SYNTHESIZATION AND CHARACTERIZATION OF GRAPHITIC CARBON NITRIDE (g-C$_3$N$_4$) AND COCONUT SHELL HUSK DERIVED-CARBON COMPOSITE.

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ABSTRAK

Salah satu masalah utama alam sekitar ialah pembuangan air pembuangan daripada industri. Air pencemaran oleh pelepasan berwarna daripada pelbagai industri seperti pembuatan kertas, pencelupan tekstil, kosmetik, cat, dan pemprosesan makanan boleh memberi kesan kepada kesihatan manusia jika dibuang ke dalam air kerana air pembungan bersifat toksik, karsinogenik, dan xenobiotik. Fotokatalis konvensional seperti titanium dioksida (TiO$_2$) umumnya digunakan di Malaysia untuk merawat air sisa perwarna. Namun, semikonduktor ini memiliki kekurangan kerana tenaga jurang jalur yang besar, yang mengakibatkan prestasi yang buruk. Matlamat penyelidikan ini adalah untuk mencipta sintesis karbon nitrida grafit (g-C$_3$N$_4$) dan komposit karbon terbitan daripada tempurung kelapa, dan mencirikan sifat dan aktivitinya sebagai pemangkin. Dalam kajian ini, semikonduktor fotokatalitik akan disediakan dalam bentuk serbuk dengan kaedah sintetik seperti kaedah hidroterma. Karbon tulen dan karbon nitrida grafit tulen (g-C$_3$N$_4$) akan dicirikan dengan menggunakan difraktometer sinar-x (XRD) dan pengimbasan mikroskop elektron-sinar penyebaran tenaga (SEM-EDX), transformasi fourier inframerah (FTIR), dan penganalisis spektroskop kelihatan ultraviolet (UV-Vis). Pencirian adalah langkah penting dalam mengkaji struktur permukaan mangkin, komposisi mangkin, dan sifat kimia mangkin. g-C$_3$N$_4$ berjaya direka kerana jurang jalur yang sempit dan ditemui sonocatalyst bebas logam. Hasilnya, g-C$_3$N$_4$ boleh digunakan dalam rawatan air sisa pewarna. Selain itu, ia boleh mencapai Matlamat Pembangunan Mampan (SDG) 6 (air bersih dan sanitasi) kerana air sisa pewarna boleh dirawat dan bahan cemar berbahaya seperti toksik, karsinogen, dan xenobiotik dapat dikurangkan. Ringkasnya, ia boleh membantu mengurangkan masalah alam sekitar di samping melindungi kesihatan manusia.

ABSTRACT

One of the main environmental issues is industrial wastewater discharge. Water contamination by dye discharges from various industries such as paper making, textile dyeing, cosmetics, paints and food processing can affect human health if discharged into water because they are toxic, carcinogenic, and xenobiotic. Conventional photocatalyst like titanium dioxide (TiO_2) is commonly used in Malaysia to treat dye wastewater. However, this semiconductor has their own drawbacks because of the huge band gap energy, which results in poor performances. The aims of this research are to create a synthesization graphitic carbon nitride ($g-C_3N_4$) and coconut shell husk derived carbon composite, and characterize its properties and activity as a catalyst. In this study, photocatalytic semiconductors will be prepared in the form of powders by synthetic methods like the hydrothermal method. Pure carbon and pure graphitic carbon nitride ($g-C_3N_4$) will characterize by using x-ray diffractometer (XRD) and scanning electron microscope-energy dispersive x-ray (SEM-EDX), fourier-transform infrared (FTIR), and ultraviolet visible spectroscope (UV-Vis) analyzer. Characterization is important step in studying the structure of the catalyst surface, composition of the catalyst, and the chemical properties of the catalyst. $g-C_3N_4$ is successfully fabricated due to the narrow band gap and discovered metal-free sonocatalyst. As a result, $g-C_3N_4$ can be used in the dye wastewater treatment. Apart from this, it can meet Sustainable Development Goals (SDG) 6 (clean water and sanitation) because dye wastewater can be treated and dangerous contaminants such as toxics, carcinogens, and xenobiotics can be reduced. In short, it can help to reduce environmental problems while also protecting human health.

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LIST OF SYMBOLS

%	Percentage
$(CH_3)_2CO$	Acetone
°	Degree
°C	Degree celcius
$BaSO_4$	Barium sulfate
CH_2Cl_2	Dichloromethane
CH_3CH_2OH	Ethanol
CH_4	Methane
CH_4N_2O	Urea
CO_2	Carbon dioxide
eV	Electron volt
Fe_2O_3	Iron (III) oxide
$FeCl_3$	Iron (iii) chloride
g	Gram
$g\text{-}C_3N_4$	Graphitic carbon nitride
H_2O_2	Hydrogen peroxide
HNO_3	Nitric acid
mg/dm^3	Miligrams per cubic decimeter
min	Minute
ml	Mililiter
mm	Milimeter
$Mn_2O_3,$	Manganese (III) oxide
Na_2CO_3	Sodium carbonate
Na_2SO_4	Sodium sulphate
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NH_2	Amino radical
nm	Nanometre
O_2	Oxygen
OH	Hydroxyl
OH	Hydroxide

rpm	Revolution per minute
SnO_2	Tin (IV) oxide
SO_3H	Sulfonic acid
TiO_2	Titanium dioxide
ZnO	Zinc oxide
θ	Theta
λ	Wavelength
μm	Micrometer

LIST OF ABREVIATIONS

AOPs	Advanced oxidation processes
BESs	Bio-electrochemical systems
BOD	Biochemical oxygen demand
CB	Conduction band
CN	Graphitic carbon nitride (g-C_3N_4)
COD	Chemical oxygen demand
FTIR	Fourier-transform infrared
GEMs	Genetic engineered microorganisms
ICDD	International Centre for Diffraction Data
IR	Infrared
MECs	Microbial electrolysis cells
MF	Microfiltration
MFCs	Microbial fuel cells
NF	Nanofiltration
PD	Photocatalytic degradation
RO	Reverse osmosis
SDG	Sustainable Development Goals
SEM-EDX	Scanning electron microscope-energy dispersive x-ray
TSS	Total suspended solids
UF	Ultrafiltration
UV	Ultraviolet
UV-Vis	Ultraviolet visible spectroscope
VB	Valence band
XRD	X-ray diffractometer

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Economic growth in Malaysia is rapidly increasing due to the transition to an urban and industrialized society. This change has resulted in a number of environmental issues, one of which is an increase in wastewater discharge, which could lead to a serious water pollution problem in Malaysia (Yean Ling Pang et al., 2022). 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. Organic matter, microorganisms, and inorganic compounds are all contained in this 0.1% (Tuser, 2020). Wastewater effluents are released into a variety of environments, such as lakes, ponds, streams, rivers, estuaries, and oceans. Water pollution is usually generated by both point and non-point sources. A point source is a pipe or channel that is used to discharge waste from an industrial facility or a city sewerage system. While non-point source is a very wide unconfined area from which a variety of pollutants enter the body of water, such as agricultural activities and surface runoffs. Some people believe the rain that falls on the street during a storm is clean, this is not true. Substances that wash off of roads, parking lots, and rooftops can pollute rivers and lakes and cause harm to human and aquatic life (Tuser, 2020; Lozanova, 2022). Untreated wastewater discharge will cause major environmental issues and must be monitored strictly.

Dye wastewater is one of the environmental issues. Dye released into water bodies comes from various industries such as paper making, textile dyeing, cosmetics, paints, and food processing. Usually, they use dyes to color the original raw material to produce their product, and it is important to add color or change the colour of something (Kumar et al., 2021). Based on Figure 1, the textile manufacturing and dyeing industries use huge quantities of a large number of dyes and release these dye pollutants into bodies of water as waste water effluents. Global dye production is estimated to be around 7×10^6 tonnes per year, with approximately 10% lost during the dyeing process and the remainder released into the environment after dying and processing. (Dihom et al., 2022). The presence of dyes in wastewater, even in small amounts (less than 1 mg/dm^3 for a few dyes), is highly unpleasant and unwanted. This is

because dyes are carcinogenic and highly toxic, causing health and environmental issues. From an environmental perspective, the discharge of dye effluents into the bodies of water poses potential threats to the quality of water and causes serious health problems for humans, plants, and animal life. Living things that drink water from these polluted sources are more likely to develop cancer, while the toxic properties of dyes will endanger human health and even animals. Therefore, dye wastewater needs to be removed from the water effluents before being released into water bodies.
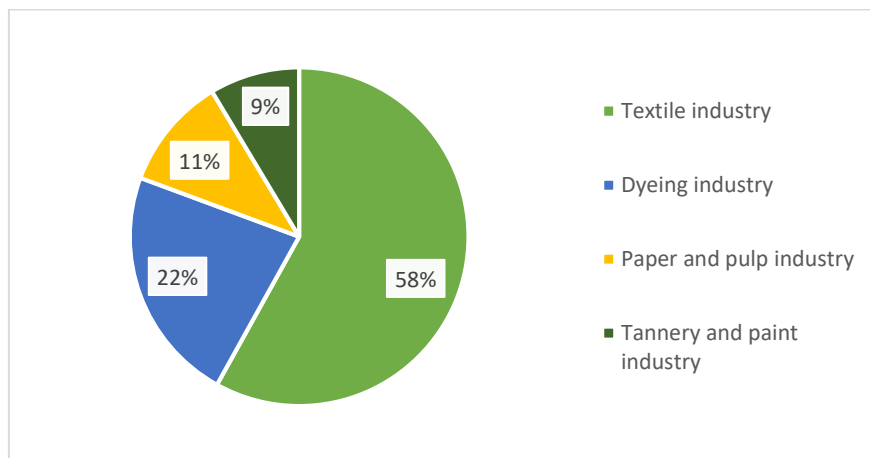
Figure 1.1   Comparison of dye effluent discharge from various
Source: Sasireka Velusamy et al. (2021).

Dye wastewater treatment is an important matter to ensure that the discharge has a minimal impact on water quality and aquatic life. There are three common methods for treating dye wastewater, which are chemical, physical, and biological treatment. Adsorption, ion-exchanger, irradiation, and filtration are common methods in physical treatment. These methods are widely used in industries that have high dye removal potential while also having low operating costs. Other than that, chemical treatments like flocculation and coagulation techniques are usually used to remove organic pollutants. Coagulation techniques work well for insoluble dye degradation but not so well for soluble dye degradation. The last method is biological treatment, which uses green technology to remove dye. It can also effectively remove the chemical oxygen demand (COD) and turbidity, but not much for decolorization. However, these methods have their own disadvantages, because organic dyes are more difficult to cure due to their chemical stability and biological resistance. Besides that, membrane filtration is an effective process, but frequent clogging of the membrane by foreign particles in wastewater is an issue, and the process is expensive, whereas the chemical coagulation process

produces a large amount of sludge and is responsible for secondary pollution if the produced sludge is not handled properly (Al-Mamun et al., 2019).

Photocatalysis can be applied to the dyeing of wastewater and can degrade organic pollutants in dye wastewater into water, carbon dioxide or other small molecules and reduce or oxidize inorganic pollutants to harmless substances under mild conditions, using a simple process and green technology (Ren et al., 2021). Photocatalytic degradation requires the use of an ultraviolet (UV) light source and photocatalysts to be added for the formation of oxidizing agents. It has gained popularity, among other things, as a tool for treating dye-contaminated water. It is because there are many advantages to the photocatalytic reaction systems, which are reusability, sufficient band gap and surface area, and the required morphology. In the presence of UV light, the photocatalysts are used to degrade organic pollutants and hazardous materials and destroy micro-organisms. It is also an eco-friendly technology where pollutants are degraded into less toxic or non-toxic components. Moreover, photocatalytic degradation is characterized by low operating costs and a technique that operates under ambient pressure and temperature, which can achieve complete mineralization for the dyes (Joshi & Gururani, 2022; Dihom et al., 2022). A few parameters, such as solution pH, dye type, UV radiation intensity, and initial dye concentration, affect photocatalytic degradation efficiency. Photocatalytic degradation is preferred because it produces no toxic byproducts that must be treated again. However, photocatalytic degradation still have some fatal defects restricting their practical applications.

In semiconductor photocatalysis, it is used to design, characterise, and potentially photocatalytical applications with doped or undoped nanostructural materials especially considering their particle sizes as well as shapes. Semiconductor photocatalysis can be classified into two types, homogeneous photocatalysis and heterogeneous photocatalysis. Homogeneous photocatalysis occurs when the photocatalyst and reaction medium are in the same phase. For example, homogeneous photocatalysis is used in the photo-assisted degradation of aqueous organic dye with water soluble carbon dots (Muzibur Rahman, 2019). On the other hand, heterogeneous photocatalysis occurs when the photocatalyst and reaction medium are not in the same phase. It is the most commonly used technique for photocatalytic water treatment because the catalyst material can be easily separated after application (Kumar et al., 2021). Moreover, the common semiconductor used for treatment methods is titanium

dioxide (TiO_2). TiO_2 is a semiconductor that can act as both a heterogeneous and homogeneous photocatalyst photoreaction. TiO_2 has the disadvantage of a large band gap energy, which results in poor performance. Since the main goal of treating the wastewater is to overcome water scarcity and pollution, a metal-free semiconductor is chosen for this research. Graphitic carbon nitride (g-C_3N_4) is a recently discovered metal-free sonocatalyst. Because it is metal-free, this semiconductor will be less expensive than TiO_2 due to the abundance and renewability of raw materials (Zhen, 2019). g-C_3N_4 has gotten a lot of attention because of its photocatalytic activity, low cost and simple synthesis, and interesting layered structure. It is also a metal-free catalyst with a medium band gap structure that can form radicals in water. This catalyst will be less expensive than other metal-based catalysts because it can be found in abundance (Alaghmandfard & Ghandi, 2022). As mentioned before, TiO_2 has disadvantages that can make the performance poor. The research towards nontoxic metal-free g-C_3N_4 shows the performance has attracted considerable attention.

In conclusion, this research is important because it focuses on treating dye wastewater easily and safely for our future. Without treating the dye wastewater properly, it will cause harm to humans, plants, and animals. It can also reduce the quality of water needed by humans. With the implementation of the 17th Sustainable Development Goals, clean water and sanitation have increased in importance to raise the quality of life and reduce environmental impact.

1.2 Problem statement

Water pollution is going to be a serious issues in Malaysia year by year because of economic growth with a rapid transition to an urban and industrialized society (Yean Ling Pang et al., 2022). Pollutants in water can cause disease or poisoning. Without treated the water pollution, then the environment and human health can be negatively impacted. These impacts can include harm to fish and wildlife populations, oxygen depletion, beach closures and other restrictions on recreational water use, and drinking water contamination. It can also degrade water quality and have an impact on plants, animals, and humans. Consuming, entering, or washing in dirty water can have a negative impact on human health. For example, by drinking the unsafe water, a lot of diseases can harm to the human health such as diarrhea, cholera, typhoid, dysentery or skin infections (Health, 2019). Sometimes it not effect immediately but it can be harmful in long term exposure. In addition, with the increase in population, water

demand will rise. So without the treated water, fresh water supply will be limited. With the growth in population, water demand will rise along with the discharge of municipal wastewater.

Water contamination by dye discharges can come from various industries such as paper making, textile dyeing, cosmetics, paints, and food processing. The textile industry is one of the world's largest producers of contaminated wastewater (Dihom et al., 2022). Textile materials are particularly popular due to their low production costs and excellent mechanical qualities. Dye is widely used in the textile industry to colorize products at all stages of the manufacturing process. Even at low quantities, organic or synthetic dyes can produce visible color in the body of water. When dye wastewater is discharged directly into water streams without being properly treated, it is one of the most harmful wastewaters for ecosystems because it reduces sunlight passage, increases biochemical oxygen demand (BOD) and chemical oxygen demand (COD), inhibits plant growth, and prevents photosynthesis. It leads to the death of aquatic life and plants because the oxygen content of the water is lower. The most dangerous effect is that it inhibits the water's self-purification process by interfering with the oxygen transport mechanism between air and water (Ardila-Leal et al., 2021). In addition, discharges of dye wastewater into bodies of water can also affect human health like cancer, allergies, and skin diseases because they contain toxic, carcinogenic, and xenobiotic substances. Usually, it happens due to the ingestion and absorption of dye-contaminated water by humans.

The dye composition in this printing and dyeing waste-water is complex, high concentration, high color, difficult to biodegrade substances, and contains a variety of organics with biological toxicity and three properties (carcinogenic, teratogenic, and mutagenic), making it difficult to achieve the desired effect using a single treatment technology (Dihom et al., 2022). There are three common methods for dye removal from wastewater, which are chemical, physical and biological method, and each of these methods has been thoroughly classified based on the basic principles involved. Textile dyes are frequently eliminated using chemical and physical methods. These methods are not harmful, and they just transfer pollutants from one stage to the other and need further treatment. Conventional wastewater treatment technologies like adsorption, coagulation or flocculation and precipitation are usually used to treat dye wastewater, but this method cannot be used individually enough to remove dye from wastewater. Generally, these methods require a long operating time and produce secondary sludge, which is costly to dispose of. For example, biological processes are

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unsuitable for the decolorization of dyes since most of the dyes are inorganic and toxic in nature to the microorganisms used in the process. Another example is that coagulation is better for insoluble dyes but not for soluble dyes, whereas activated carbon is only suitable for soluble dyes (Zhen, 2019).

Among the various methods for treating dye-contaminated water, photocatalytic degradation has gained popularity as a treatment tool for colored water. The research towards nontoxic metal-free g-C_3N_4 shows the performance of hydrogen evolution from water has attracted considerable attention. However, they still have some fatal defects, limiting their practical applications. There are several factors that affect the degradation performance of a photocatalyst. Firstly, the pH of the solution. Photocatalytic water treatment is highly dependent on pH because it affects the charge on the catalyst particles, the size of aggregates and the position of conductance and valance bands. In order to achieve maximum degradation efficiency, the pH must be chosen carefully. Next, the size and structure of the photocatalyst. Organic compounds and photocatalyst surface coverage have a direct relationship (Zhen, 2019). The number of photons striking the photocatalyst controls the rate of reaction, which means that the reaction takes place only in the absorbed phase of the photocatalyst.

This research focuses on problem statements that need to be improved to focus on dye wastewater treatment. It also focuses on the carbon materials that are obtained from coconut shell husks. The use of unwanted husks as carbon material can reduce and reuse this type of biomass. Since the raw materials used are not hazardous, g-C_3N_4 doped with carbon derived from coconut shell husk will be a green material.

1.3 Objective

The objectives of the proposed study are summarized as:

i. To prepare g-C_3N_4 and coconut shell husk derived carbon composite for sonocatalytic degradation of dye.

ii. To correlate the synthesization technique of g-C_3N_4 and coconut shell husk derived carbon composite with the catalyst properties and activity.

1.4   Scope of study

In this study, photocatalytic semiconductors were prepared in the form of powders by synthetic methods like the hydrothermal method. Hydrothermal synthesis is a method of synthesis of single crystals that depends on mineral solubility in hot water under high pressure. This method is usually a widely used technique because of its low cost, low temperature, high yield, scalable process, and large scale method. It is able to control the shape and dimension of nanomaterials by reaction time, temperature, pH value, and capping agent during the hydrothermal process. Hydrothermal processing involves heating aqueous slurries of organic wastes at high pressures to create an energy carrier with a higher energy density, which is similar to how the earth produced fossil fuels over millions of years. Several pieces of equipment were used to characterise the prepared catalyst to achieve this research. This was a necessary stage because it provided information on the structure of the catalyst surface, the composition of the catalyst, and the chemical properties of the catalyst. The characterization of the catalyst may provide an explanation for the catalyst's performance. The characterization that were used in this research were physical, chemical and optical characterization. X-ray diffractometer (XRD) and scanning electron microscope-energy dispersive x-ray (SEM-EDX) are categorised as physical characterization. XRD is an analytical technique based on the diffraction of X-rays by matter, especially crystalline materials. SEM produces detailed high-resolution pictures of the sample by rastering a focussed electron beam across the surface and detecting a secondary or backscattered electron signal, whereas EDX gives elemental identification and quantitative compositional information. Besides that, fourier-transform infrared (FTIR) is chemical characterization that are used in this research. FTIR analysis uses infrared light to scan the samples as it identifies organic, inorganic, and polymeric components. Lastly is an optical characterization which are ultraviolet visible spectroscope (UV-Vis). It is used to quantify light absorbance across the electromagnetic spectrum's ultraviolet and visible regions.

1.5   Significance of study

The coconut shell husk can be used to produce several important products. In this study, coconut shell husk was used to derive a carbon composite. It is a readily renewable, pH-neutral, non-hydrophobic soil amendment that aerates, improves water retention, and is more environmentally friendly. The implementation of eco-friendly raw materials introduces a more sustainable catalyst for the wastewater treatment process. Since coconut shell husk products are all natural, they are easily recyclable and hence environmentally friendly.

Next, this type of biomass is also cost-effective. Usually, coconut shell husks are rarely used for human consumption, and sometimes consumers just throw them away. Therefore, the price of this coconut shell husk is cheap and can be easily found. In addition, it can make the use of the studied samples more practical. If the sample is found to be reusable, it will be less expensive, which is favorable for industrial applications. As we know, the cost of treating the dye wastewater is expensive because the dye waste wastewater is difficult to achieve the desired effect using a single treatment technology. Therefore, to achieve a cost-effective product, coconut husk is used to derive a carbon composite.

Last but not least, this study can achieve SDG 6 that produce clean water and sanitation. It is important because quality water is in higher demand nowadays and it can also reduce environmental issues like water pollution. Without treating the dye wastewater, it can harm the environment and humans. As a result, this research will aid in the treatment of dye wastewater more easily than the method currently used by most industries.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Water is a very important resource for human survival and development. Water contamination is a major environmental issue because water covers more than 70% of the Earth's surface (Denchak, 2022; Lorenz, 2019). Generally, water pollution is the contamination of a stream, river, lake, ocean, or other body of water, lowering its quality and making it dangerous to humans and the environment. Environmental pollution is the greatest challenge in maintaining safe water sources (Evans et al., 2019). Water pollution is classified according to its source or the characteristics of the water body it affects. There are some of the most common types of pollution which are surface water pollution, groundwater pollution, chemical pollution, nutrients pollution, oxygen depletion pollution, microbiological pollution and suspended matter (Lorenz, 2019).

Table 2.1　　　Types of pollution

Types of pollution	Description
Surface water pollution	Water that is found naturally on the Earth's such as lagoons, rivers, oceans, and lakes. Contamination of surface water features occurs when contaminants dissolve or mix with the water, for example oil spills in the ocean or intentional, like industries eliminating their wastes into rivers or sea.
Groundwater pollution	Happens when dangerous chemicals and particles applied to the ground by humans seep into the ground by rainwater. The contaminants pollute underground water features such as underground rivers and waterbeds.

Chemical pollution	The most common water pollutants, affecting both surface and underground water bodies. The major cause is industrial and agricultural activities.
Nutrients pollution	Even while nutrients are necessary for plant and aquatic life, too much of them can be harmful. When wastewater and fertilizers are released into the water, they contain high levels of nutrients essential for plant growth, resulting in the rapid and uncontrolled growth of vegetation and algae on the water's surface.
Oxygen depletion pollution	Biodegradable chemicals are beneficial to aquatic microbes. When a lot of these items end up in the water, the number of microbes grows and consumes all of the oxygen. The lack of oxygen causes aerobic microbes to die, while anaerobic species thrive, and oxygen depletion pollution occurs.
Microbiological pollution	Natural existing microorganisms such as protozoa, viruses, and bacteria in water cause microbiological pollution. Water containing some of these microorganisms can cause diseases such as cholera and bilharzia. The effects of microbiological pollution are common in areas where people drink untreated water.

| Suspended matter | Some of the particulate matter such as cans, straws, and other large objects may settle at the bottom of the lake, ocean, or river, impacting life on the river, lake, or ocean's floor. |

Source: Lorenz (2019)

2.2 Dye wastewater

A dye is a substance derived from plants or chemicals that is mixed into a liquid and used to alter the color of something such as paper, leather, cosmetics, plastics and textile material (Zhang et al., 2022; Kumar et al., 2021). They are also the compounds that possess the ability to stick to things that want to dye. A dye is a colored compound that has a chromophore and is fixed to acid or basic groups such as OH, SO_3H, NH_2, and NR_2 (Kumar et al., 2021). In addition, 20% of the water pollution with a high contribution to environmental contamination by textile wastewater effluent, where about 50,000 tons/year of dyes are dumped into the environment (Dihom et al., 2022). As mentioned before, dyes give a highly dense color to water and cause diseases like nausea, severe irritation of skin, dermatitis, and hemorrhage. Generally, the dyes presence is unacceptable because of their color, and it can also cause huge environmental problems because of their carcinogenicity, toxicity, and nonbiodegradability (Sasireka Velusamy et al., 2021; Shindhal et al., 2020). Moreover, dyes exhibit high solubility in water and make it more difficult to be removed by conventional procedures (Zhang et al., 2022).

2.2.1 Sources of dye

Natural dye and synthetic dye are two main sources of the dyes. Natural dyes are obtained from natural sources, which are plants, invertebrates, or minerals. For example, most are of plant origin and are extracted from woods, barks, roots, leaves, flowers, seeds, and lichens. Others come from shellfish, insects, and mineral compounds (Abrahart, 2022; Hossain, 2021). It shown that, natural dyes are easily available, renewable, and environmentally safe bioresource products (Singh et al., 2021). Despite all the advantages, natural dyes has flaws that must be acknowledged. It is have a limited color range and susceptible pH. It also insoluble

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in water but soluble in organic solvent and fat. Moreover, natural dyes can form weak hydrogen and van der Walls bonds with the fabric, thus, natural dyes is not an easy process to obtain and maintain a specific color (Witono et al., 2022). However, for natural dyes to be applied in industry, usage of mordants is one of the preferred solution (Zhen, 2019). It not only improves the affinity of the dyes for the fiber but it also changes the shade and tone of some dyes (Singh et al., 2021). The use of mordants has resulted in improved dye performance by providing a wider range of colors as well as improved fastness. Even so, the use of mordants can result in the formation of metal ions, which can pose a risk to the environment when discharged as wastewater effluent from the dyeing process.

Synthetic dyes started with the development of synthetic organic chemistry. It are organic compounds that used for imparting color to textile, paper, plastic reasonably permanent fashion, leather or permanent manner (Mazharul Islam Kiron, 2021). Mostly pharmaceutical, textile, food, paper & pulp and cosmetic industries uses synthetic dyes for manufacturing process (Zhang et al., 2022). Synthetic dyes have replaced natural dyes, even though natural dyes have been used for a long time to dye fabrics. Synthetic dyes are very inexpensive and come in a variety of colors and shades (Singh et al., 2021). In addition, it dries quickly and the color of the dyes is more long-lasting than using natural dyes. As a result, synthetic dye is more advantageous in industries than natural dye, which is more environmentally friendly. However, synthetic dyes also have pros and cons. The disadvantages of the synthetic dyes are it involves extreme conditions such as high pH, strong acids, high temperature, and heavy metal catalyst that are not environmentally friendly. It also generates a large amount of effluent which contains toxic chemicals due to their synthetic origin and complex molecular structures, which decrease their ability to biodegrade (Sajda .S. Affat, 2021). This means that synthetic dyes will harm the welfare of humans and the environment.

2.2.2   Type of dyes

There are several types of dye. Firstly, acid dyes are water-soluble anionic dyes that are applied to fibers like silk, wool, nylon, and modified acrylic fibers in neutral acid dye baths. It also has one or more sulfonic acid substituents or acidic groups. Moreover, at least part of the dye's attachment to the fiber is attributed to salt formation between anionic groups in the dyes and cationic groups in the fiber. Acid dyes have no effect on cellulosic fibers. The majority of

synthetic food colors fall into this category. Examples of acid dye are Alizarine Pure Blue B, Acid Red 88, and Acid Yellow 36 (Mazharul Islam Kiron, 2021; Abrahart, 2022).

Next, basic dyes are water-soluble cationic dyes that are mostly used on acrylic fibers but can also be used on wool and silk. They can also be used on basic dyeable nylon and polyester variants. Typically, basic acid is added to the dye bath to aid in dye uptake on the fiber. It is also used in paper coloring. Moreover, basic dyes produce brilliant colors that are exceptionally fast on acrylic fibers. This was the first group of synthetic dyes extracted from coal-tar derivatives. As textile dyes, they have been largely replaced by later developments and still used in discharge printing and for preparing leather, paper, wood, and straw. In addition, basic dyes were used to color wool, silk, linen, or hemp without the use of a mordant or an agent. Usually, mordants like tannic acid are used on cotton and rayon (Mazharul Islam Kiron, 2021; Abrahart, 2022).

Direct dyes are a type of dye as well. Because of their sulfonic acid groups, they are water soluble. They are typically performed in a neutral or slightly alkaline dye bath at or near boiling temperature, with the addition of sodium chloride (NaCl), sodium sulfate (Na_2SO_4), or sodium carbonate (Na_2CO_3). Direct dyes are commonly used on cotton, paper, leather, wool, silk, and nylon. These dyes typically have a high molecular weight and an azo linkage (N=N). It also serves as a pH indicator and a biological stain. Because direct dyes can form hydrogen bonds, they can be applied directly to fabrics from an aqueous solution. Furthermore, direct dyes, particularly basic dyes, were widely hailed because they eliminated the need for a mordant or binder when dyeing cotton. The colors are not as bright as those in basic dyes, but they are more resistant to light and washing, and this resistance can be significantly improved by treatments (Mazharul Islam Kiron, 2021; Abrahart, 2022).

In addition, azoic dyes are a method of producing an insoluble dye directly onto or within the fiber. This is accomplished by combining diazoic and coupling components on a fiber. The two components react to produce the required insoluble azo dye when dyebath conditions are adjusted appropriately. Next, azo dyes have at least contain one azo group (-N=N-) attached to one or often two aromatic rings. Since other classes of fast dyes lack good red dyes, these dyes are primarily used for bright red shades in dyeing and printing. Azoic dyes, also known as naphthols in the industry, are created in the fabric by applying one half of the dye. The other half is then put on, and they combine to form the finished color. They are not

resistant to rubbing or crocking unless applied carefully and thoroughly. This dyeing technique is unique in that the final color is determined by the diazoic and coupling components used. This method of dyeing cotton is becoming less popular due to the toxicity of the chemicals used (Mazharul Islam Kiron, 2021; Abrahart, 2022; Shindhal et al., 2020).

Other than that, disperse dyes are water insoluble and were developed for the dyeing of cellulose acetate. In the presence of a dispersing agent, the dyes are finely ground and sold as a paste, or spray-dried and sold as a powder. Their primary application is in polyester, but they can also be used to color nylon, cellulose triacetate, and acrylic fibers. In some cases, a dyeing temperature of 130°C is required, and a pressurized dyebath is used. Because of the small particle size, there is a large surface area, which aids in dissolving and fiber uptake. The dispersion agent used in the grinding process may have a significant impact on the dyeing rate (Mazharul Islam Kiron, 2021; Abrahart, 2022).

Furthermore, mordant dyes do not directly dye the fabric but require a binding agent known as mordant. The mordant acts as a binding agent between the fiber and the dye, improving the dye's resistance to water, light, and perspiration. Some dyes combine with metal salts (mordanting) to form insoluble colored complexes (lakes). These substances are commonly used in the dyeing of cotton, wool, and other protein fibers. The metallic precipitate forms in the fiber, resulting in extremely fast colors that are highly resistant to light and washing. It is important to note that many mordants, particularly those containing heavy metals, can be hazardous to health and must be used with extreme caution (Mazharul Islam Kiron, 2021; Abrahart, 2022).

Next, reactive dyes react with the cellulosic fiber to form a covalent bond. It also utilizes a chromophore attached to a substituent that is capable of directly reacting with the fiber substrate. It also makes use of a chromophore attached to a substituent that can directly react with the fiber substrate. Because of the covalent bonds that hold reactive dyes to natural fibers, they are among the most permanent of dyes. This produces dyed fiber with extremely high wash fastness properties. These are the dyeing of fabrics which contain a reactive group which combines directly with the hydroxyl or the amino group of the fibre. Because of the chemical reaction, the colour is fast and has a very long life. Cotton, wool or silk can be dyed with this types of dye (Mazharul Islam Kiron, 2021; Abrahart, 2022).

Last but not least, sulphur dyes produce very deep shades that are resistant to washing but not to sunlight. They will dye cotton, linen, and rayon, but not in a vibrant manner. Furthermore, they are low-cost dyes used to color cotton in dark colors. The fabric is dyed by heating it in a solution of an organic compound, typically a nitrophenol derivative, and a sulfide or polysulfide. When the organic compound reacts with the sulfide source, it produces dark colors that adhere to the fabric. Sulphur dyes, particularly the black colors, have the disadvantage of making the fabric tender or weakening its structure, causing it to break easily. Sulfur dyes are applied to cotton using an alkaline reducing bath that contains sodium sulfide as the reducing agent. They are inexpensive and have good light, washing, and acid resistance (Mazharul Islam Kiron, 2021; Abrahart, 2022).
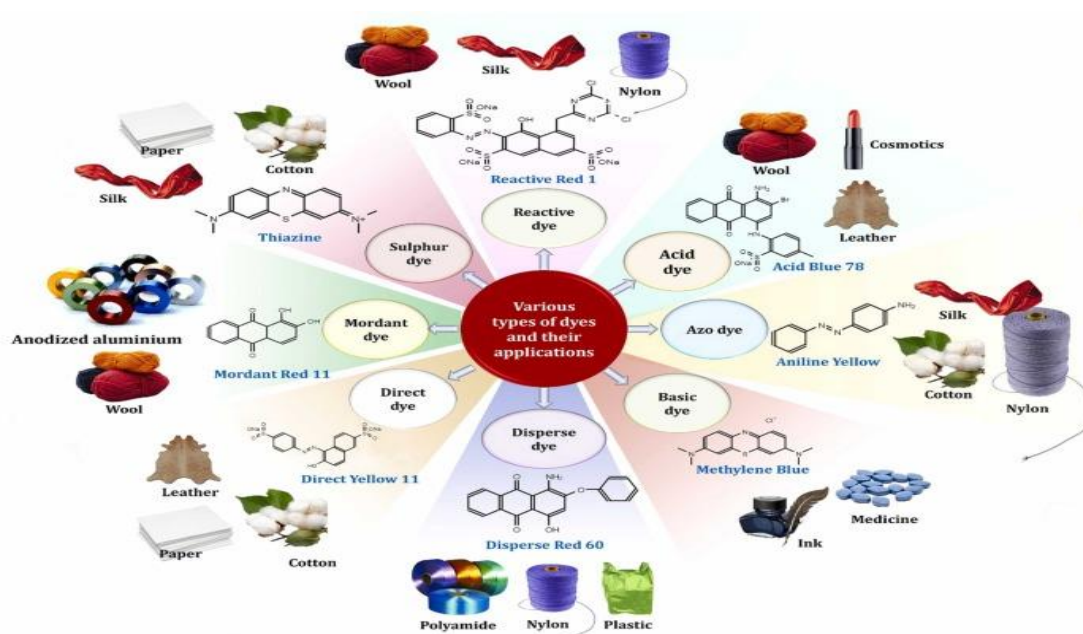
Figure 2.1   Various categories of dyes and their possible industrial applications
Source: Al-Tohamy et al. (2022).

2.3   Conventional dye wastewater treatment

Dye wastewater treatment is very important nowadays, because dye wastewater contains a variety of dyes in different concentrations, and usually the dye contaminants in water are toxic, carcinogenic, and xenobiotic (Dihom et al., 2022; Sasireka Velusamy et al., 2021; Shindhal et al., 2020). As mentioned before, this contain can cause harm to human health and the environment. Thus, the dye wastewater needs to be treated by removing the dye color in

order to protect humans and the environment (Yaseen and Scholz, 2019). Dye containing wastewater should be effectively treated using eco-friendly technologies to avoid negative effects on the environment, human health, and natural water resources. Various conventional treatment processes are used to treat the dye wastewater which are physical-chemical treatment and biological treatment (Ceretta et al., 2021). All these methods have different COD and color removal capabilities, depending on the types of dyes present in the wastewater.

2.3.1 Physical-chemical treatment

Physical-chemical treatment involves chemicals that can modify the physical state of colloidal particles, which helps in making them more stable and coagulable for further treatment. These treatment methods have been used for over a century in conjunction with biological treatment methods. The process consists of a series of physical treatments and chemical reactions. Physical-chemical plants are commonly used for industrial effluents purification. They can treat, in addiction to specific chemicals, a wide range of pollutants, depending on inlet flow and effluent characteristic. A wastewater treatment plant of a dyeing and finishing industrial park including 24 companies in Guangxi Province in China used hydrolytic acidification/aerobic process combined with selective physicochemical technology to treat wastewater (Jin et al., 2019). The disadvantages of this treatment are that they are expensive, have high chemical and energy requirements, and produce secondary by products, which can endanger their full-scale implementation (Ceretta et al., 2021).

2.3.1.1 Coagulation

Coagulation is the chemical water treatment process used to remove solids from water, by manipulating electrostatic charges of particles suspended in dye wastewater. This process introduces small, highly charged molecules into water to destabilize the charges on particles, colloids, or oily materials in suspension (Bradley, 2019). Coagulation is most effective at removing suspended solids and natural organic matter like gravel, sand, algae, clay, iron, protozoa, and even bacteria (Campbell, 2021). Moreover, coagulant chemicals with charges opposite those of the suspended solids are added to the water to neutralize the negative charges on non-settlable solids such as clay and color-producing organic substances (Mazille & Spuhler, 2019). Once the charge is neutralized, the small suspended particles are capable of sticking together. These slightly larger particles are called microflocs, and are not visible to the

naked eye. Water surrounding the newly formed microflocs should be clear. If not, coagulation and some of the particles charge have not been neutralized and more coagulant chemicals may need to be added. Moreover, a high-energy, rapid-mix to properly disperse coagulant and promote particle collisions is needed to achieve good coagulation (Mazille & Spuhler, 2019). Over-mixing does not affect coagulation, but insufficient mixing will leave this step incomplete. Contact time in the rapid-mix chamber is typically 1 to 3 minutes.

In the coagulation process, there are many variables can influence the removal percentage, such as the effect of dose, rapid mixing speed, slow mixing speed, rapid mixing time, slow mixing time and settling time. The optimisation of these parameters may influence the process efficiency. For example, $FeCl_3$ at pH 9 was chosen as a coagulant for coagulation/flocculation because it demonstrated the most effective removal of COD, TSS, colour, TN and turbidity (Karam et al., 2020). In most cases coagulation has been effective in removing color especially for wastewaters, containing dissolvable solids. However, high chemical dosages are usually required and large amounts of sludge volume must be disposed of. Besides that, the cost of sludge disposal results in relatively high process costs (Mazille & Spuhler, 2019). Coagulation and rapid mixing with short contact times helps in destabilizing the colloid surfaces so they can clump together and thus conditioning them for next step of flocculation. Selecting the right coagulant for a system will enhance overall system performance, and particularly improve solids removal efficiency by enhancing filter and clarifier performance (Bradley, 2019). Coagulation is a necessary dye wastewater treatment process, but it cannot work alone. Flocculation, filtration, sedimentation and disinfection are also required to ensure that dye wastewater is reduce or free from harmful contaminants (Campbell, 2021).

2.3.1.2 Flocculation

Flocculation goes hand in hand with coagulation in wastewater treatment. The addition of flocculation process is highly recommended to improve coagulation process effluents by enlarging the size of flocs and, consequently causing rapid settling (Karam et al., 2020). Flocculation is a process in which a chemical coagulant added to water acts to facilitate particle bonding, resulting in larger aggregates that are easier to separate. This chemical also binds the collected mass together, preventing it from dissolving even when the water is slightly agitated. After that, the larger aggregates can be removed from the wastewater stream. This is done

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either through settling where the floc drops to the bottom for removal or through the use of filters which capture the floc in the filter material. Care must be taken when cleaning the filters to ensure that the phosphorus rich floc is contained and treated (Bradley, 2019). The flocculation process takes 10 to 30 minutes, although the maximum flocculation time varies based on the quality of raw water and the dosage used.

Flocculants are lightweight, medium weight and heavy polymers that cause the destabilized clumps of particles to agglomerate and drop out of the solution, removing them from the filtered water. The weight used depends on the type of particle. In addition, organic flocculants are derivatives of algins (seaweed based), starch or cellulose (plant based) and are usually less effective. On the other hand, synthetic flocculants such as polyelectrolytes are highly effective (Chatsungnoen & Chisti, 2019). They are water soluble synthetic macromolecules which may have charges on them. Due to their high efficiency, lower doses are more effective and excessive dosage may be detrimental to the whole process and at the same time increase the costs.

2.3.1.3 Sedimentation

Sedimentation is the process of separating small particles and sediments in water. It removes undesirable small particulate suspended matter and some biological contaminants from water under the influence of gravity. The more the suspended solids and pathogens will settle to the bottom of the container if the longer the water is held undisturbed. The sedimentation process is used to reduce particle concentration in the water. In addition, sedimentation can also be used after coagulation to improve the efficiency of ongoing filtration in the process (Balsom, 2020). Besides that, the advantage of sedimentation is that it minimizes the need for coagulation and flocculation. Typically, chemicals are needed for coagulation and flocculation, but improved sedimentation controls the need for additional chemicals. Additionally, sedimentation can be used after coagulation to increase the effectiveness of ongoing filtration in the process.

2.3.1.4 Filtration

Filtration is used to remove colloidal and suspended matter that remains after sedimentation, as well as the bacterial load. Using filtration in water treatment, solid particles are entirely removed from the water. This can be from ground water, surface water or even pre-

treated wastewater. Filtration generally involves passing water through a thick layer of sand or porous material that retains coarse impurities on its surface and in its pores. The filtration apparatus is known as a filter, and the porous material that fills the filter is known as the filtering medium. There are a few disadvantages of this process which are a filter process does not capture all contaminants or bacteria. It still need require an additional wastewater treatment process because only smaller particles pass through the membrane. Moreover, filters in an effluent treatment plant will clog and become ineffective at removing suspended particles if they are not properly maintained. The maintenance periods must be carefully considered dependent on the fluctuating levels of pollutants in the passing wastewater. The maintenance can sometimes be disruptive to treatment and require staff training (Arvia, 2022).

2.3.2 Biological treatment

Biological treatment refer to the strategies that use the abilities of microorganisms, enzymes or plants to remove a contaminant from a matrix such as water, sediment, air, or soil, therefore it will reducing the toxicity and also minimize the negative impact to the human health and environment. Thus, treatments that use microorganisms (bacteria, algae, and fungi) are the most widespread (Ceretta et al., 2021). There are numerous references that use microorganisms in pure cultures like an Aeromonas hydrophila was able to reduce 72% of dyes present in simulated wastewater (Thanavel et al., 2019). Moreover, biological treatment are cost effective, simple and environment friendly alternatives. Although these treatments can reduce toxicity, pollutant mineralization is rarely achieved. Furthermore, the presence of toxic substances frequently inhibits microorganism growth and catalytic activity and making extrapolation to large scale processes is difficult. This necessarily requires the modification of natural effluent conditions in order to conduct research, such as the use of simulated or diluted effluents, the addition of nutritional supplements, or prior acclimatization (Ceretta et al., 2021). In addition, aerobic and anaerobic process is a biological treatment method that uses to treat dye wastewater. This anaerobic-aerobic treatment method will improve the colour reduction of the biological treatment methods greatly. Since anaerobic treatment alone is insufficient to treat organic dyes effectively, the combination of biological treatment with other methods are applied (Zhen, 2019). In comparison to physical-chemical methods, anaerobic digestion, is considered as the most suitable approach for the treatment of dyeing wastewater due to its low input requirements, cost-effectiveness, and environmental safety (Che et al., 2022).

2.3.2.1 Anaerobic digestion

Anaerobic digestion is used as part of the process to treat biodegradable waste and sewage sludge. The process is use for industrial or domestic purpose to manage waste. Anaerobic digestion is a biological process that uses microorganisms to break down organic contaminants found in wastewater in the absence of oxygen. Anaerobic biological treatment will decolorize organic dyes by breaking them down into amines. The amines produced have been found to be extremely hazardous, making this treatment method undesirable. Following anaerobic treatment, aerobic biological treatment can be used to degrade the amines produced by anaerobic bacteria when dye is digested. (Pinheiro et al., 2022). Anaerobic digestion is commonly considered as an environmentally friendly technology for a wide range of organic waste, including sewage sludge. Nevertheless, the anaerobic digestion process remains vulnerable to several external environmental factors, such as the biological toxicity of dyes and their degradation products, and shorter hydraulic retention time (HRT), resulting in a lower anaerobic biodegradation efficiency of azo dyes (Guo et al., 2020).

Anaerobic digestion completed in 4 stages which are hydrolysis, acidogenesis, acetogenesis and methanogenesis (Spuhler, 2019; Kieren, 2021). The overall process can be described by the chemical reaction, where organic material such as glucose is biochemically digested into carbon dioxide (CO_2) and methane (CH_4) by the anaerobic microorganisms. The input components are first hydrolyzed by bacteria, which starts the digestion process. Organic polymers that are insoluble, such as carbohydrates, are broken down into soluble derivatives that can be used by other bacteria. The sugars and amino acids are then converted to carbon dioxide, hydrogen, ammonia, and organic acids by acidogenic bacteria. Bacteria transform these organic acids into acetic acid, along with extra ammonia, hydrogen, and carbon dioxide, among other chemicals, during acetogenesis. Finally, methanogens decompose these compounds into CH_4 and CO_2 (Hanum et al., 2019). The populations of methanogenic archaea are important in the treatment of anaerobic wastewater.

2.3.2.2 Aerobic digestion

Bacteria and fungi are the most common microorganisms used for dye decolorization under aerobic conditions (Shindhal et al., 2020). In fact, bacteria can grow faster than fungi. Usually, aerobic microorganisms require oxygen to support their metabolic activity. For more than three decades, aerobic bacteria capable of degrading various dyes have been used. There

have been numerous reports of bacteria that can degrade dyes. The use of bacteria and fungi for the complete decolorization and degradation of dyes from textile effluent has the advantages of being a low-cost process that can complete dye mineralization with nontoxic by-products. However, degradation of dyes in textile wastewater by white-rot fungi has some inherent drawbacks, such as a long growth phase and the need for nitrogen-restricted environments, unreliable enzyme production, and large reactor size due to the long holding time (14 days) for complete degradation. Because it is a very slow process that provides a suitable environment for the growth of autochthonous microorganisms, this process is not applicable to full-scale textile wastewater treatment (Shindhal et al., 2020).

This treatment is ineffective because dyes are made to resist oxidative biodegradation. As a result, the degradation of textile wastewater will proceed at a much slower rate than that of normal domestic wastewater. Aerobic microorganisms will be introduced into the wastewater as activated sludge. Several studies have shown that activated sludge is the major contributor to this type of dye removal. Instead of being biodegraded by aerobic microorganisms, dyes will be adsorbed on activated sludge. As a result, aerobic treatment of dyes is ineffective. (Zhen, 2019).

2.3.3 Advanced wastewater treatment

Since dye wastewater contains toxic and highly conjugated structure compounds and also nonbiodegradable molecules that are harmful to human health and the environment, it requires advanced treatment technology (Rojviroon et al., 2021). Advanced wastewater treatment processes can be biological processes, physicochemical processes, or a combination of both (Tuser, 2021). Usually, wastewater treatment not always treat wastewater efficiently, which can generate a number of concerns like health problems. To face the challenges, new wastewater treatment techniques are being implemented. So, advanced wastewater treatment is required as society mitigates the impacts of increased population, urbanization, industrialization, and the depletion of potable water. With the use of these treatment technologies, it is possible to improve the quality of wastewater beyond the limitations of conventional technologies in order to achieve the goal of resource recovery or resource conservation (Tuser, 2021).
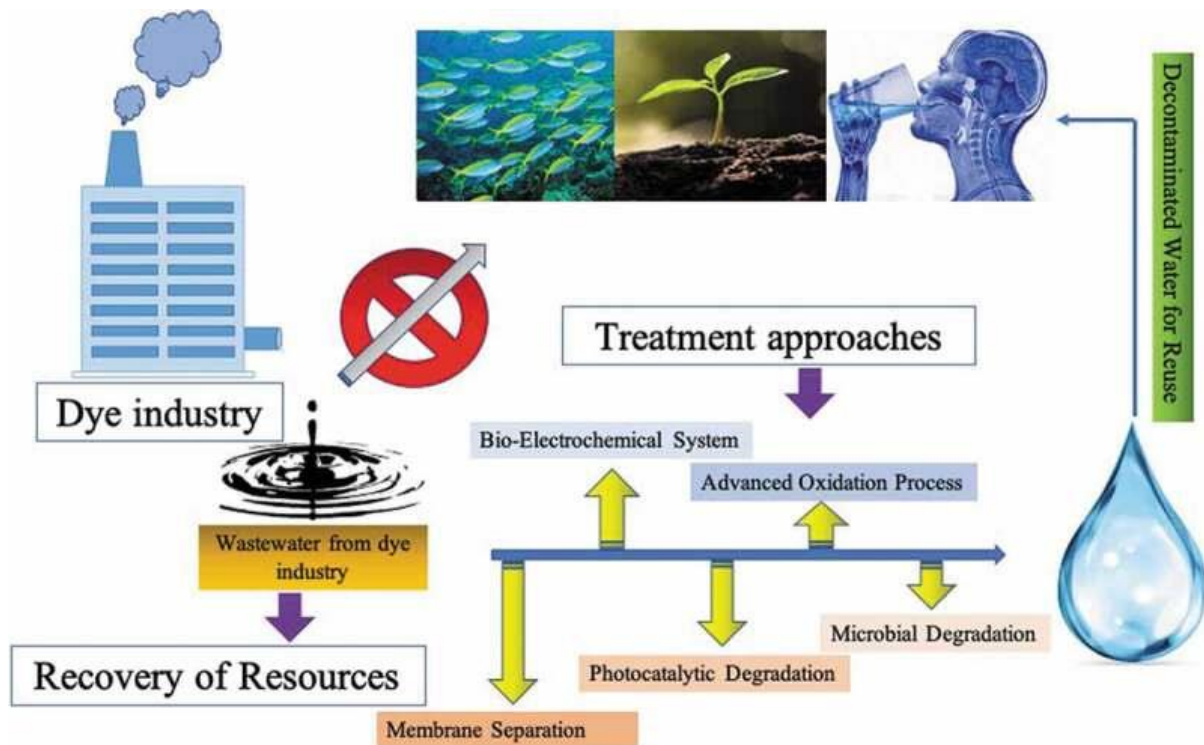
Figure 2.2   Advanced wastewater treatment

Source: Shindhal et al. (2020).

2.3.3.1 Membrane Filtration

In this process, the wastewater is allowed to pass through a porous membrane. If any solute is larger than the pore size of the membrane, it will be trapped, while the rest of the solution will pass through the membrane. During the filtration process, trapped solutes from the filter cake or layer are constantly removed (Shindhal et al., 2020). Membrane filtration techniques are classified according to the size of the porous membranes. There are four different types of membrane filtration, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Lemmons, 2022; Shindhal et al., 2020).

Figure 2.3   Classification of membrane filtration based on size exclusion

Source: Lemmons (2022).

Based on Figure 2.3, a different type of filtration process is used for different sized particles. MF membranes have pore sizes ranging from 0.1 μm to 5.0 μm, and suspended particles, for example, will be trapped in these m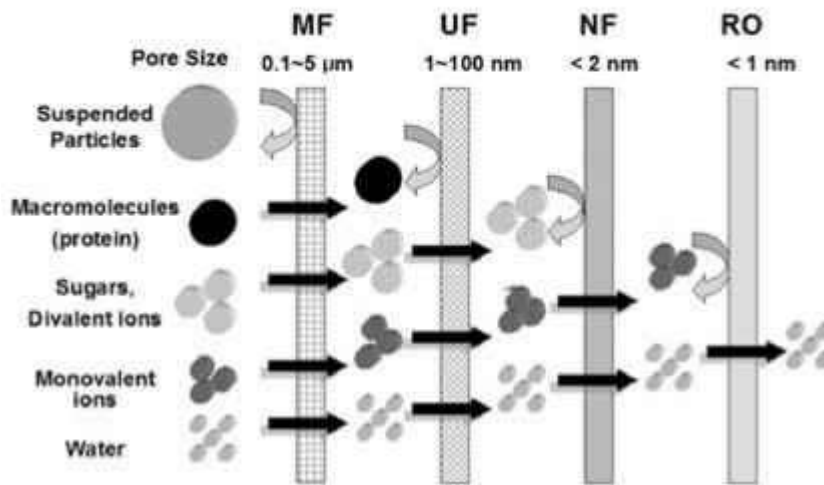embranes. Next, macromolecules, for example, will be trapped in UF membranes due to their 1 nm to 100 nm pore size, with high applied pressure, and low water permeability. Besides that, NF membranes contain less than 2 nm of pore size, while RO membranes contain less than 1 nm of pore size, so only water will pass through these membranes. In addition, MF and UF use the same sieving mechanism, which is an innovative and sustainable technology. According to Shindhal et al. (2020), UF is used for the recycling and separation of water-insoluble dyes such as disperse dye and indigo dye, whereas NF and RO procedures are used to hydrolyze reactive dyes from dye wastewater. MF is generally not used for wastewater treatment because of their large pore size. Usually, the type of membrane filtration is determined by a variety of factors, including the nature of the dye, the dyeing process, and the chemical composition of the pollutants. Moreover, membrane filtration has a high resistance to harsh chemical environments and a significant potential for the reclamation of dye effluents. However, due to membrane fouling and high initial and operating costs, its application is limited (Zhang et al., 2021).

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2.3.3.2 Microbial degradation

Various microorganisms like bacteria, algae, fungi and yeast can be used for dye degradation. Genetic engineered microorganisms (GEMs) play important role in achieving complete dye degradation. For bacterial biodegradation, many bacterial strains are used in aerobic or anaerobic dye degradation. In azo dye degradation, Pseudomonas luteola, Xanthophilus azovorans, Klebsiella pneumonia, and Clostridium perfringens are used. For degradation of various dyes different microbes can be used, they have different mechanisms and pathways for degradation of dyes. Azo dyes are useful class of dyes with highest diversity of colors. Under anaerobic condition and with help of azoreductase, microorganisms degrade azo dyes and as end product they form colorless aromatic amines (Dong et al., 2019). Microbial degradation is environment friendly technique to control pollution. (Varjani et al., 2020) and inexpensive nature. Microbes could decolorise the dyes by both aerobic and anaerobic metabolism.

2.3.3.3 Bio-Electrochemical system

Bio-electrochemical systems (BESs) use electroactive microorganisms for degrading organic materials in wastes for energy or chemical production. (Sayed et al., 2020). It also are unique systems capable of converting the chemical energy of organic waste including low strength wastewaters and lignocellulosic biomass into electricity or hydrogen/chemical products in microbial fuel cells (MFCs) or microbial electrolysis cells (MECs) respectively, or other products formed at the cathode by an electrochemical reduction process. As compared to conventional fuel cells, BESs operate under relatively mild conditions, use a wide variety of organic substrates and mostly do not use expensive precious metals as catalysts. The bio-electrocatalytic reaction combined with extracellular electron transfer can drive several procedures such as synthesizing chemicals, producing electricity from wastewater, removing pollutants and desalinating seawater (Sayed et al., 2020). Removal of untreated wastewater from different industries such as textile, dyestuff and paper involves 70% identified commercial dyes which includes common chromophores in reactive dyes. Bio-electrochemical systems (BESs) contain great potential for azo dye removal (Yang et al., 2019).

2.3.3.4 Advanced Oxidation Process (Photocatalysis)

Photocatalysis is composed of two parts, which are photo and catalyst, and uses light to activate a substance which modifies the rate of the chemical reaction without being involved itself. The advanced oxidation processes (AOPs), which includes photocatalytic degradation (PD) using nanophotocatalysts, is a rising technology causing in completing the mineralization of the dyes, compared to traditional treatment techniques such as the absorption method, which transfers the pollutants to other stages. Photolysis is capable of partially degrading 50% to 80% of micro-pollutants like dyes using nanophotocatalysts. (Dihom et al., 2022). The photocatalytic degradation requires the use of an ultraviolet (UV) light source and photocatalysts to be added for the formation of oxidizing agents. The addition of hydrogen peroxide, H_2O_2 can further increase the generation of hydroxyl (OH) radicals in the wastewater to increase the efficiency of degradation. The efficiency of photocatalytic degradation is affected by a few parameters such as solution pH, types of dye, UV radiation intensity, and the initial dye concentration. The photocatalytic degradation is favoured since it does not produce any toxic products that need to be treated again. Moreover, the highest photolysis efficiency was found at low dye concentrations and pH to improve the initial operating parameters. Photolysis increases with increasing photocatalysis in the surface area and with an optimum amount of photocatalyst. (Dihom et al., 2022). Furthermore, 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).

A photocatalytic reaction is a chemical reaction that occurs when light and a photocatalyst interact. This technology has several advantages, including environmental protection complete pollutant degradation, and no secondary pollution. Figure 2.4 shows that the reaction mechanism of the photocatalytic. A semiconductor has an energy band structure that consists of a low energy valence band (VB) and a high energy conduction band (CB), and the band gap between the two is known as a forbidden band. When the incident light has a higher energy than the semiconductor's band gap, photons excited electrons in the VB of the semiconductor to the CB, and corresponding holes are generated in the VB. An electric field separates photogenerated electrons and holes, which move to the surface of semiconductor particles. The photogenerated pores have strong oxidizing properties and can oxidize substances adsorbed on the semiconductor's surface or solution. When exposed to a specific

amount of light energy, electrons on a VB are excited and jump to a CB, while holes remain on the VB. The electrons on the CB diffuse to the catalyst surface and participate in a reduction reaction, whereas the holes on the VB diffuse to the photocatalyst surface and participate in an oxidation reaction. During the reaction, the electrons can form H_2O_2 or a superoxide radical O_2 with H+ and dissolved O_2 in the aqueous solution, and the holes can oxidize OH to produce hydroxyl radicals OH, resulting in the degradation of pollutants (Zhang et al., 2019).
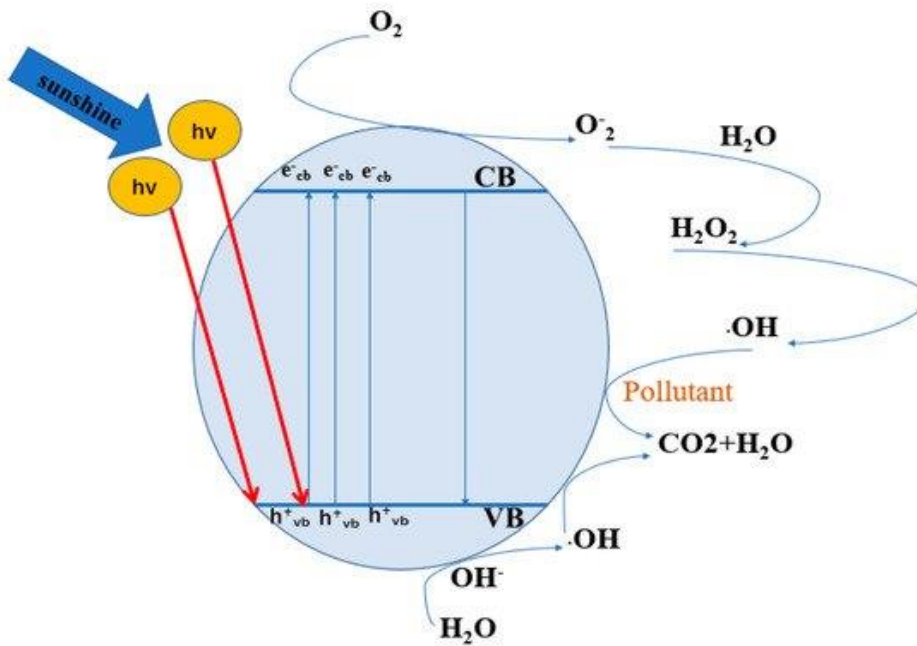
Figure 2.4   Photocatalytic reaction mechanism

Source: Zhang et al. (2019).

2.4   Semiconductor photocatalyst

In semiconductor photocatalysis, it is used to design, characterize, and potentially photocatalytical applications with doped or undoped nanostructural materials especially considering their particle sizes as well as shapes. Nanostructured materials, such as porous metal oxides, metal nanoparticles, porous carbons, and their composites, are being investigated for potential applications in energy conversion/storage devices, gas storage, photocatalysis, and electrocatalysis. Semiconductor photocatalysis can be divided into two types which are homogenous photocatalysis and heterogeneous photocatalysis, based on the phase differences of reactants and catalysts, which triggered the concept of advanced oxidation processes at the end of twentieth century. (Muzibur Rahman, 2019) Homogeneous photocatalysis occurs when the photocatalyst and reaction medium are in the same phase while heterogeneous

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photocatalysis occurs when the photocatalyst and reaction medium are not in the same phase. For wastewater treatment, a variety of semiconductor photocatalysts, such as ZnO, TiO_2, Fe_2O_3, Fe_3O_4, SnO_2, and Mn_2O_3, have been developed but TiO_2 has the most efficient photocatalytic degradation of pharmaceutical pollutants of all reported photocatalysts due to a variety of advantages such as low processing cost, non-toxicity, and high environmental stability (Kar et al., 2021).

2.4.1 Titanium dioxide (TiO_2)

TiO_2 is a semiconductor that can perform both heterogeneous and homogeneous photocatalyst photoreactions. Titanium is one of the most widely used metals on the earth, but it does not occur naturally in this elemental form. TiO_2, commonly known as titanium (IV) oxide or titania, is a naturally occurring compound formed when titanium interacts with oxygen. Titanium is present in the earth's crust as an oxide in minerals. TiO_2 is an abundant, biocompatible, and low-cost semiconductor with unique optoelectronic properties and high chemical stability (Parrino et al., 2021). TiO_2 has a lot of unique properties that make it appropriate for a wide range of applications. It has a melting point of 1,843°C and a boiling temperature of 2,972°C, therefore it exists naturally as a solid, and it is insoluble in water even in particle form (Hejazi, 2020). Moreover, TiO_2 is an insulator as well. Unlike other white materials that may appear slightly yellow in light, TiO_2 does not have this appearance and appears as pure white due to the way it absorbs UV radiation. TiO_2 also has a high refractive index (the ability to scatter light), which is even greater than diamond. They also considered as an inert and safe material which means it doesn't react with other chemicals and is thus a stable substance that may be employed in a wide range of industries and applications (Abd Aziz et al., 2021)

Furthermore, TiO_2 is a functional substance that has uses in a variety of fields, including photocatalysis and energy fields (Hussain et al., 2019). Applications of TiO_2 nanomaterials in photocatalysis have seen widespread development in recent decades especially researches semiconductor in photocatalysis but its photocatalytic efficiency can be increased even further by designing the material as a nanostructure with unique surface and structural properties (Andronic & Enesca, 2020; Zhou & Schmuki, 2020). It also an important inorganic chemical product and mainly contains white pigment. In general, the physical characteristics that determine the photocatalytic activity of TiO_2 are crystallinity, impurities, specific surface area,

and density of the surface hydroxy groups (Abd Aziz et al., 2021). Different preparation methods, such as sol-gel procedures, hydrothermal treatments, and flame spray pyrolysis, can be used to produce TiO_2 nanoparticles (Uddin et al., 2020). Moreover, if UV light is present, the photocatalytic activity of TiO_2 nanoparticles may occur. For example, the photocatalytic activity of TiO_2 nanoparticles shows that when methylene blue is degraded under UV light, 97% of the dye is removed in 3 hours, however when methylene blue is degraded without UV light, only 15% of the dye is removed in 3 hours. (Nasikhudin et al., 2019). The use of TiO_2 photocatalytic waste treatment for environmental preservation has been shown to successfully degrade many organic contaminants. Because of its chemical stability and commercial availability, TiO_2 has been widely used as a photocatalytic material. (Nasikhudin et al., 2019). TiO_2 also has a low toxicity, a high photochemical solidity, a high corrosion resistance, and a moderately low cost of manufacture (Ahmed et al., 2022).

2.4.2 Drawbacks and limitation of TiO_2

Although TiO_2 has been widely utilized as a photocatalyst, it still has a number of drawbacks, including low absorption of visible or solar radiation, rapid recombination of electron and hole as well as low stability limits its practical applications especially for wastewater treatment. (Hendra Saputera et al., 2021). Moreover, they also have a large band gap energy (3.0–3.2 eV), which limits their light response to the UV region (Allaker & Yuan, 2019). It also effective only upon irradiation with UV light at levels that could cause damage to human cells. In addition, the low rate of degradation for certain organic compounds, insufficient photon energy, and mass contact for TiO_2 at the high concentration of organic pollution make the capability of TiO_2 limited. These limits may develop as a result of undesirable TiO_2 features, such as low affinity towards organic pollutants and the instability of nanosized particles, which may aggregate and reduce the active sites (Dharma et al., 2022). In addition, other disadvantages of TiO_2 including agglomeration, the low efficiency of the catalyst, high electron-hole recombination rate. Last but not least, TiO_2 has a low inactivation efficiency for bacteria due to its low utilization (4%) of the incoming solar spectrum (ultraviolet light) caused by anatase's large band gap (3.2 eV), and the great challenge in forming nanostructured materials (Ni et al., 2021).

2.5 Graphitic Carbon Nitride (g-C$_3$N$_4$)

g-C$_3$N$_4$ is a very important organic material which is used mostly as semiconductors. It have some special properties like photocatalytic activity, super hardness, low density, and chemical stability. g-C$_3$N$_4$ is has a unique two-dimensional layered structure which are non-metallic and л-conjugated polymeric material. It can be produced by polymerizing the carbon and nitrogen containing compounds such as cyanamide, dicyandiamide, or melamine (Ghalkhani et al., 2021). The extent of polymerization and condensation process determines the final product's properties and reactivity. g-C$_3$N$_4$ is a metal-free polymeric semiconductor with a mild band gap (2.7 eV), excellent optical properties, physicochemical stability and large specific surface area, has become a hot-spot in photocatalytic sterilization (Ni et al., 2021). The g-C$_3$N$_4$ based compounds have shown interesting applications in varied interdisciplinary areas such as photocatalysis, photoelectronics, and photodegradation due to their large specific surface area and high chemical stability (Ghalkhani et al., 2021).

The g-C$_3$N$_4$ can overcome the limitations of TiO$_2$ because TiO$_2$ has the disadvantage of a large band gap energy, which results in poor performance. Since the main goal of treating the wastewater is to overcome water scarcity and pollution, a metal-free semiconductor is chosen for this research. Graphitic carbon nitride (g-C$_3$N$_4$) is a recently discovered metal-free sonocatalyst. Because it is metal-free, this semiconductor will be less expensive than TiO$_2$ due to the abundance and renewability of raw materials (Zhen, 2019).

2.6 Synthesization method of photocatalyst

Photocatalytic semiconductors can be prepared in the form of powders, fibers, and films by different synthetic methods including sol-gel process, precipitation method, hydrothermal and solvothermal techniques, chemical vapour deposition, and electrodeposition method.

Table 2.2   Advantage and disadvantage of the synthetic method

Synthetic methods	Advantage	Disadvantage
Sol gel	• High purity • High uniformity • Low synthesis temperature	• Use raw material, generally titanium alkoxide • Required a large amount of organic solvent

	• Easy control of the reaction conditions • The process not require special or expensive equipment	• The obtained film is heat-treated at a relatively high temperature. Therefore, the film forming cost is relatively high
Precipitation	• Good light absorption capability and can promote the separation of holes • Can improve photocatalytic performance	• Many of the heavy metals added do not readily react in solution and may introduce impurities into the solution, which limits the application of the precipitation method
Hydrothermal	• Good grain development • Small particle size • Uniform distribution, and low-cost raw photocatalysts. • High crystallinity and morphology control • Suitable for the growth of large good quality crystals while maintaining control over their composition	• Need expensive autoclaves • The impossibility of observing the crystal as it grows if a steel tube is used
Chemical vapour deposition	• The process is flexible for designing, and new technology can be developed on the base of existing producing unit.	• The organic exhaust gas is usually hazard and toxic to human healthy and can be serious environmental problem without proper treatment.

| Electrodeposition | • The deposition rate is high and thick coatings can be readily obtained and the process is generally competitive, and it is relatively easier to cause chemical reactions on the surface of substrate than physical change.

• Its relatively low cost and improved interfacial bonding between the coating material and the substrate before heat treatment or sintering | • The high temperature supply. The particle material of process (also named as precursor) usually has a high evaporation temperature. Normally precursors evaporates at 600°C, at which temperature substrates are not stable.

• Its tendency towards non-conformal growth on non-planar surfaces. |

Source: Zhang et al. (2019)

2.6.1 Hydrothermal synthesis method

Hydrothermal synthesis is one of the most commonly used methods for preparation of nanomaterials. It is basically a solution reaction-based approach. In hydrothermal synthesis, the formation of nanomaterials can happen in a wide temperature range from room temperature to very high temperatures. To control the morphology of the materials to be prepared, either low-pressure or high-pressure conditions can be used depending on the vapor pressure of the main composition in the reaction (Gan et al., 2020). Moreover, hydrothermal synthesis is a method of synthesis of single crystals that depends on mineral solubility in hot water under high pressure. This method is usually a widely used technique because of its low cost, low temperature, high yield, scalable process, and large scale method. It is able to control the shape and dimension of nanomaterials by reaction time, temperature, pH value, and capping agent

during the hydrothermal process. Hydrothermal processing involves heating aqueous slurries of organic wastes at high pressures to create an energy carrier with a higher energy density, which is similar to how the earth produced fossil fuels over millions of years.

Normally this method were conducted in steel pressure vessels called autoclave with or without Teflon lines under controlled temperature or pressure with the reaction in aqueous solutions. It also provide a high-pressure and closed environment to facilitate solvation of the reagents and reactions between liquid precursors. Compared with other synthesis methods, this method can synthesize high-crystalline nanomaterials under relatively mild conditions (Qiu et al., 2021).

2.7   Material chemistry

2.7.1   Characterization of photocatalyst

The characterization of heterogeneous catalysts is an important study because it provides data that can be used to better understand the synthesis catalyst. There are various methods that can be used to characterize g-C_3N_4 which are physical characterization, chemical characterization, and optical characterization.

2.7.1.1 Physical characterization

For this research, there are 2 types of physical characterization that will be used, which are XRD and SEM-EDX. XRD plays a major role in characterisation because it can analyse and provide structural properties of the sample at an atomic scale (Ali et al., 2022). XRD also a technique used in materials science to determine a material's crystallographic structure. According to El Bourakadi et al. (2021), XRD is a technique for analyzing crystalline materials that uses the diffraction of X-rays by matter. It provides information on crystal structure, phase, preferred crystal orientation (texture), and other structural parameters such as average grain size, crystallinity, strain, and crystal defects. XRD peaks are created by the constructive interference of a monochromatic beam of X-rays diffracted at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the distribution of atoms within the lattice. As a result, the XRD pattern is the fingerprint of a material's periodic atomic arrangements. The International Centre for Diffraction Data database (ICDD) of XRD patterns can be used to identify the phase of a wide range of crystalline samples (Ali et al., 2022).

Moreover, XRD is well suited to determining the bulk structure and composition of crystalline heterogeneous catalysts (Hiden, 2021).

Other than that, it is used for phase analysis, crystalline variants, and to study the grain and particle size of nanomaterials (Ghalkhani et al., 2021). XRD is an elastic scattering (no loss of photon energy) technique that produces increasing interference as more ordered materials are analyzed. The term "diffusion" is more appropriate for noncrystalline materials. This is a powerful nondestructive crystalline material characterization technique that provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters such as average grain size, crystallinity, tension, and crystal defects (El Bourakadi et al., 2021). The X-ray source in an XRD device is a metal (normally cobalt or copper) that irradiated with a high energy electron beam. X-rays is an electromagnetic wave radiation, and crystals are ordered arrays of atoms. When an X-ray hits a crystal lattice, secondary spherical waves are diffracted according to Bragg's law.

Besides that, XRD works by irradiating a material with incident X-rays and then measuring the X-ray intensities and scattering angles that leave the material. The main usage of XRD analysis is the identification of materials based on their diffraction pattern. In addition to phase identification, XRD provides information on how the actual structure differs from the ideal one due to internal stresses and defects. Usually, this method is extremely useful in science, engineering, and technology (El Bourakadi et al., 2021). Besides that, XRD also can detected amorphous phase (non-cystalline material). The best way to differentiate between amorphous and crystalline materials is to measure XRD patterns. Based on Figure 2. crystalline material always exhibit sharp diffraction peaks while amorphous does not (Ali et al., 2022). There are a few limitations for XRD analysis which are the sample must exhibit crystalline structure or else no result will be detected, and the analysis of samples at high angles will cause peaks to overlap and provide inaccurate results.
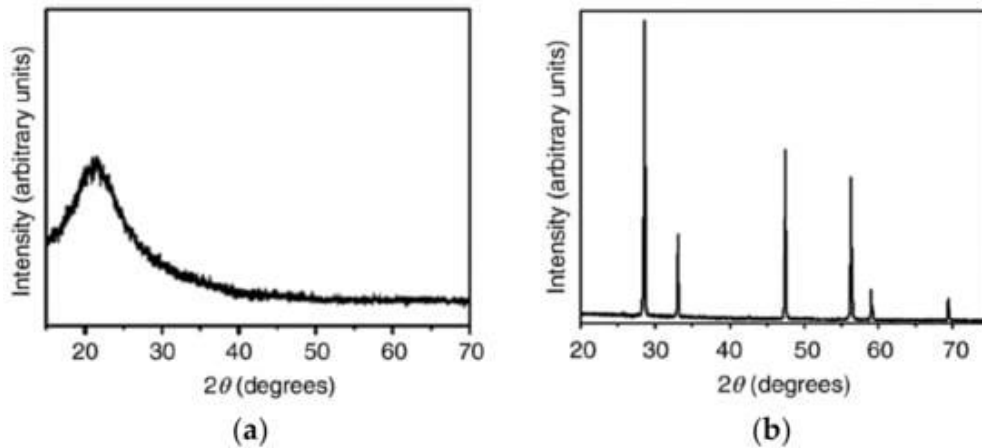
Figure 2.5　　XRD qualitative graphs that represent (a) an amorphous material and (b) a crystalline material

Source: Ali et al. (2022).

SEM-EDX is another kind of physical characterisation that is applied in this study. SEM-EDX is the most well-known and commonly utilized surface analytical technology for obtaining compositional and morphological information. Using a primary electron beam that is highly focused and scanning to hit the sample with high-energy electrons, high-resolution images of surface topography are created (Zhen, 2019). Since light is replaced with electron beams in this technique, it is analogous to light microscopy. Electron beams will delivered to the sample in a vacuum region, where they will be directed and focussed by electromagnetic lenses and metal apertures. Different types of electrons will be created after the sample's surface is struck by the electron beam. Backscattered electrons, secondary electrons, auger electrons, X-rays, and cathodoluminescence are among the types of electrons that are produced. The backscattered and secondary electrons will produce magnified picture information, whilst the auger electron and X-ray will produce compositional information. Since electron beams are employed as the light source, the main disadvantages of SEM are that the image produced will only be in black and white, and it can only detect materials that are solid, inorganic, and tiny enough to be put on the specimen holder. Additionally, the size of the electron microscope chamber restricts the size of the sample (Gleichmann, 2020). Furthermore, the relative abundance of the elements present on the specimen's surface can be determined using the EDX technique, which can examine the composition (Scimeca et al., 2018). The difference in energy detected in the x-ray can provide the compositional information of the specimen by detecting the x-rays that will be produced when the sample is struck by the electron beam (Erdman et al.,

2019). Only x-rays produced by atoms with atomic numbers greater than four can be detected. To put it briefly, the use of SEM-EDX can reveal topographical, morphological, and even compositional details regarding g-C_3N_4 and the dopant present for a clearer understanding.

2.7.1.2 Chemical characterization

FTIR spectroscopy is a non-invasive and label-free spectroscopic technique that can be used to examine molecular structure with no restrictions on molecular mass. The energy of infrared light helps chemical molecules change between their vibrational energy levels. If the frequency of the radiation matches the vibrational frequency of the molecule then the radiation will be absorbed, causing the change in the amplitude of the molecular vibration (Munajad & Subroto, 2018). This difference in frequency absorption allows FTIR to detect specific compounds that are present in the specimen. The combination with the mathematical fourier transform for IR spectroscopy allows quantitative and qualitative information to be obtained rapidly. The range of the infrared region is 12800 cm^{-1} to10 cm^{-1} and can be divided into three regions which are the near-infrared region (12800 cm^{-1} to 4000 cm^{-1}), mid-infrared region (4000 cm^{-1} to 200 cm^{-1}) and far-infrared region (1000 cm^{-1} to 50 cm^{-1}). FTIR spectroscopy can be used to learn more about the functional groups, chemical structure, and composition of a compound or combination of compounds because the energy of these vibrational transitions is specific to particular chemical bonds (Munajad & Subroto, 2018). Furthermore, by using the FTIR, it can identify unknown materials and find additives (Titus et al., 2019). It can also determine the quality or consistency of a sample as well as the number of components in a mixture. Moreover, FTIR is easy to use because it only takes a few seconds to measure the sample.

2.7.1.3 Optical characterization

UV-Vis is an optical characterization technique used in this study because it is low-cost, fast, and facile (Faraji et al., 2021). Spectrometers are devices that are used to measure the spectra of samples, especially the electromagnetic radiation intensity as a function of the wavelength of the radiation. There are many types of spectrometers designed to measure different types of spectra and yield different types of information about their material samples. For example, a spectrophotometer measures ultraviolet, visible, and near-infrared light that is either reflected from or transmitted through a sample. The energy of light has a fixed value that is inversely proportional to its wavelength. As a result, shorter light wavelengths carry more

energy while longer ones carry less. In order to promote electrons in a substance to a higher energy state, which we can observe as absorption, a certain amount of energy is required. In a substance, electrons in various bonding conditions require different amounts of energy to move them to higher energy states. This is why light absorbs at different wavelengths in different substances. Usually, the graph that will be obtained from this analysis is absorbance versus wavelength. The ultraviolet region is defined as 200 nm to 400 nm, while the visible region is between 400 nm to 800 nm. If the wavelength exceeds 800 nm, it is classified as infrared (Nivetha et al., 2022). The band gap can be define from the data of UV-Vis by using the Tauc equation. It represents the direct transition of band gap energy by plotting the graph between ahv versus energy. The distance between the conduction band and the valence band of electrons is known as a band gap. The minimal energy needed to excite an electron up to a condition in the conduction band where it can engage in conduction is essentially represented by the band gap.

2.8   Summary

The literature review for this report is contained in this chapter. Since the target for this research is to reduce dye wastewater, the theory of the dye wastewater, sources of dyes, and types of dyes are discussed. Moreover, the conventional dye wastewater was also studied. Among various proposed photocatalysts, TiO_2 has been studied because it is considered the most widespread photocatalyst for several reasons. Other than that, the theoretical aspects of $g\text{-}C_3N_4$ and carbon were also studied. The hydrothermal synthesis method was studied since it is used for the synthesis method of photocatalysts. Last but not least, the material chemistry, like physical characterization, chemical characterization, and optical characterization, was studied.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This study has been done based on the specified research objectives. A general diagram detailing about the flow of research work are shown in the following flowchart (Figure 3.1).
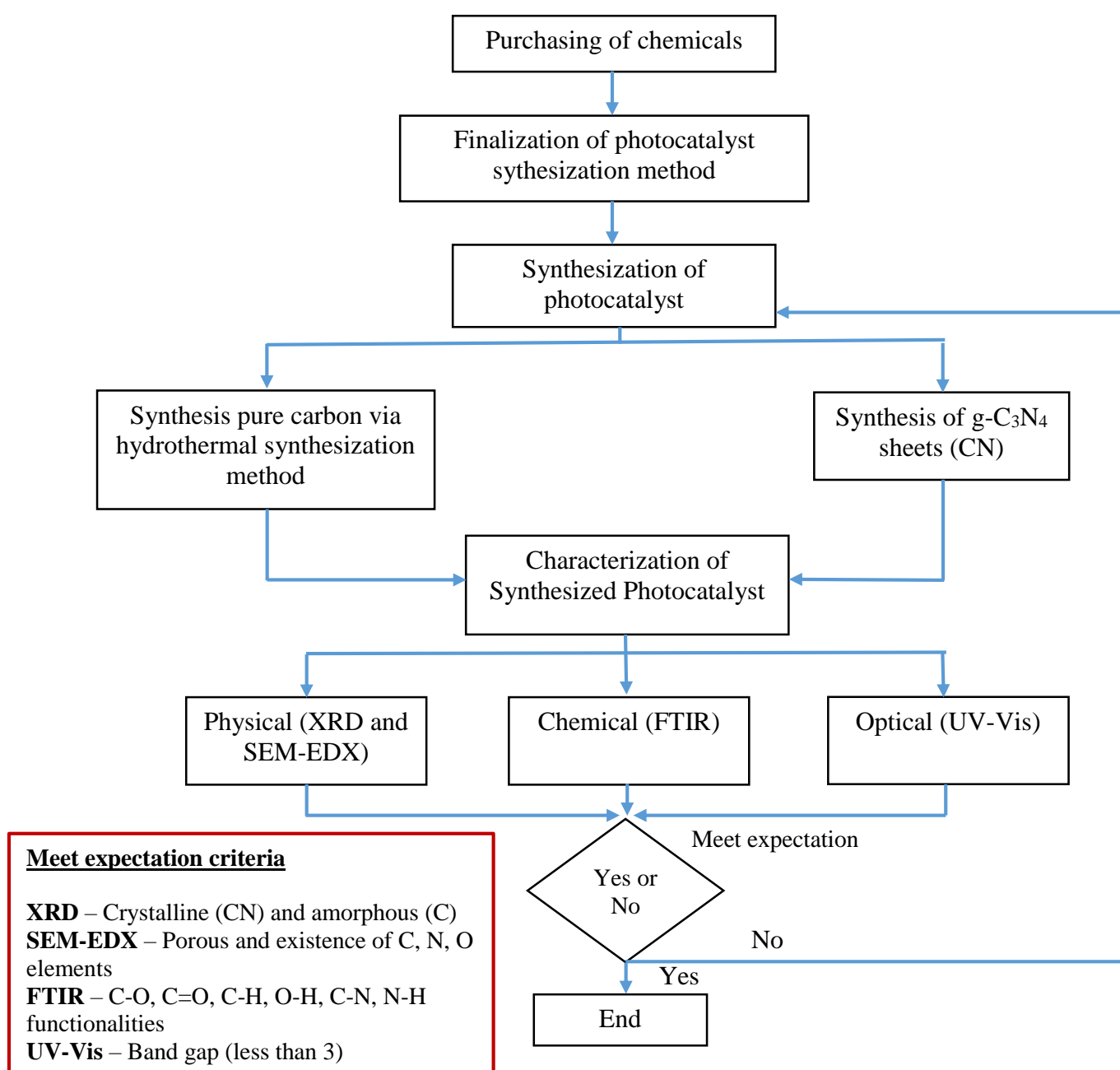

Figure 3.1   Flowchart of the overall g-C$_3$N$_4$ and coconut shell husk process

3.2   Reagent and material

All the chemical reagents that will be used in this study are analytical grade and purchased from Sigma-Aldrich Chemical Co. For the synthesis of carbon, ethanol (CH_3CH_2OH, 190 proof, ACS spectrophotometric grade, 95.0%), dichloromethane (CH_2Cl_2, anhydrous, $\geq$99.8%, contains 40-150 ppm amylene as stabilizer), and acetone (($CH_3)_2CO$, ACS reagent, $\geq$99.5%) will be used. Moreover, coconut shell husks will also be used and were collected from 'A' Santan Segar, Kuantan, Pahang. In addition, urea (CH_4N_2O), nitric acid (HNO_3, ACS reagent, $\geq$90.0%) solution, sodium hydroxide (NaOH, ACS reagent, $\geq$97.0%, pellets), and barium sulfate ($BaSO_4$) will be used to create g-C_3N_4.

3.3   Preparation of pure carbon via hydrothermal synthesization method

The mixture of coconut shell husk and ethanol was synthesized via hydrothermal treatment. The coconut shell husk was thoroughly washed with distilled water and drained to remove excess water. The coconut shell husk was cut into smaller pieces, and grinded into fine paste using universal blender, and filtered using a 0.1 mm sieve. 40 ml of the juice was mixed with 30 ml of ethanol under vigorous stirring for 5 minutes. The mixture was then poured into a Teflon-lined stainless steel autoclave and heated in the oven at a constant temperature of 120 °C for 150 minutes. The resulted dark brown solution was washed with dichloromethane (CH_2Cl_2) and centrifuged at 3000 rpm for separation of the less fluorescent deposit. Excess acetone (($CH_3)_2CO$) was added to the upper parts of the solution and centrifuged at 4,000 rpm to obtain highly fluorescent carbon of size ranging from 1.5 – 4.5 nm.
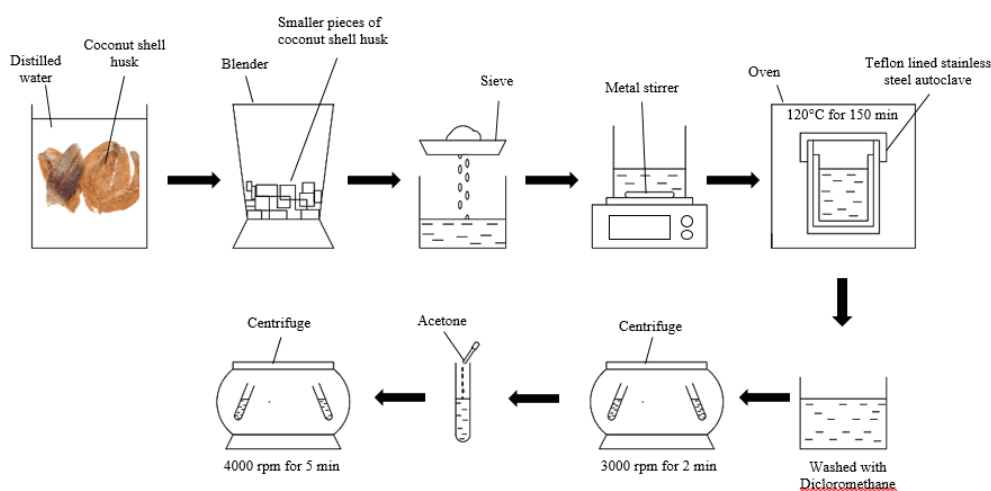

Figure 3.2   Step to prepare the pure carbon

3.4 Preparation of g-C₃N₄ sheets (CN)

10 g of urea was placed in an alumina crucible with a cover and, then, heated to 550 °C with a heating ramp of 2°C/min and maintained at this temperature for 2 hours. After calcination, the light-yellow powder indicated the formation of bulk g-C₃N₄. Then, 100 mg of bulk g-C₃N₄ was stripped in a 40 mL HNO_3 solution (VHNO3 /VH_2O = 1:1) at 80°C for 1 hour. The obtained mixture was diluted with deionized water and adjusted to neutrality with sodium hydroxide. The g-C₃N₄ sheet was then collected by centrifuged at 4000 rpm for 15 minutes and washed three times with water to remove salt.
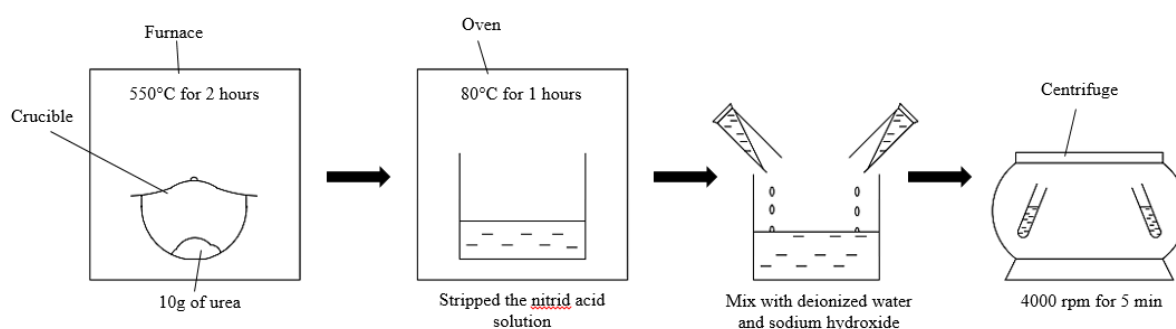

Figure 3.3   Step to prepare the g-C₃N₄ sheets (CN)

3.5 Materials chemistry

Several piece of equipment were used to characterize the synthesized samples. Characterization is important step in studying the structure of the catalyst surface, composition of the catalyst, and the chemical properties of the catalyst. The characterization of the catalyst could provide the explanation for its catalytic activity. The analysis techniques applied in this research involved XRD, SEM-EDX, FTIR, and UV-Vis.

XRD is an analytical technique based on the diffraction of X-rays by matter, especially crystalline materials. SEM produces detailed high-resolution pictures of the sample by rastering a focussed electron beam across the surface and detecting a secondary or backscattered electron signal, whereas EDX gives elemental identification and quantitative compositional information. Besides that, FTIR analysis uses infrared light to scan the samples as it identifies organic, inorganic, and polymeric components. Lastly, UV-Vis is used to quantify light absorbance across the electromagnetic spectrum's ultraviolet and visible regions.

3.5.1 XRD

The prepared photocatalysts crystallite phase composition were analysed through X-ray diffractometer (Brand: Bruker, Model: D8 Advance). In this analysis, Cu-Kαradiation (wave length, λ = 0.15418 nm) was used as the source. All the samples were characterized to know the characteristics of solid (crystalline or amorphous). The X-ray diffraction patterns were set for the 2θ range of 10 to 80° with 2θ of 5° per minute for this study. Prior to this analysis, the solid samples were cleaned through ethanol, acetone and ultrapure water with sonication each for 10 min.

The crystallite size of the prepared photocatalyst has been calculated by following Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Where,

D = Coherent scattering length (crystallite size).

β = Full width half maximum (FWHM) for the 2θ peak.

K = Shape factor taken as 0.89 nm for calculations.

λ = Wavelength of X-ray (0.154 nm).

θ = Diffraction angle.

The lattice space of the prepared photocatalyst has been calculated by following Bragg's equation:

$$d = \frac{\lambda}{2 \sin \theta}$$

Where,

d = Distance between crystal planes.

λ = X-ray wavelength.

θ = Diffraction angle of crystal plane

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3.5.2 SEM-EDX

The crystallite structure and surface characteristic of the prepared photocatalysts were determined using SEM analysis. In this experiment, the SEM images were obtained at accelerating voltage of 15 kV using Hitachi Tabletop TM3030 Plus machine. EDX was used to determine the occurrences of important elements present in prepared photocatalysts in conjunction with SEM. All the sample powder was sputter-coated with gold (Au). The coating process can help to reduce the charging effect on the electron so that the electron did not stay at only one place.

3.5.3 FTIR

The FTIR analysis was used to determine the particular functional groups existed within the prepared catalysts. All spectra were identified with a FTIR spectrometer (Brand: Perkin Elmer, Model: Spectrum 100) in a transmission mode and scanned over the range between 400 and 4000 cm^{-1} wavenumbers with a resolution of 4 cm^{-1}. The sample were cleaned through ethanol, acetone and ultrapure water before FTIR analysis.

3.5.4 UV-Vis

The optical absorbance and photochemical properties of the prepared photocatalysts was certified by UV-Vis analysis. The visible light absorption ability was tested based on the band gap energy of the prepared photocatalysts. The visible light absorption spectrum that works in the 300-900 nm of the prepared photocatalyst was performed by UV- 2600, SHIMADZU, and quartz cell (10 mm path length). Eg of the photocatalysts were determined by plotting Tauc's plot as shown in equation below. The Eg was obtained by extending the gradient of the graph to x- axis.

$$(\alpha h v)\ 2 = K(h v - E g)$$

where:
h = the plank constant
v = the frequency of the photon
Eg = band gap energy
K = a constant

3.6   Summary

A flowchart for overall research activities is included in this chapter. It also consists of the materials, reagents, and equipment that are used to conduct the experiment. Moreover, this chapter also involves the preparation of pure carbon, and CN. The material chemistry for the characterization of the synthesis samples is also included in this chapter.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

In this chapter, the characterization of pure carbon and pure g-C$_3$N$_4$ were performed by using x-ray diffractometer (XRD) and scanning electron microscope-energy dispersive x-ray (SEM-EDX), fourier-transform infrared (FTIR), and ultraviolet visible spectroscope (UV-Vis) analyzer. By analyzing the samples, the difference between pure carbon and pure g-C$_3$N$_4$ could be observed.

4.2 X-ray Diffraction (XRD) Analysis

The XRD results for pure carbon and pure g-C$_3$N$_4$ are shown in Figure 4.1 and Figure 4.2 respectively. By analyzing the pure carbon peak, it is looks like broad humped peak then the material will be amorphous with short range ordering. As mentioned before, if the graph gets a very broad humped peak, then the material will be amorphous with short range ordering (Ali et al., 2022). According to Kumar Rout (n.d.), the fiber contains high amounts of amorphous material such as lignin, hemicellulose, and amorphous cellulose; these two peaks are smeared, thus appearing as one broad peak. Based on Figure 4.1, it shows three significant peaks which are at 21°, 22.3°, and 23°, respectively. According to Zhen (2019), the pyrolyzed coconut shell also had a peak around 28.3°, implying that the carbon produced was indeed carbon. Therefore, in this study, the carbon was created using the right synthesis method.

By analyzing the pure g-C$_3$N$_4$ peak, it was observed that there were 14.8°, 18.7°, 22.4°, 26.7°, and 29.0° appeared in by the XRD pattern. According to Liu et al. (2019) the peak at 13.1° and 28.33° is in good agreement with graphitic phase carbon nitride. The lower angle diffraction peak at 13.1° corresponds to tris-triazine units (100), while the stronger one at 27.3° is caused by aromatic segment interlayer stacking (002). Moreover, the CN graph indicates that nitrogen is present since nitric acid is used in the synthesis of CN. Therefore, the nitrogen was part of the CN's containment. Furthermore, it was demonstrated that g-C$_3$N$_4$ could be produced in good form due to the use of urea in the synthesis process. Thus, it clearly shows that the

catalyst produced was indeed g-C₃N₄ because the information or substance of the CN is comparable to other articles.
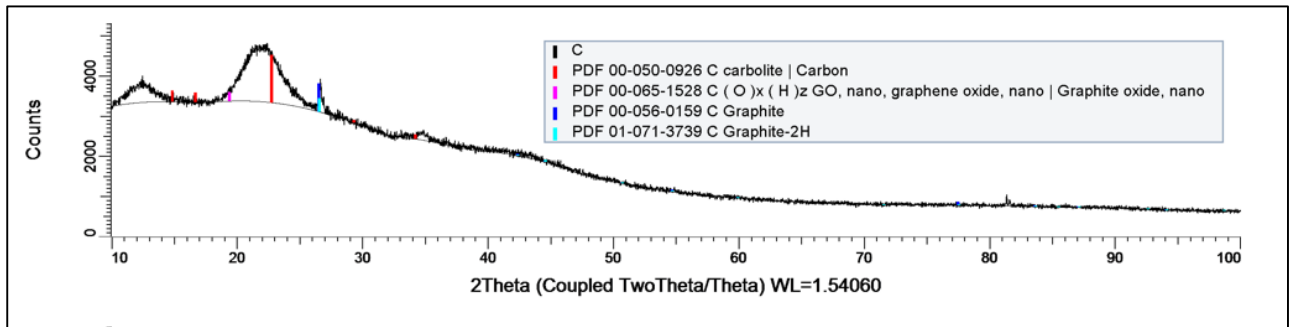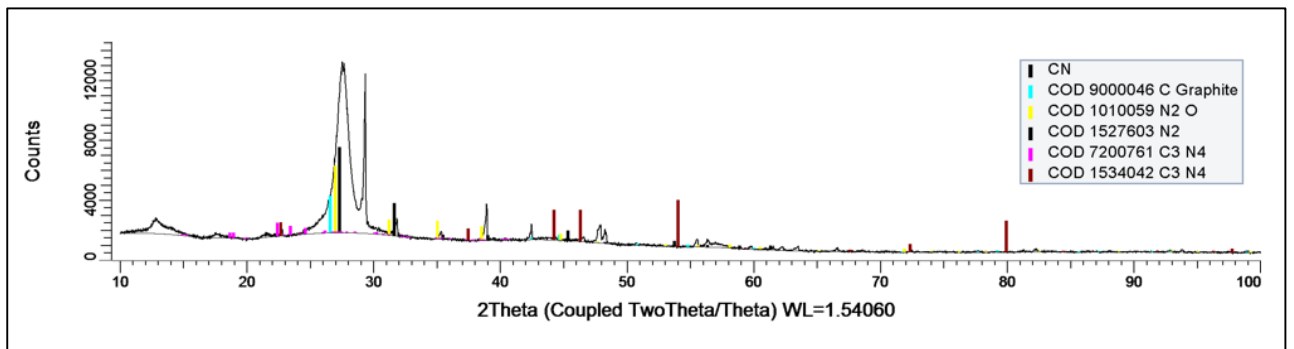

Figure 4.1   XRD of C

Figure 4.2   XRD of CN

4.3   Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX)

Figure 4.7 and Figure 4.8 illustrate the surface morphology of C and CN composites at 2,500 magnification by using SEM. Figure 4.3 demonstrates that C has a smoother surface with fewer irregular shapes.Based on Zhen (2019), he also found that the carbon material had cracks and residues, but there were no particles of an unusual shape. According to Saiyyidah Tus Zuhroh et al. (2022), the coconut husk structure looks long, smooth, organized, tight, and strong. This is due to the fact that the cellulose is still firmly encased with hemicellulose and lignin.

Figure 4.4 shows that CN has a structure that resembles overlapping sheets with irregular shapes and irregular porous. According to Paul et al. (2019), the shape of the product will be different based on its calcination temperature during the preparation of the product. The morphology of the sample prepared at 450 °C and 500 °C appears to be lumpy, whereas the

sample prepared at 550 °C has a stacked, layered morphology. Samples prepared at 600 °C and 650 °C resulted in the contraction of layered flakes of g-C₃N₄, suggesting the possibility of a reduction in the surface area at calcination temperatures above 550 °C. For better formation of g-C_3N_4, the calcination temperature must range from 350 °C to 550 °C because it can enhance the absorption of visible light (Lu et al., 2018). Additionally, it contains a lumpy structure formed by nitrogen (N) that aids in the absorption of visible light.

In conjunction with SEM, energy dispersive x-ray spectroscopy (EDX) was performed to identify the elemental composition of the powder. The EDX spectrum of C in Table 4.1 unveils the elements that are present in C, and it consist of carbon (C) and oxygen (O). Furthermore, the mass of the carbon (52.38 %) is higher than the oxygen (47.62 %). This is because coconut shell husk is basically an organic structure with large amounts of carbon and oxygen in its structure. Table 4.2 shows the percentage of mass and atoms of the elements that are present in CN. The EDX analysis of all samples shows the presence of approximately 17.06 % oxygen on the surface of the powder. According to Aghamir et al. (2019), it can be attributed to ambient contamination of the graphite substrate with oxygen. Moreover, the percentages of mass for carbon and nitrogen are 25.12 % and 57.82 % respectively. This is due to the use of g-C_3N_4 and nitric acid in the synthesis of CN.
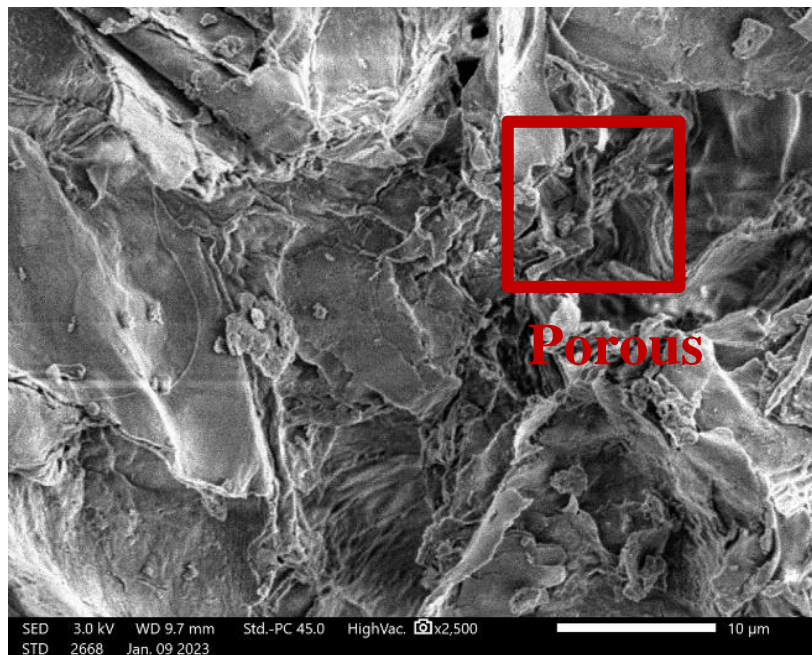

Figure 4.3   SEM image of C

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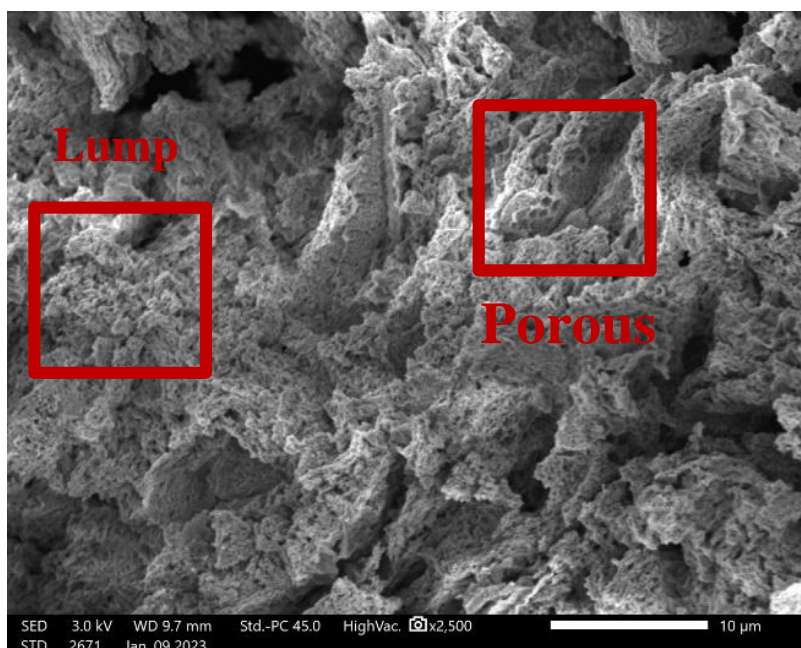
Figure 4.4   SEM image of CN

Table 4.1   EDX analysis of C

Element	Mass (%)	Atom (%)
C	52.38	59.44
O	47.62	40.56

Table 4.2   EDX analysis of CN

Element	Mass (%)	Atom (%)
C	27.71	31.17
N	64.79	62.50
O	7.49	6.33

4.4   Fourier Transform Infrared (FTIR) Analysis

The FTIR spectrum has been used to identify the functional groups of the prepared samples and is presented in Figure 4.5 and Figure 4.6. FTIR absorption spectrum for C and CN were obtained in the 400 cm^{-1} to 4000 cm^{-1} range. For the result for pure carbon, it shows a few peaks that were observed in this study. According to Zhen (2019), there is no distinct peaks were observed from 400 cm^{-1} to 4000 cm^{-1}. Moreover, C had a broad peak at 3348 cm^{-1} because the O-H stretching was attributed to the presence of chemical compounds with hydroxyl functional groups such as phenolic or aliphatic alcohol and carboxylic acid in both the activated carbons from coconut husk, which indicates the presence of chemical compounds with hydroxyl functional groups in the activated carbons from coconut husk. According to Jeanne Rampe et al. (2021), the absorption appears at a wave number of around 3400 cm^{-1} is indicates the presence of an O-H group. Besides that, the wave number with an absorption band peak of 2921 cm^{-1} indicates the vibration of the aliphatic C-H group which indicates a hydrocarbon compound. Based on the literature review by Jeanne Rampe et al. (2021), the absorption that appears at a wave number of 2800 cm^{-1} to 2900 cm^{-1} are indicates the presence of an aliphatic C-H group. Furthermore, the absorbance also appears at 1609 cm^{-1} and 1035 cm^{-1}. Based on Jeanne Rampe et al. (2021), they also found at 1800 cm^{-1} to 2300 cm^{-1} indicates the presence of a C=O group which is a carbonyl group, while absorbance at wavenumber 800 cm^{-1} to 1300 cm^{-1} indicates the presence of a CO group. The presence of O-H, C-H, C=O, and CO groups refers to the chemicals used in the synthesis method to produce C. O-H groups come from cellulose, hemicellulose, and lignin that are found in the coconut shell husk, while C=O groups were assigned from the hemicelluloses of the coconut shell husk.

By analyzing the pure graphitic carbon nitride graph, a sharp peak at 805.48 cm^{-1} was observed. According to Wang et al. (2018), the peak of graphitic carbon nitride at 810 cm^{-1} is attributed to the breathing vibration of tri-s-triazine units however, an alternative view assigns it to an out-of-plane collective wagging mode of the N and C atoms in the heptazine (Ben-Refael et al., 2020). Based on Zhen (2019), he also found at 805.6 cm^{-1} indicates the characteristic of heptazine rings. Moreover, there are many peaks in the range 1200 cm^{-1} until 1700 cm^{-1} due to in plane stretching modes of the rings, such as typical aromatic vibrations at 1312 cm^{-1} (C-N stretch), 1457 cm^{-1} (s – triazine ring), and 1653.04 cm^{-1} (C=N stretch). The other broad absorption bands in the 1200 cm^{-1} until 1600 cm^{-1} region are assigned to the typical stretching vibration modes of C-N heterocycles (Wang et al., 2018). Besides that, a sharp peak

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was observed at 3284 cm^{-1} which represents the presence of N-H stretch. The broad absorption band from 3000 cm^{-1} to 3300 cm^{-1} originates from the stretching vibration of the N-H bond, associated with uncondensed amino groups (Wang et al., 2018), and can be assigned to the stretching modes of secondary and primary amines and their intermolecular hydrogen-bonding interactions. Based on Zhen (2019), he also found at 3170 cm^{-1} indicated the stretching vibration modes for the N-H groups. All the functional groups in this study refer to the chemicals used in the synthesis method to produce CN. N-H groups were designated as an amino group that is found in urea, while the C=O group is also found in urea.
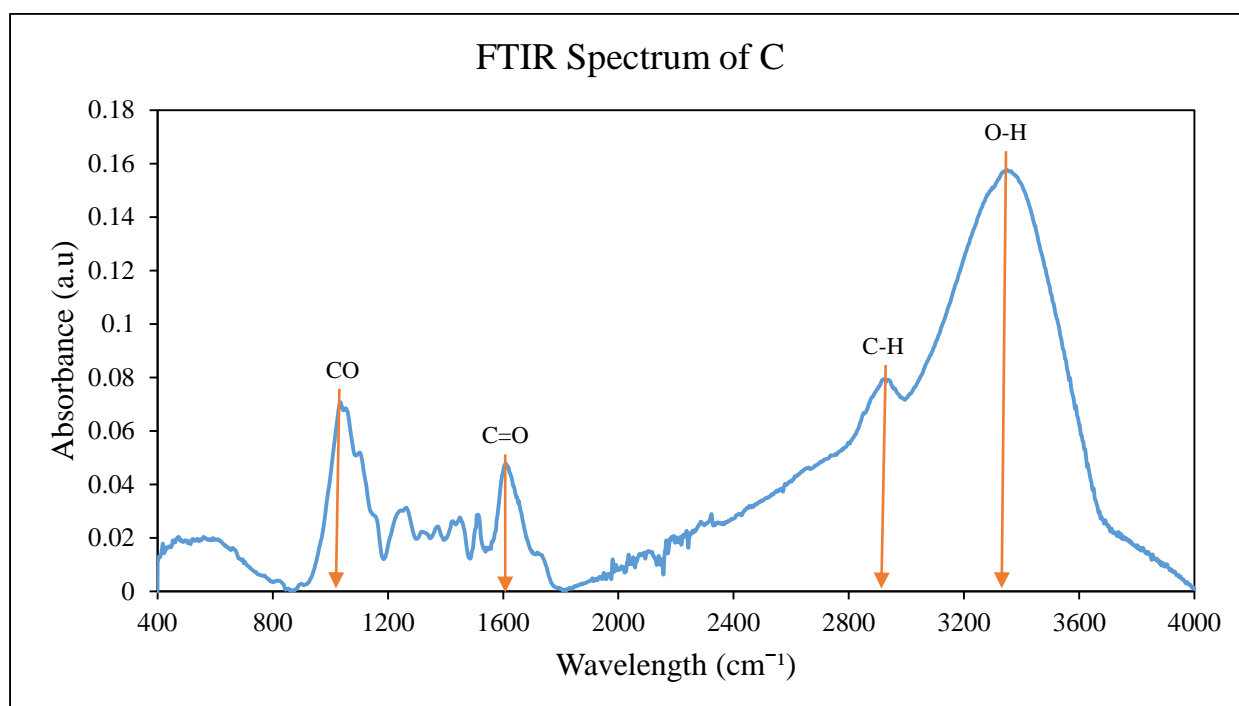
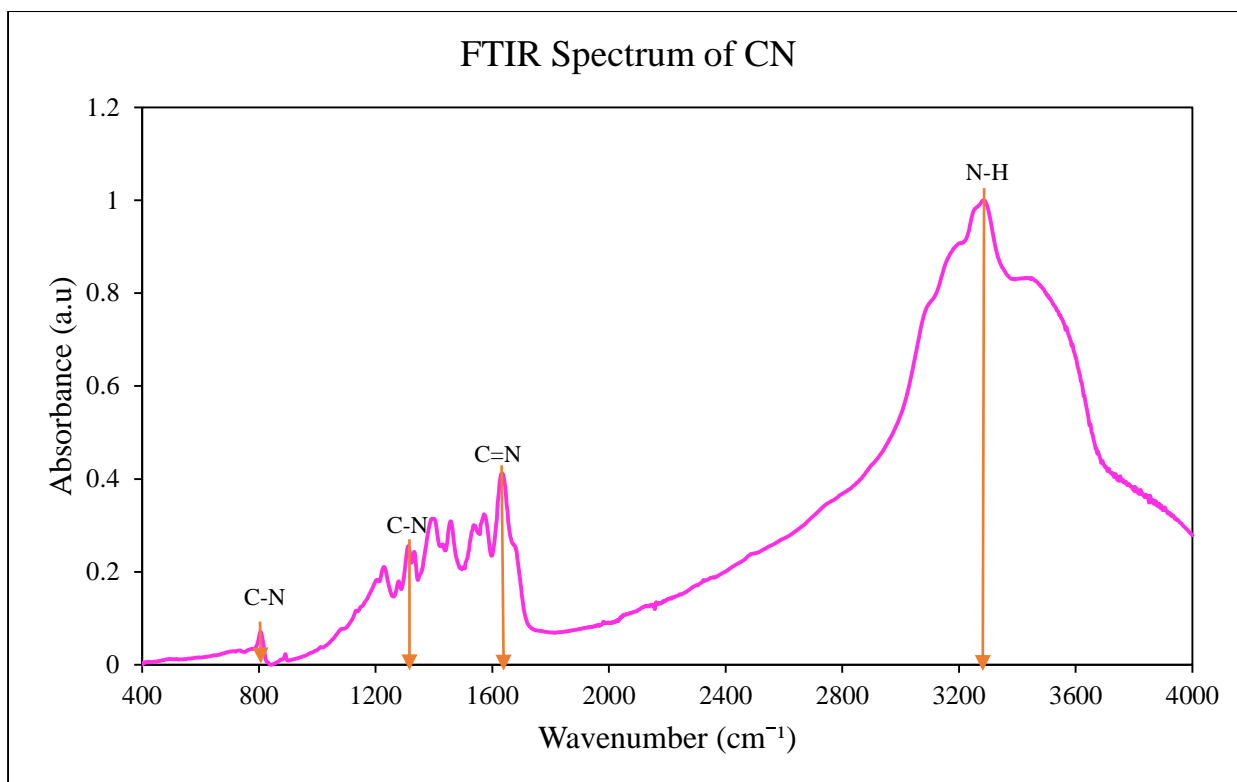

Figure 4.5   FTIR Spectrum of C

Figure 4.6   FTIR Spectrum of CN

4.5   Ultraviolet-Visible (UV-Vis) analysis

The UV-Vis absorption spectrum has been attributed to the analysis of the optical properties of the synthesized catalysts. Figure 4.1 shows the graph of the absorbance against wavelength for the C and CN results. The UV-Vis absorption spectrum for C and CN were obtained in the 200 nm to 800 nm range because only molecules with the proper energy difference between their bonding and anti-bonding orbitals can thus absorb UV-Vis light. UV-Vis can be divided into ultraviolet and visible. The ultraviolet region is defined as 200 nm to 400 nm, while the visible region is between 400 nm and 800 nm. In addition, the absorption intensity in the UV region was high while the visible region was low in the catalyst, however, it is still possible for optical purposes (Nivetha et al., 2022).

Based on Figure 4.7, this result for both samples indicates a wide absorption range in the UV area, which are 261 nm and 257 nm for the C and CN, respectively. Besides that, by analyzing the pure carbon graph, it was observed that the absorbance region for visible started from 0.46 a.u. until 0.95 a.u. while for the g-C_3N_4 graph, it started from 0.17 a.u until 0.71 a.u. The pure carbon catalyst exhibits an expanded absorption wavelength region compared to that

of CN. Moreover, the majority of CN has been reported to have an absorbance tail at longer wavelengths (Zhang et al., 2018). It is worth noting that the weak absorption tails were observed due to structure defects in heated samples, which may improve the visible absorption of materials, and this is most likely due to structure defects formed in high-temperature samples. The occurrences of nitrogen (64.79%) based on the EDX results also contributed to the absorption under visible light.

Figure 4.8 shows the band gap energy of the catalyst. The Tauc equation was used to calculate the band gap energy (Eg). It represents the direct transition of band gap energy by plotting ahv versus energy. The results show that the bandgap energy increases as particle size decreases. The band gap energy of the prepared catalyst were acquired as 3.6 eV and 2.9 eV, shown in Figure 4.2 for the C and CN, respectively. According to Ragupathi et al. (2020), g-C_3N_4 is a versatile polymeric, organic semiconducting material and has a band gap of 2.7 eV. The photocatalytic performance of a photocatalyst strongly depends on its electronic band structure and band-gap energy, Eg. For an efficient photocatalyst, the band-gap energy should be smaller than 3 eV to extend the light absorption into the visible region to efficiently utilize the solar energy. The ability to absorb UV light is limited due to the wide band gap (Zhao et al., 2018). As stated by Kusmierek, (2020), a decrease in the band gap enables the performance of a photocatalytic degradation process under visible light irradiation or even sunlight, which is safer and more economic than UV irradiation. This is because the narrow band gap can improve electron transport (Ding et al., 2020) and gives rise to strong thermal excitation of intrinsic carriers. According to Hen (2019), the g-C_3N_4 with the phase of g-h-heptazine is mainly focused due to the small band gap energy that has the potential of water splitting efficiency. Compared to their wide band gap counterparts, narrow band gap semiconductors have the characteristics of high carrier concentration, difficulty in controlling p-type and n-type doping, and being soft mechanically. In this study, it is shown that, the absorption spectra of this catalyst can go up to the visible light region without any doping.
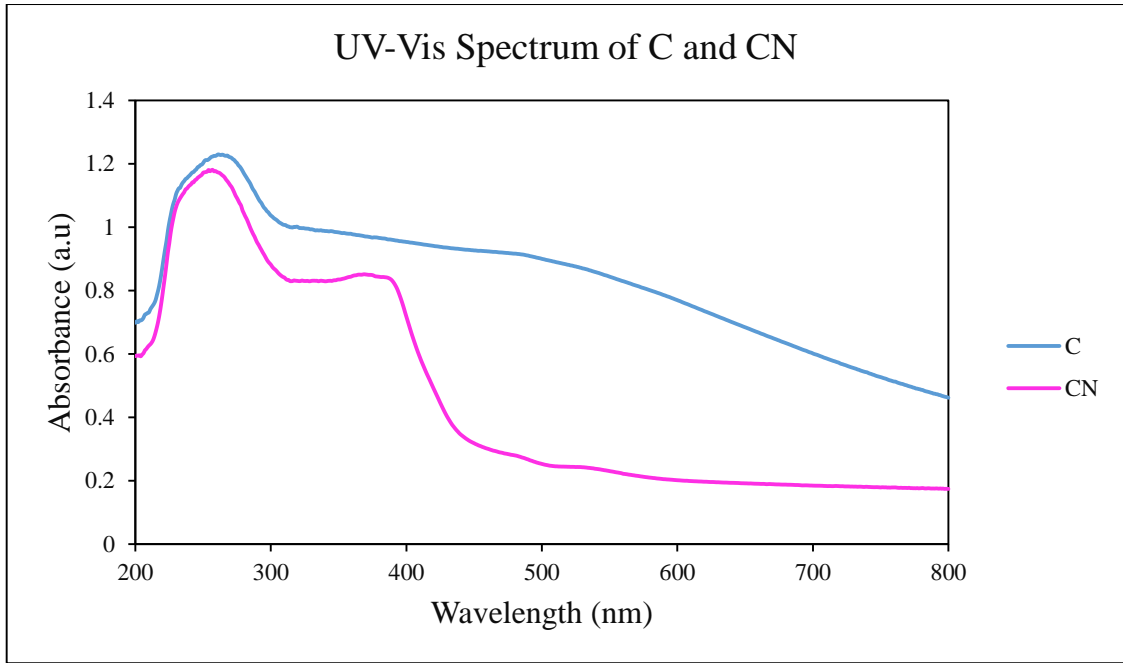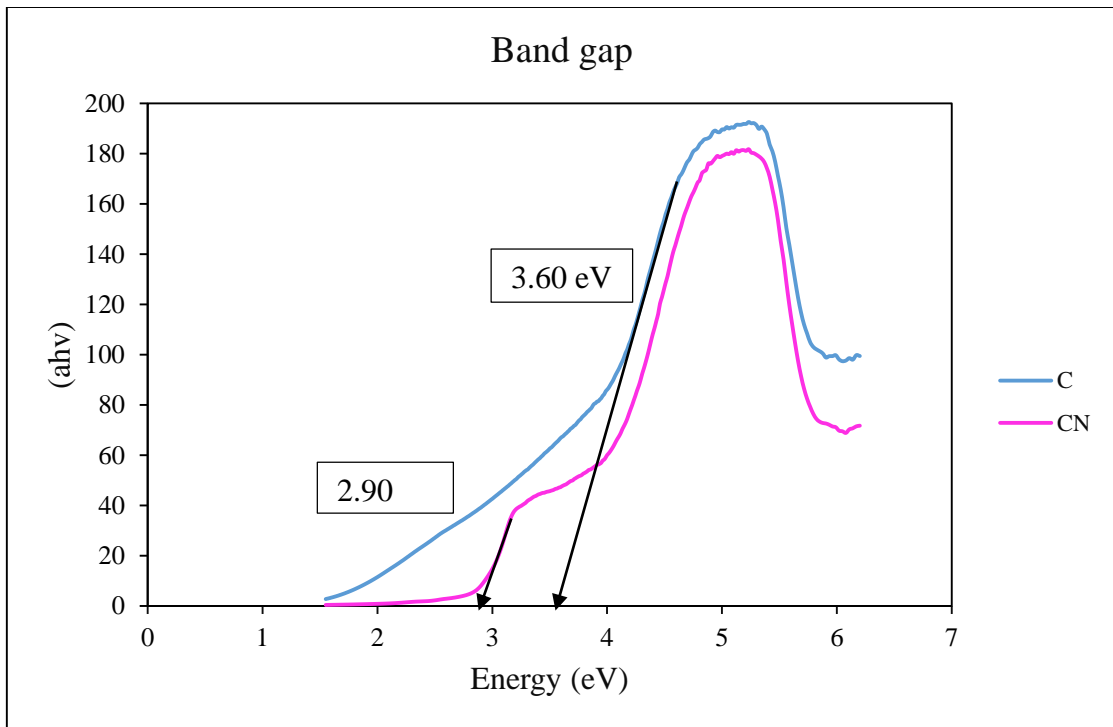
Figure 4.7   The UV-Vis spectrum of C and CN

Figure 4.8   The band gap of C and CN

CHAPTER 5

CONCLUSION

5.1   Conclusion

In conclusion, pure carbon and pure g-C_3N_4 were synthesized successfully using coconut shell husk and urea respectively. The SEM-EDX results shows that the structure of C smoother surface with the no irregular shapes and it is consisting of C and O. For the CN results, it shown that shows that CN has a structure that resembles overlapping sheets with irregular shape and irregular porous, and it is consists C, O, and N. It is shown that the catalyst was created using the right synthesis method because the information of the characteristic is comparable to other articles. Furthermore, the XRD results shows that the C peak looks like broad humped peak then the material will be amorphous with short range ordering, while the peak of CN looks like sharp peak that the material will be crystalline. Among the samples, CN shows the reduced band gap energy which is 2.90 eV, while for C is 3.60 eV. As mentioned before, a decrease in the band gap enables the performance of a photocatalytic degradation process under visible light irradiation or even sunlight, which is safer and more economic than UV irradiation. Furthermore, the FTIR results show that the functional group for C is O-H, which is derived from cellulose, hemicellulose, and lignin, and the C=O group is derived from hemicelluloses that are contained in the coconut shell husk. While for CN, N-H, and C=O groups were found because of the use of urea to produce bulk g-C_3N_4. Thus, it clearly shows that all the functional groups refer to the chemicals used in the synthesis method to produce C and CN. As a result, g-C_3N_4 can be used in the dye wastewater treatment. Apart from this, it can meet SDG 6 because dye wastewater can be treated and dangerous contaminants such as toxics, carcinogens, and xenobiotics can be reduced. In short, it can help to reduce environmental problems while also protecting human health.

5.2   Recommendation

In this study, there are several recommendations that can be proposed to overcome the process limitation as well as to enhance the project performance of CN. Therefore, to enhance this study, some guidelines for future research work are outlined here:

i.   Catalyst synthesis procedure should be improved in accordance with time and cost.

ii.   Vary the time and temperature of the calcination process.

iii.   The modification of g-C_3N_4 using carbon can increase the surface area of the sample. According to Zhen (2019), the addition of carbon materials will increase the surface area of the sonocatalyst because of its porous structure. Therefore, the surface area of contact between the pollutant in the solution and the carbon-based sonocatalyst will be increased. Aside from that, it can also provide more catalytic sites for the sonocatalytic degradation process.

iv.   The characterization of Brunauer-Emmett-Teller (BET) should be used to study the surface area of the samples are important for better insight.

REFERENCES

Abd Aziz, A., Khatun, F., Uddin Monir, M., Lan Ching, S., & Kah Hon, L. (2022). TiO$_2$: A Semiconductor Photocatalyst. *Titanium Dioxide - Advances and Applications*. https://doi.org/10.5772/intechopen.99256

Abrahart, E. N. (2022). dye | Definition, Uses, Properties, & Types | Britannica. In *Encyclopædia Britannica*. https://www.britannica.com/technology/dye

Alaghmandfard, A., & Ghandi, K. (2022). A Comprehensive Review of Graphitic Carbon Nitride (g-C3N4)–Metal Oxide-Based Nanocomposites: Potential for Photocatalysis and Sensing. *Nanomaterials*, *12*(2), 294. https://doi.org/10.3390/nano12020294

Ali, A., Chiang, Y. W., & Santos, R. M. (2022). X-ray Diffraction Techniques for Mineral Characterization: A Review for Engineers of the Fundamentals, Applications, and Research Directions. *Minerals*, *12*(2), 205. https://doi.org/10.3390/min12020205

Al-Mamun, M. R., Kader, S., Islam, M. S., & Khan, M. Z. H. (2019). Photocatalytic activity improvement and application of UV-TiO2 photocatalysis in textile wastewater treatment: A review. *Journal of Environmental Chemical Engineering*, *7*(5), 103248. https://doi.org/10.1016/j.jece.2019.103248

Ardila-Leal, L. D., Poutou-Piñales, R. A., Pedroza-Rodríguez, A. M., & Quevedo-Hidalgo, B. E. (2021). A Brief History of Colour, the Environmental Impact of Synthetic Dyes and Removal by Using Laccases. *Molecules*, *26*(13), 3813. https://doi.org/10.3390/molecules26133813

Arvia. (2022, January 24). *Water technology comparison pros and cons | Arvia Technology*. Arviatechnology.com. https://arviatechnology.com/water-technology-comparison-with-nyex/

Balsom, P. (2020, January 23). *Understanding Sedimentation Water Treatment*. High Tide. https://htt.io/understanding-sedimentation-water-treatment/

Ben-Refael, A., Benisti, I., & Paz, Y. (2020). Transient photoinduced phenomena in graphitic carbon nitride as measured at nanoseconds resolution by step-scan FTIR. *Catalysis Today*, *340*, 97–105. https://doi.org/10.1016/j.cattod.2018.11.010

Bock, S., Kijatkin, C., Berben, D., & Imlau, M. (2019). Absorption and Remission Characterization of Pure, Dielectric (Nano-)Powders Using Diffuse Reflectance Spectroscopy: An End-To-End Instruction. *Applied Sciences*, *9*(22), 4933. https://doi.org/10.3390/app9224933

Ceretta, M. B., Nercessian, D., & Wolski, E. A. (2021). Current Trends on Role of Biological Treatment in Integrated Treatment Technologies of Textile Wastewater. *Frontiers in Microbiology*, *12*. https://doi.org/10.3389/fmicb.2021.651025

Chatsungnoen, T., & Chisti, Y. (2019). Flocculation and electroflocculation for algal biomass recovery. *Biofuels from Algae*, 257–286. https://doi.org/10.1016/b978-0-444-64192-2.00011-1

Denchak, M. (2022, April 18). *Water Pollution: Everything You Need to Know*. NRDC. https://www.nrdc.org/stories/water-pollution-everything-you-need-know

Dihom, H. R., Al-Shaibani, M. M., Radin Mohamed, R. M. S., Al-Gheethi, A. A., Sharma, A., & Khamidun, M. H. B. (2022). Photocatalytic degradation of disperse azo dyes in textile wastewater using green zinc oxide nanoparticles synthesized in plant extract: A critical review. *Journal of Water Process Engineering*, *47*, 102705. https://doi.org/10.1016/j.jwpe.2022.102705

Ding, C., Fu, K., Pan, Y., Liu, J., Deng, H., & Shi, J. (2020). Comparison of Ag and AgI-Modified ZnO as Heterogeneous Photocatalysts for Simulated Sunlight Driven Photodegradation of Metronidazole. *Catalysts*, *10*(9), 1097. https://doi.org/10.3390/catal10091097

Escobedo-Morales, A., Ruiz-López, I. I., Ruiz-Peralta, M. deL., Tepech-Carrillo, L., Sánchez-Cantú, M., & Moreno-Orea, J. E. (2019). Automated method for the determination of the band gap energy of pure and mixed powder samples using diffuse reflectance spectroscopy. *Heliyon*, *5*(4), e01505. https://doi.org/10.1016/j.heliyon.2019.e01505

Faraji, M., Yamini, Y., & Salehi, N. (2021). Characterization of magnetic nanomaterials. *Magnetic Nanomaterials in Analytical Chemistry*, 39–60. https://doi.org/10.1016/b978-0-12-822131-0.00014-5

Ghalkhani, M., Khosrowshahi, E. M., & Sohouli, E. (2021). Carbon nano-onions: Synthesis, characterization, and application. *Handbook of Carbon-Based Nanomaterials*, 159–207. https://doi.org/10.1016/b978-0-12-821996-6.00006-3

Gleichmann, N. (2020, February 25). *SEM vs TEM*. Analysis & Separations from Technology Networks; Technology Networks. https://www.technologynetworks.com/analysis/articles/sem-vs-tem-331262

Guo, G., Tian, F., Zhang, L., Ding, K., Yang, F., Hu, Z., Liu, C., Sun, Y., & Wang, S. (2020). Effect of salinity on removal performance in hydrolysis acidification reactors treating textile wastewater. *Bioresource Technology*, *313*, 123652. https://doi.org/10.1016/j.biortech.2020.123652

Hadi, Jaafar, J., Nurul Widiastuti, & Nur Hashimah Alias. (2022, March 19). *A Review of Titanium Dioxide (TiO2)-Based Photocatalyst for Oilfield-Produced Water Treatment*. ResearchGate; MDPI AG. https://www.researchgate.net/publication/359352261_A_Review_of_Titanium_Dioxide_TiO2-Based_Photocatalyst_for_Oilfield-Produced_Water_Treatment

Hanum, F., Yuan, L. C., Kamahara, H., Aziz, H. A., Atsuta, Y., Yamada, T., & Daimon, H. (2019). Treatment of Sewage Sludge Using Anaerobic Digestion in Malaysia: Current State and Challenges. *Frontiers in Energy Research*, *7*. https://doi.org/10.3389/fenrg.2019.00019

Hendra Saputera, W., Egiyawati, C., Setyani Putrie, A., Fathoni Amri, A., Rizkiana, J., & Sasongko, D. (2021). Titania Modified Silica from Sugarcane Bagasse Waste for Photocatalytic Wastewater Treatment. *IOP Conference Series: Materials Science and Engineering*, *1143*(1), 012073. https://doi.org/10.1088/1757-899x/1143/1/012073

Hossain, I. (2021, February 26). *Sources and Applications of Natural Dyes*. Textile News, Apparel News, RMG News & Articles. https://textilefocus.com/sources-applications-natural-dyes/

Jeanne Rampe, M., Santoso, I. R. S., Rampe, H. L., Tiwow, V. A., & Apita, A. (2021). Infrared Spectra Patterns of Coconut Shell Charcoal as Result of Pyrolysis and Acid Activation

Origin of Sulawesi, Indonesia. *E3S Web of Conferences*, *328*, 08008. https://doi.org/10.1051/e3sconf/202132808008

Joshi, N. C., & Gururani, P. (2022). Advances of graphene oxide based nanocomposite materials in the treatment of wastewater containing heavy metal ions and dyes. *Current Research in Green and Sustainable Chemistry*, *5*, 100306. https://doi.org/10.1016/j.crgsc.2022.100306

Kar, P., Shukla, K., Jain, P., Sathiyan, G., & Gupta, R. K. (2021). Semiconductor based photocatalysts for detoxification of emerging pharmaceutical pollutants from aquatic systems: A critical review. *Nano Materials Science*, *3*(1), 25–46. https://doi.org/10.1016/j.nanoms.2020.11.001

Karam, A., Bakhoum, E. S., & Zaher, K. (2020). Coagulation/flocculation process for textile mill effluent treatment: experimental and numerical perspectives. *International Journal of Sustainable Engineering*, *14*(5), 983–995. https://doi.org/10.1080/19397038.2020.1842547

Kieren. (2021, July 16). *What is Anaerobic Wastewater treatment?* Hynds Wastewater. https://www.hyndswastewater.co.nz/what-is-anaerobic-wastewater-treatment/

Kumar Rout, T. (n.d.). *Pyrolysis of coconut shell*. https://core.ac.uk/download/pdf/53189855.pdf

Kumar, A., Dixit, U., Singh, K., Prakash Gupta, S., & S. Jamal Beg, M. (2021). Structure and Properties of Dyes and Pigments. *Dyes and Pigments - Novel Applications and Waste Treatment*. https://doi.org/10.5772/intechopen.97104

Kumar, N., Yadav, S., Mittal, A., & Kumari, K. (2021). Photocatalysis by zinc oxide-based nanomaterials. *Nanostructured Zinc Oxide*, 393–457. https://doi.org/10.1016/b978-0-12-818900-9.00005-x

Lakshmi, B., Joe Thomas, B., & Gopinath, P. (2021). Accurate band gap determination of chemically synthesized cobalt ferrite nanoparticles using diffuse reflectance spectroscopy. *Advanced Powder Technology*, *32*(10), 3706–3716. https://doi.org/10.1016/j.apt.2021.08.028

Lemmons, R. (2022, January 7). *Membrane Processes for Advanced Wastewater Treatment - Wastewater Treatment*. Climate Policy Watcher. https://www.climate-policy-watcher.org/wastewater-treatment/membrane-processes-for-advanced-wastewater-treatment.html

Liu, D., Dong, J., Liu, F., Gao, X., Yu, Y., Zhang, S., Dong, L., & Guo, Y. (2019). SYNTHESIS AND PHOTOCATALYTIC PERFORMANCE OF g-C 3 N 4 COMPOSITES. *Journal of Ovonic Research*, *15*(4), 239–246. https://chalcogen.ro/239_LiuF.pdf

Lorenz, A. (2019). *Types and Effects of Water Pollution | FairPlanet*. FairPlanet. https://www.fairplanet.org/story/types-and-effects-of-water-pollution/

Lozanova, S. (Feinstein). (2022, January 18). *What Can You Do About Nonpoint Source Pollution?* Earth911. https://earth911.com/earth-watch/what-can-you-do-about-nonpoint-source-pollution/

Lu, L., Wang, G., Zou, M., Wang, J., & Li, J. (2018). Effects of calcining temperature on formation of hierarchical TiO2/g-C3N4 hybrids as an effective Z-scheme heterojunction photocatalyst. *Applied Surface Science*, *441*, 1012–1023. https://doi.org/10.1016/j.apsusc.2018.02.080

Martín de Vidales, M. J., Nieto-Márquez, A., Morcuende, D., Atanes, E., Blaya, F., Soriano, E., & Fernández-Martínez, F. (2019). 3D printed floating photocatalysts for wastewater treatment. *Catalysis Today*, *328*, 157–163. https://doi.org/10.1016/j.cattod.2019.01.074

Mazharul Islam Kiron. (2021, September 8). *Synthetic Dyes in Textiles - Textile Learner*. Textile Learner. https://textilelearner.net/synthetic-dyes-in-textiles/

Mazille, F., & Spuhler, D. (2019). *Coagulation-Flocculation | SSWM - Find tools for sustainable sanitation and water management!* Sswm.info. https://sswm.info/sswm-university-course/module-6-disaster-situations-planning-and-preparedness/further-resources-0/coagulation-flocculation

Munajad, A., & Subroto, C. (2018). Fourier Transform Infrared (FTIR) Spectroscopy Analysis of Transformer Paper in Mineral Oil-Paper Composite Insulation under Accelerated Thermal Aging. *Energies*, *11*(2), 364. https://doi.org/10.3390/en11020364

Muzibur Rahman, M. (2019). Introductory Chapter: Fundamentals of Semiconductor Photocatalysis. *Concepts of Semiconductor Photocatalysis*. https://doi.org/10.5772/intechopen.89586

Nasikhudin, Diantoro, M., Kusumaatmaja, A., & Triyana, K. (2019). Study on Photocatalytic Properties of TiO_2 Nanoparticle in various pH condition. *Journal of Physics: Conference Series*, *1011*, 012069. https://doi.org/10.1088/1742-6596/1011/1/012069

Ni, Y., Wang, R., Zhang, W., Shi, S., Zhu, W., Liu, M., Yang, C., Xie, X., & Wang, J. (2021). Graphitic carbon nitride (g-C3N4)-based nanostructured materials for photodynamic inactivation: Synthesis, efficacy and mechanism. *Chemical Engineering Journal*, *404*, 126528. https://doi.org/10.1016/j.cej.2020.126528

Paul, D. R., Sharma, R., Nehra, S. P., & Sharma, A. (2019). Effect of calcination temperature, pH and catalyst loading on photodegradation efficiency of urea derived graphitic carbon nitride towards methylene blue dye solution. *RSC Advances*, *9*(27), 15381–15391. https://doi.org/10.1039/c9ra02201e

Piccard, B. (2020). *Solutions to water pollution: how to improve water quality?* @Solarimpulse. https://solarimpulse.com/water-pollution-solutions

Qiu, J., Li, Y., & Jia, Y. (2021). Synthesis methods. *Persistent Phosphors*, 31–67. https://doi.org/10.1016/b978-0-12-818637-4.00002-1

Ren, G., Han, H., Wang, Y., Liu, S., Zhao, J., Meng, X., & Li, Z. (2021). Recent Advances of Photocatalytic Application in Water Treatment: A Review. *Nanomaterials*, *11*(7), 1804. https://doi.org/10.3390/nano11071804

Rojviroon, T., Rojviroon, O., Sirivithayapakorn, S., & Angthong, S. (2021). Application of TiO2 nanotubes as photocatalysts for decolorization of synthetic dye wastewater. *Water Resources and Industry*, *26*, 100163. https://doi.org/10.1016/j.wri.2021.100163

Saiyyidah Tus Zuhroh, Akbarningrum Fatmawati, & Widjaja, A. (2022, August 22). *Coconut Husk to Reducing Sugar Conversion Using Combined Ultrasound and Surfactant Aided Subcritical Water*. ResearchGate; Universitas Gadjah Mada. https://www.researchgate.net/publication/362849652_Coconut_Husk_to_Reducing_Su

gar_Conversion_Using_Combined_Ultrasound_and_Surfactant_Aided_Subcritical_Wa
ter

Sajda .S. Affat. (2021, May 16). *Classifications, Advantages, Disadvantages, Toxicity Effects of Natural and Synthetic Dyes: A review*. ResearchGate; unknown. https://www.researchgate.net/publication/351885086_Classifications_Advantages_Disadvant ages_Toxicity_Effects_of_Natural_and_Synthetic_Dyes_A_review

Sasireka Velusamy, Roy, A., Sundaram, S., & Mallick, T. K. (2021, February 4). A Review on Heavy Metal Ions and Containing Dyes Removal Through Graphene Oxide-Based Adsorption... ResearchGate; Chemical Society of Japan. https://www.researchgate.net/publication/349060955_A_Review_on_Heavy_Metal_Io ns_and_Containing_Dyes_Removal_Through_Graphene_Oxide- Based_Adsorption_Strategies_for_Textile_Wastewater_Treatment

Sayed, E. T., Shehata, N., Abdelkareem, M. A., & Atieh, M. A. (2020). Recent progress in environmentally friendly bio-electrochemical devices for simultaneous water desalination and wastewater treatment. *Science of the Total Environment*, *748*, 141046. https://doi.org/10.1016/j.scitotenv.2020.141046

Scimeca, M., Bischetti, S., Lamsira, H. K., Bonfiglio, R., & Bonanno, E. (2018). Energy Dispersive X-ray (EDX) microanalysis: A powerful tool in biomedical research and diagnosis. *European Journal of Histochemistry*. https://doi.org/10.4081/ejh.2018.2841

Singh, M., Vajpayee, M., & Ledwani, L. (2021). Eco-friendly surface modification of natural fibres to improve dye uptake using natural dyes and application of natural dyes in fabric finishing: A review. *Materials Today: Proceedings*, *43*, 2868–2871. https://doi.org/10.1016/j.matpr.2021.01.078

Spuhler, D. (2019). *Anaerobic Digestion (General) | SSWM - Find tools for sustainable sanitation and water management!* Sswm.info. https://sswm.info/arctic-wash/module-4- technology/further-resources-wastewater-treatment/anaerobic-digestion- %28general%29#:~:text=The%20process%20is%20generally%20carried,acidification%3B% 20acetogenesis%2C%20and%20methanogenesis.

Titus, D., James Jebaseelan Samuel, E., & Roopan, S. M. (2019). Nanoparticle characterization techniques. *Green Synthesis, Characterization and Applications of Nanoparticles*, 303–319. https://doi.org/10.1016/b978-0-08-102579-6.00012-5

Tuser, C. (2020, January 9). *What is Wastewater?* Water & Wastes Digest. https://www.wwdmag.com/wastewater-treatment/what-wastewater

Wang, M., Ma, F., Wang, Z., Hu, D., Xu, X., & Hao, X. (2018). Graphitic carbon nitride, a saturable absorber material for the visible waveband. *Photonics Research*, *6*(4), 307. https://doi.org/10.1364/prj.6.000307

Witono, J. R., Ramadhany, P., Santoso, H., & Putri, A. (2022). The potency of norbixin as an active compound of natural dye in textile industry. *Materials Today: Proceedings*. https://doi.org/10.1016/j.matpr.2022.02.437

Yang, H.-Y., Liu, J., Wang, Y.-X., He, C.-S., Zhang, L.-S., Mu, Y., & Li, W.-H. (2019). Bioelectrochemical decolorization of a reactive diazo dye: Kinetics, optimization with a
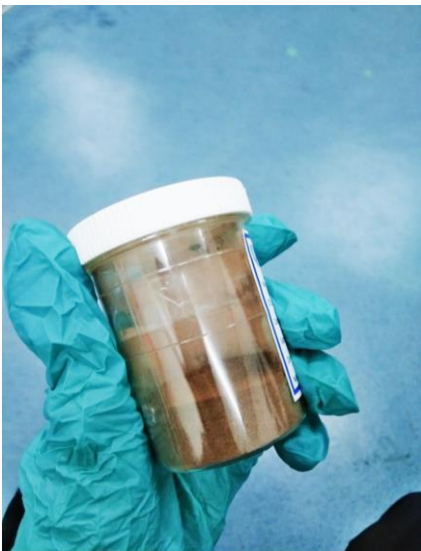
response surface methodology, and proposed degradation pathway. *Bioelectrochemistry*, *128*, 9–16. https://doi.org/10.1016/j.bioelechem.2019.02.008

Yao, S., Xue, S., Peng, S., Jing, M., Qian, X., Shen, X., Li, T., & Wang, Y. (2018). Synthesis of graphitic carbon nitride at different thermal-pyrolysis temperature of urea and it application in lithium–sulfur batteries. *Journal of Materials Science: Materials in Electronics*, *29*(20), 17921–17930. https://doi.org/10.1007/s10854-018-9906-2

Zhang, F., Wang, X., Liu, H., Liu, C., Wan, Y., Long, Y., & Cai, Z. (2019). Recent Advances and Applications of Semiconductor Photocatalytic Technology. *Applied Sciences*, *9*(12), 2489. https://doi.org/10.3390/app9122489

Zhang, Y., Shaad, K., Vollmer, D., & Ma, C. (2021). Treatment of Textile Wastewater Using Advanced Oxidation Processes—A Critical Review. *Water*, *13*(24), 3515. https://doi.org/10.3390/w13243515

Zhao, P., Ma, Y., Lv, X., Li, M., Huang, B., & Dai, Y. (2018). Two-dimensional III2-VI3 materials: Promising photocatalysts for overall water splitting under infrared light spectrum. *Nano Energy*, *51*, 533–538. https://doi.org/10.1016/j.nanoen.2018.07.010

Zhen, A. (2019). Synthesis of Graphitic Carbon Nitride (G-c3n4) / Coconut Shell Husk Derived-carbon Composite for Sonocatalytic Degradation of Organic Dye - UTAR Institutional Repository. *Utar.edu.my*. https://doi.org/http://eprints.utar.edu.my/3358/1/CL%2D2019%2D1401446%2D1.pdf

APPENDICES

Appendix A:

Preparation of sample

Appendix B: Characterization