition.

This makes sense since a higher adsorption rate would allow more organic pollutants to be degraded (Nas, 2021).

2.8 Summary

This chapter contains the literature review done for this report. The dye wastewater problem, classification of dyes, the textile wastewater treatment methods, advanced oxidation process, ozonation, reverse osmosis and photocatalysis are discussed in this chapter. This report focused on the sonophotocatalytic degradation of pure g-C_3N_4. Mechanism of sonophotocatalysis, sonophotocatalytic reactor, the parameter studies for sonocatalytic degradation and the dye concentration are also discussed.

CHAPTER 3

METHODOLOGY

3.1 Research Work Plan

The performance of the prepared photocatalysts was investigated on the degradation of MO solution through photocatalytic degradation process. In order to have a better understanding on the photocatalytic degradation of MO solution using Carbon, C and g-C_3N_4, CN the parameters that governing the photocatalytic reaction were studied. The parameters studied in this research are effect of catalyst loading, and effect of pH towards photodegradation of MO solution. Figure 3.1 shows the schematic diagram that ruled out the overall steps that involved in this study. The results and outcomes obtained throughout each stage in this chapter were presented and discussed in next chapter.

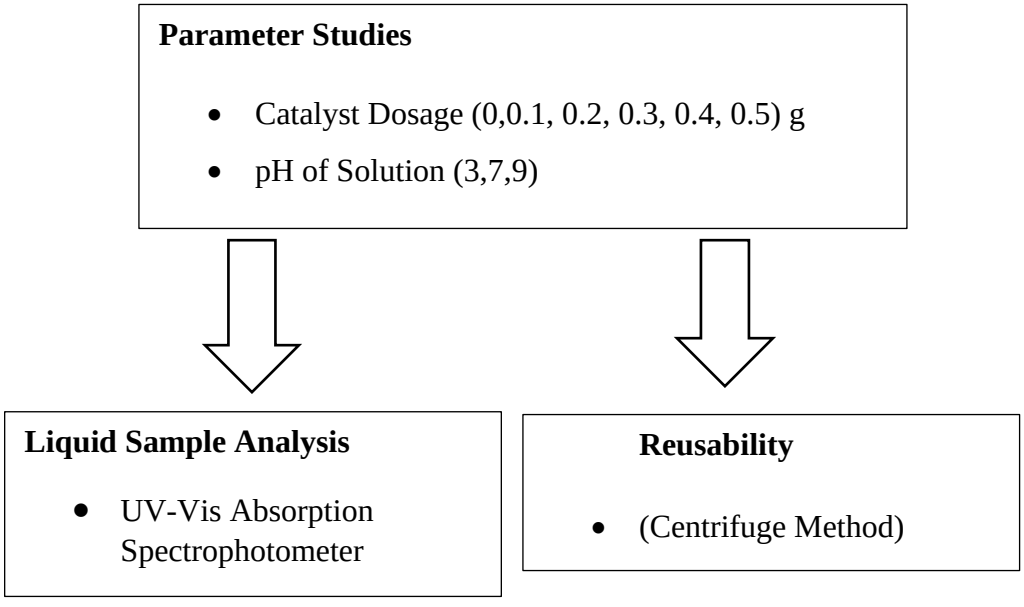


Figure 3.1: Research Flow Work

3.2 Photocatalytic Reaction

The parameters of the ultrasonic bath set at medium. The conical flask is filled with the organic dye solution and sample catalysts. The beaker is place on the stage of the ultrasonic processor and the beaker will be lifted with the stage to allow the ultrasonic processor to come in contact with the solution. The factors that would be include in the study are initial dye concentration and pH of solution.

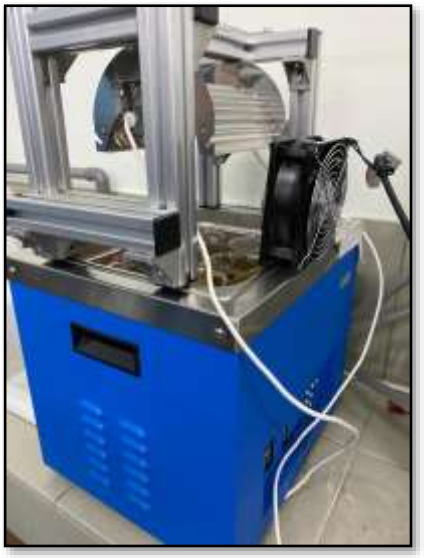


Figure 3.2: Sonocatalytic Reactor

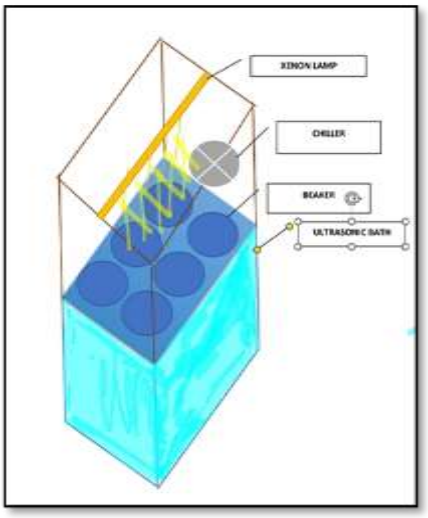


Figure 3.3: Schematic diagrams of photoreaction apparatus

3.3 Photocatalytic Activity of Prepared Catalysts

Methyl Orange (MO) was applied as the probe molecules. Before light irradiation, 0.1g of prepared sample added into 150 mL of dye solution (5 mg/L). Then the suspension stirred for 30 min to achieve the adsorption-desorption equilibrium. A 300 W Xenon lamp (320 to 780 nm) is used as a light source, which is positioned 10 cm away from the reactor with an average light intensity of 168 mW/cm^2. After irradiation, the suspension taken out and centrifuged to remove the photocatalysts before measurement. The concentration changes of MO have been monitored by measuring the UV-Vis absorption of the liquid supernatants. The photocatalytic activity was carried out in a photoreaction apparatus.

The photocatalytic activity of Carbon and g-C_3N_4 were conducted by monitoring the removal rate of MO. The reaction temperature was maintained at ambient temperature throughout all tests to avoid any thermal effects. Control experiments were carried out prior to starting the main experiments to make sure that the MO were degraded due to photocatalytic degradation. In first control experiment, 150 mL of MO solution was mixed with 0.1g of Carbon and g-C_3N_4 for 30 min at room temperature to confirm the formation of an adsorption/desorption equilibrium between the photocatalyst and dye solution. Under artificial lighting, 150 mL of the dye solution was added to the reactor without any photocatalyst. At regular intervals, 15.00 mL of sample were withheld, and the concentration of the reaction solution was determined both before and after photolysis.

After completing the control tests, a 250 mL beaker was filled with 150 mL of MO solution to serve as the reaction vessel. A predetermined quantity of Carbon and g-C_3N_4 were dissolved in dye solution before being exposed to radiation. Following that, a 300 W xenon lamp was turned on and placed above 10 cm from the reaction of solution surface. Every 20 minutes, the solutions were collected during the 120 minutes reaction. Before performing the UV/Vis examination, the samples were filtered to remove any solid debris. A UV-DR 5000 Spectrophotometer was used to measure the solutions' absorbance in the 200–900 nm range. For the degradation of dye, two parameters are typically investigated, the impact of catalyst loading and the pH of the dye solution.

3.4 Parameter Studies

The effect of various factors on degrading efficiency was investigated. The sonocatalytic dye wastewater purification has been done accordingly by different catalyst dosage and different pH solution to find the optimum. To isolate the influence of a given parameter on degrading efficiency, some factors has been held constant during the research of these parameters. The ultrasonic frequency, treatment period, and amount of dye solution are all kept consistent throughout the trial. Before adding the sonocatalyst to the dye solution, the volume of the solution was held at 150 ml. The light source is a 300 W Xenon lamp (320 to 780 nm) position 10 cm distant from the reactor with an average light intensity of 168 mW/cm^2.

3.4.1 Effect of catalyst dosage

The impact of catalyst dosage has been investigated. The catalyst dosage affected the degradation efficiency of the sonocatalyst. For the effect of catalyst loading, the photocatalyst loading was varied at 0.1 g, 0.2 g, 0.3 g, 0.4 g and 0.5 g. The remaining parameters was kept constant, including the starting dye concentration of 5 mg/L and natural solutions. Photocatalyst dosage is another important process-control factor because required dose of catalyst varies depending on the wastewater conditions. Basically, catalyst doses are dependent on the concentration of dissolved organic compounds in most surface waters. Higher concentrations of catalyst reduce the time of particles in the degradation process by reducing the efficiency of collision-attachment. The catalyst that has the best degradation efficiency used for the subsequent studies.

3.4.2 Effect of pH of solution

The effect of pH of solution has been treated and carried out by identify which one is optimum. To investigate the effect pH on the removal of MO, the desired initial solution pH of 3.00, 7.00, and 9.00 were obtained using either HNO_3 or NaOH solutions. Catalyst dosage were set at natural 0.1g. Furthermore, (Yaseen & Scholz, 2019) mentioned that higher

microbial dye color removal requires pH values between 6 and 10 as optimum and that the removal efficiency in strongly acid or alkaline environments noticeably drops. The dye that provides the best degradation efficiency was carried forward and used in the subsequent studies.

3.5 Sample Analysis

The concentration changes of MO were monitored by measuring the UV-Vis absorption of the liquid supernatants. The solution has been measured by using a pH meter. The ultrasonic irradiation is provided by an ultrasonic processor. The concentration of organic dye present detected by UV-Vis spectrophotometer. To quantify the organic dye concentration, a calibration curve of absorbance against concentration has been plotted. According to the Beer-Lambert Law, the absorbance should be directly proportional to the concentration. The concentrations of the liquid sample were determined, and the degradation efficiency was compute. Equation 3.5 used to compute the deterioration efficiency of any system.

$$Degradation\ efficiency = (1 - \frac{Co}{Ct}) \times 100\ \% \quad (3.5)$$

Where,

C_0 = initial dye concentration, mg/L

C_t = dye concentration at time t, mg/L

3.6 Reusability Study

To separate the utilize catalyst from the deteriorate solution, the Carbon and g-C_3N_4 was centrifuged at 4000 rpm for 30 minutes. The catalyst was cleaned after centrifugation by washing it with distilled water and collecting it on filter paper. After that, it was dry in

the oven for 3 hours at 80 ^{O}C. After that, the catalyst was employed to decompose another batch of MO.

3.7 Summary of Chapter 3

This chapter consists of the parameter used which were, catalyst dosage and pH of solution for the experiment conducted. This chapter includes feature a flowchart and an experimental setup. The sonocatalytic reactor also shown here. The reusability study technique and experimental work for various parameters are demonstrated. The deterioration efficiency calculation is also demonstrated.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

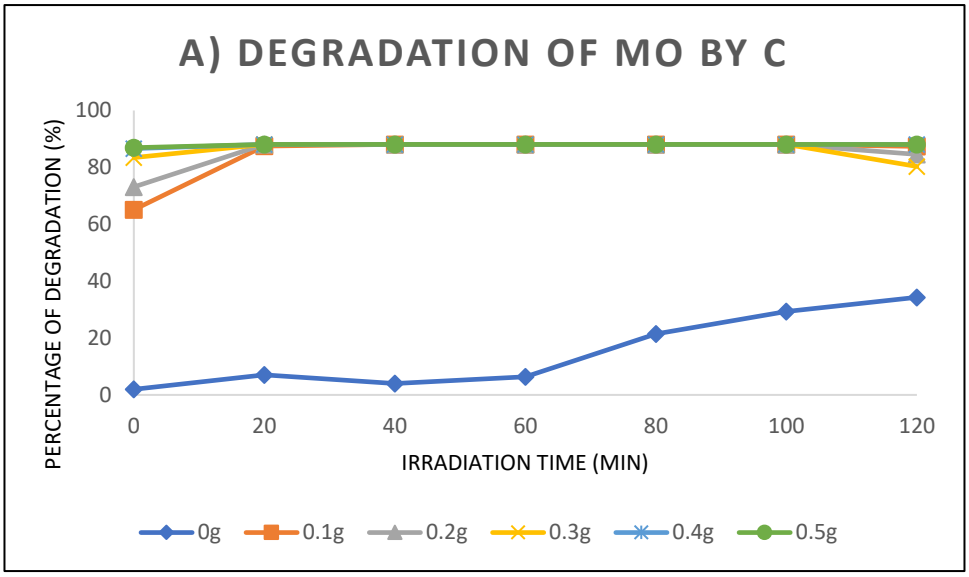
This chapter focusses on the results obtained from the experimental work. The performance of the synthesized photocatalysts in the degradation of MO solution were further discussed. The performance of synthesized photocatalysts based on several parameters tested were explained in detailed. The two parameters that were involved including catalyst loading and pH value of MO solution.

4.2 Parameter Studies in Sonocatalytic Process

4.2.1 Effect of Catalyst Loading Amount

In order to investigate the impacts of catalyst loading quantity on the photodegradation efficiency of MO, a number of variables were kept constant. The initial MO dye concentration in this investigation was set at 5 ppm, the cooling water system was set at 28 ^{o}C, and a 300 W Xenon lamp was used with a medium rpm. Catalyst loading amounts in the research range of 0.1 g, 0.2 g, 0.3 g, 0.4 g, and 0.5 g were taken into consideration. All the graphs presented in this section were for photocatalysis of the two photocatalysts after achieved the adsorption- desorption equilibrium.

a)



b)

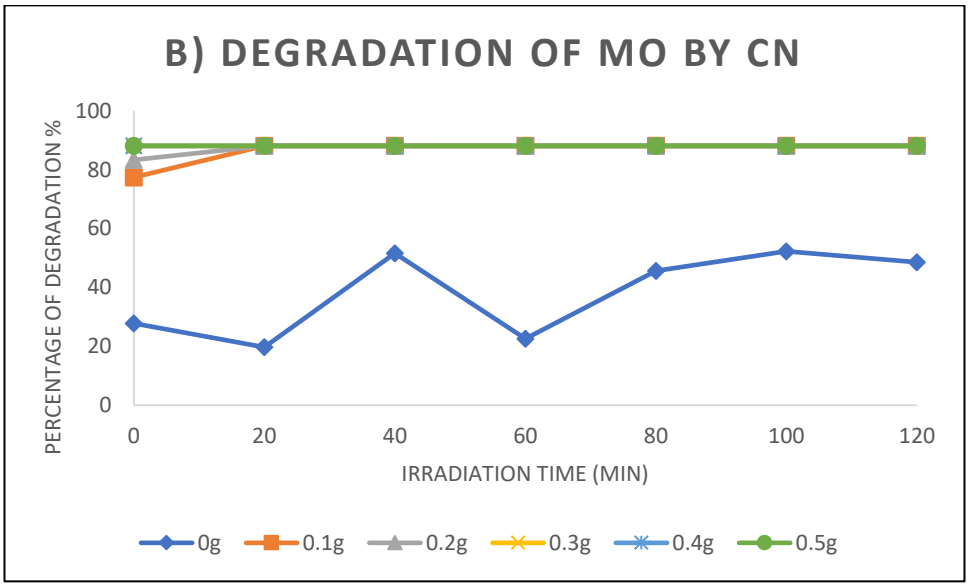


Figure 4.1: The effect of catalyst a) Carbon (C), b) g-C_3N_4 loading on photodegradation of MO at C_o = 5mg/L, t = 120 min, T = 30 ^oC

Figure 4.1 shows the effect of catalyst loading amount on the photodegradation of MO. It was found that the photodegradation percentage of MO was increased with the increased of catalyst loading amount. Larger effective surface area leads to a higher adsorption of organic molecules leading to a better photocatalytic activity (Chowdhury et al., 2018). It was observed that percentage of MO degraded for carbon catalyst loading, after 120 min increased from 34.31% to 88% with increase in catalyst loading from 0 – 0.5 g/L. This occurs for two reasons, first there is more radiation intensity and the second one is lower wavelength that resulted in electron exiting of materials. Other than that, the excessive amount of sonocatalyst in the solution will reduce the amount of cavitation bubbles formed because they will hinder the circulation of ultrasonic waves(Nie et al., 2021). Furthermore, there was very slight fluctuation in case of high catalyst amount. This was because it's achieved the optimum catalyst dosage at 0.1g - 40min. Thus, the optimum catalyst dosage shall be the one where the degradation efficiency is the highest at the lowest catalyst dosage.

In addition, percentage of MO degraded for g-C_3N_4 catalyst loading, after 120 min increased from 48.6% to 88.07% with increase in catalyst loading from 0 – 0.5 g/L. The percentage of degradation was increase from 0 min to 20 min for every catalyst loading. After it was reached to 88.07%, it was remained constant. Here, it was proven that the g-C_3N_4 attained optimum level at 0.1g – 20min. An excessive amount of photocatalysts may hinder the further penetration of light into the reactor. This would limit the photocatalysts presence in the internal solution from being excited by the light to form electron-hole and prevent the efficient charge transfer. As a result, less OH- will be generated which led to the decreasing of MO degradation percentage. According to the Ragupathi et al. (2020), g-C_3N_4 is versatile polymeric, organic semiconducting material and have the band gap of 2.7 eV. The photocatalytic performance of a photocatalyst strongly depends on its electronic band structure and band-gap energy. Among the two catalysts, g-C_3N_4 recorded the highest MO degradation. Smaller crystallites would have a greater surface area, which would enhance photocatalytic degradation since increased photocatalytic activity often depends on crystallite size. Hence, the percentage of degradation of g-C_3N_4 took the highest value at the lowest catalyst dosage among the other catalyst.

4.2.2 Effect of pH

Table 4.1 presents the percentage degradation of MO under the influence of different pH conditions (i.e., acidic, neutral, and alkali). In general, the percentage degradation of MO obtained was ranging from 62.79 – 88.7 % in which it was increasing with pH. Carbon shows the highest and lowest degradation percentage at the pH of 9 and 3 respectively. On the other hand, g-C_3N_4, CN shows the highest degradation percentage at the pH of 9 too.

Table 4.1 Percentage degradation of MO under different pH conditions

pH	Percentage degradation of MO	
	C	CN
3	62.79	70.82
7	72	74.91
9	88.7	81.65

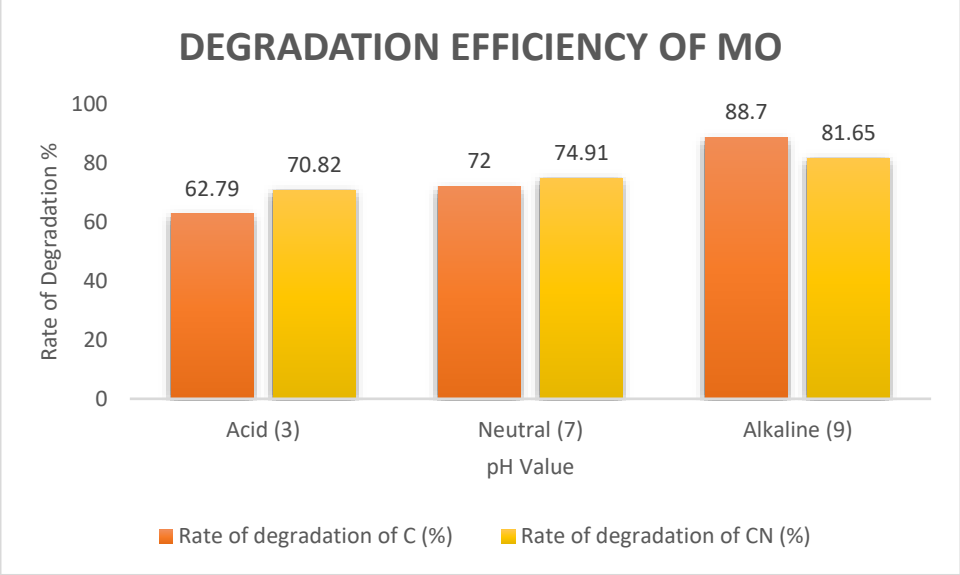


Figure 4.2: The effect of pH value in degradation of MO

Based on Figure 4.2, it demonstrated that, carbon in comparison to g-C_3N_4, it was discovered that carbon worked as the greatest photocatalyst for the degradation of MO. Since a larger percentage of MO degradation was obtained with a higher pH of the photocatalyst in use, the results also showed that alkali conditions are more conducive for MO degradation. This could be the result of the electrostatic interaction between the positively charged MO dye and the negative surface functional group of the photocatalysts (such as hydroxyl). According to (Jiaqi et al., 2019), when the pH of reaction medium was increased to alkali condition, the MO molecule would be deprotected and became positive charge. The increased percentage of degradation obtained under higher pH conditions is due to more positively charged MO molecules attaching to the negative charge functional group present on the photocatalyst to engage in photocatalytic activity. Similar results were published, showing that MO breakdown was greater under conditions of higher pH. (Lima et al., 2019). Because the catalyst loading chosen is already the optimal loading, it is advised that the porosity properties of the catalysts be improved in order to give more active sites for more MO degradation. This is because the influence of mass-transfer-limited reaction was already excluded.

4.3 Mechanism of MO

It was interesting to see that over the spectrum of pH values in MO degradation, Carbon had a greater degradation percentage than g-C_3N_4. There are several potential pathways for MO deterioration. Figure 4.3 depicts Methyl Orange's structural composition. Additionally, Figures 4.4 illustrate how MO degrades in the presence of C and CN catalyst. An electron was excided from the valance band into the conduction band when CN received light energy.

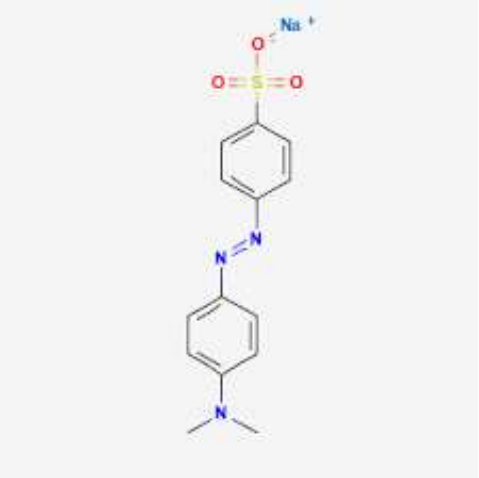


Figure 4.3: Structure of Methyl Orange

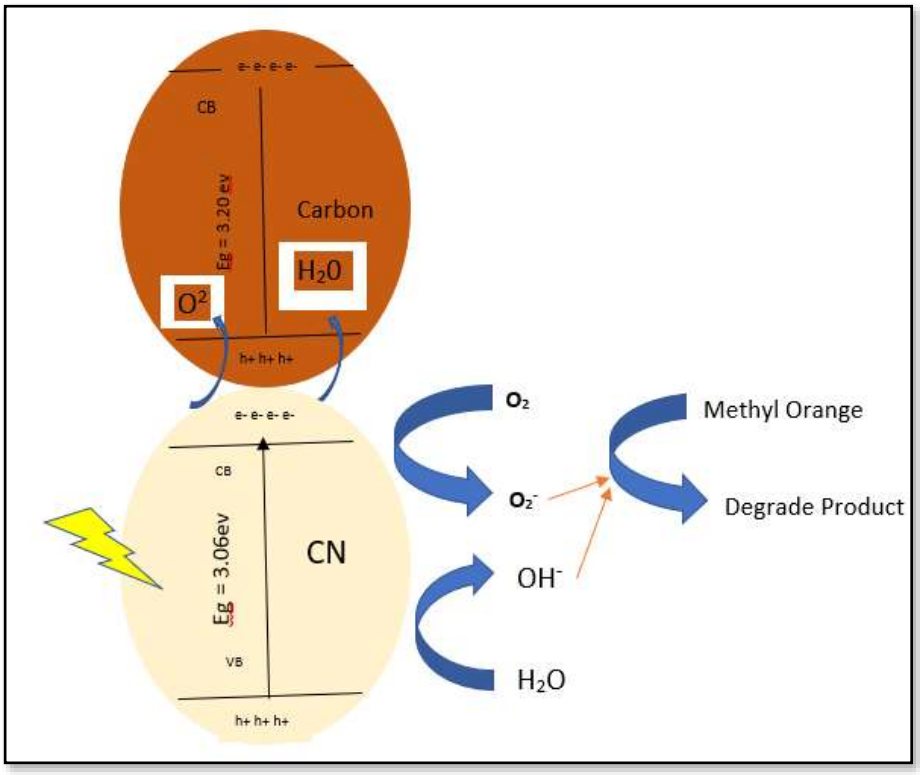


Figure 4.4: Possible degradation mechanism of MO by Carbon and g-C_3N_4 catalyst.

4.4 Reusability

The reusability of a catalyst was an important factor to determine the practicality of using the studied catalyst for wastewater treatment processes. Although the cost of producing was low since it was derived from biomass and urea, the reusability of the catalyst was still an important factor to reduce waste production.

CHAPTER 5

CONCLUSION

5.1 Conclusion

In summary, the application of Carbon (C), and g-C_3N_4 (CN), as photocatalyst in MO degradation was investigated. Moreover, the effect of various parameters was studied to determine the optimum conditions for sonocatalytic degradation of organic dyes. The parameters studied were the effect of catalyst dosage and the effect of pH of solution. Based on the results obtained from the effect of catalyst dosage, CN, showed the best percentage of degradation efficiency in catalyst loading of 0.1g in 20 min, compared to carbon C, which the degradation efficiency was occurred at 0.1g in 40 min. The CN achieved the optimum level of degradation efficiency at first than the C (88.07%). Therefore, CN showed the best sonocatalytic degradation efficiency of dye wastewater. This was due to the band gap energy of the prepared catalyst for CN is 2.90 eV, while for C is 3.60 eV. Furthermore, a decrease in the band gap enables the performance of a photocatalytic degradation process under visible light irradiation or even sunlight, which was safer and more economic than UV irradiation. For the effect of catalyst loading, 0.1 g showing the best percentage of MO removal compared to other catalyst loading. Thus, 0.1 g was selected as optimum catalyst loading throughout the experiment due to its ability showing higher degradation and to avoid the agglomeration that can occur due to excessive catalyst loading.

On the other hand, the pH results showed that MO degradation works better at the highest level of pH value for both catalysts. It was also discovered that carbon worked as the greatest photocatalyst for the degradation of MO. Here it was proven that alkaline pH condition was more suitable for the degradation of MO solution. The reusability of catalyst was also prepared in this studied.

5.2 Recommendation

Several uncertainties are yet to be confirmed and some improvements need to be done in order to achieve more comprehensive work on the application of Carbon in photocatalytic process. Hence, these are several recommendations for further research on the application of Carbon: -

i. Due to the lack of this treatment approach in photocatalytic degradation, it is also recommended to improve the photocatalyst utilized in this study to further extend its capability to be evaluated under visible light.
ii. In order to have a better understanding on the effect of the initial catalyst loading, larger range of values should be used for future study.
iii. In future, maybe can combine the C and CN to produce CCN to work more effectively in dye wastewater degradation.
iv. Extend the irradiation time and the catalyst loading, to see the degradation of dye wastewater more clearly.
v. Kinetic study based on Langmuir-Hinshelwood to identify the rate of reaction more specifically.

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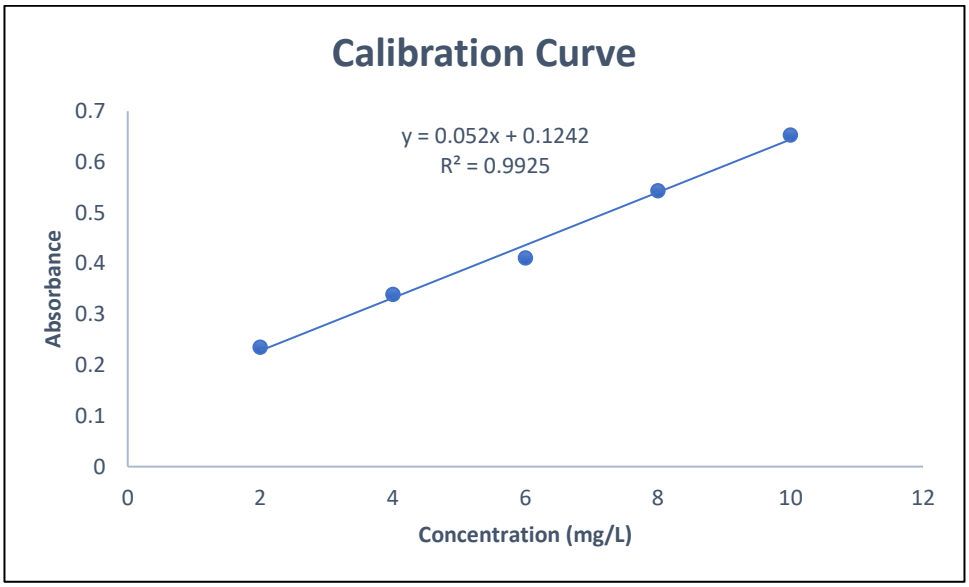
APPENDICES

Appendix A: Calibration Curve



Appendix B: Methyl Orange (5ppm)

Appendix C: Reusability of C and CN

Carbon $g\text{-}C_3N_4$