REMOVAL OF PHARMACEUTICAL COMPOUNDS USING PHOTOCATALYSIS ON FERRIC OXIDE DOPED TITANIUM DIOXIDE

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By

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ABSTRAK

Kehadiran pencemaran mikro dalam persekitaran akuatik amat membimbangkan dalam beberapa tahun kebelakangan ini. Pencermaran air akibat kontaminasi yang berlaku akibat bahan tercemar boleh memberi kesan pada kehidupan manusia, haiwan dan alam sekitar. Kajian ini menggunakan nanokomposit Fe_2O_3-TiO_2 sebagai pemangkin foto bagi mengkaji degradasi keberkesanan ATL, CBZ dan DIC dalam air kumbahan dalam skala makmal. Objektif kajian ini ada dua. Pertama adalah untuk mengkaji kesan degradasi pemangkin foto bahan farmaseutikal (ATL, CBZ dan DIC) dengan menggunakan Fe_2O_3-TiO_2 dengan pelbagai kandungan dos. Hasil kajian menunjukkan terdapat kesan positif terhadap degradasi pemangkin foto ke atas ketiga-tiga PhCs (ATL, CBZ dan DIC) bila menggunakan Fe_2O_3-TiO_2 dalam pelbagai kandungan dos. Di samping itu, hasil kajian yang hampir sama diperolehi apabila pemangkin nanokomposit Fe_2O_3-TiO_2 menggunapakai kaedah seperti pembasuhan menggunakan air (H_2O) dan Hidrogen Peroksida (H_2O_2) dalam menghilangkan ketiga-tiga PhCs (ATL, CBZ dan DIC), di samping berkeupayaan untuk mengguna semula pemangkin nanotkomposit Fe_2O_3-TiO_2 dalam 5 kitaran.

ABSTRACT

The presence of the micropollutants in the aquatic environment has caused significant concern in recent years. The occurrence of water pollution comes from the contamination of harmful substances that bring harm to human life, animals, and the environment. The present study uses Fe_2O_3-TiO_2 nanocomposites as a photocatalyst to investigate the degradation efficiency of ATL, CBZ, and DIC in synthetic wastewater on a laboratory scale. The objectives of this study are twofold. Firstly, is to examine the effect of photocatalytic degradation of pharmaceutical compounds (ATL, CBZ, and DIC) using Fe_2O_3-TiO_2. In an attempt to degrade the pharmaceutical compounds in synthetic wastewater, a synthesized Fe_2O_3 doped TiO_2 photocatalyst with different dose loading was applied. Secondly, is to investigate the efficiency of recovered nanocomposite catalyst Fe_2O_3-TiO_2 using different method after photocatalysis treatment. Results have shown that there was positive effect of photocatalytic degradation on the three PhCs (ATL, CBZ, and DIC) when using Fe_2O_3-TiO_2 with different dose loading. Furthermore, using recovered nanocomposite catalyst Fe_2O_3-TiO_2 by adopting method such as washed with water (H_2O) and Hydrogen Peroxide (H_2O_2) have slightly similar results in removing the three PhCs (ATL, CBZ, and DIC) and able to reuse the recovered nanocomposite catalyst Fe_2O_3-TiO_2 until 5 cycles.

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LIST OF ABBREVIATIONS

AOPs	Advanced Oxidation Processes
ATL	Atenolol
CB	Conductive Band
CBZ	Carbamazepine
DIC	Diclofenac
ECB	Electron Cofactor Binding Site
ECs	Emerging Contaminants
ENPs	Emerging New Pollutants
eV	Electron-volt
HPLC	High Performance Liquid Chromatography
LUX	Luminous Intensity
mol	Mole
NSAIDs	Nonsteroidal Anti-Inflammatory Drug
PhCs	Pharmaceutical Compounds
SSA	Specific Surface Area
TCA	Tricyclic Antidepressants
UV	Ultraviolet
VB	Valence Bond
WWTPs	Wastewater Treatment Plants

LIST OF SYMBOLS

°C	Degree Celsius
Ct	Final concentration
g	Gram
Fe_2O_3	Ferric Oxide
hr	Hour
H^+	Hydrogen ion
H_2O_2	Hydrogen peroxide
HO2•	Hydrogen peroxide radical
OH-	Hydroxide ion
•OH	Hydroxyl radical
Co	Initial concentration
kg	Kilogram
L	Liter
µg	Microgram
mg	Miligram
ng	Nanogram
nm	Nanometers
O_2	Oxygen
hv	Photon energy
hvb^+	Positive valence band hole
NaOH	Sodium Hydroxide
H_2SO_4	Sulphuric acid
$O_2^{-\bullet}$	Superoxide radical anion

SnO_2	Tin (IV) oxide
TiO_2	Titanium dioxide
H_2O	Water
λ	Wavelength
ZnO	Zinc oxide

CHAPTER ONE

INTRODUCTION

1.1 Background

The occurrence of water pollution comes from the contamination of harmful substances such as chemical mixture and various microorganisms into the river, lake, ocean, and other part of the water body that brings harm to human life, animals, and the environment. According to the United Nations, the environment receives more than 80 percent of untreated or reused world wastewater (Denchak, 2018). The contaminant's occurrence can be found from the residue coming from the industrial and municipal wastewater treatment plant and sewage effluent. These contaminants are generally toxic to aquatic and terrestrial animals and hazardous to human life since the flow of the food chain started from the water consumption by aquatic life and living organism.

Because of their persistence, toxicity features, and bioaccumulation, the increased pollution of a water body by chemicals of emergent concern (CECs) such as pharmaceuticals, personal care products, chemical products, and pesticides has caused concern (Ebele, Abou-Elwafa Abdallah and Harrad, 2017; Yang *et al.*, 2017). The CECs are generally detected in concentrations that range from parts per trillion (ng/L) to parts per billion (µg/L) in water(Dai *et al.*, 2015; Yang *et al.*, 2017). The presence of pharmaceutical compounds (PhCs) like antibiotics, NSAIDs, lipid-regulators, hormones-blockers, and anticonvulsants in aquatic compartments and wastewater treatment plants (WWTPs) has received a lot of attention from researchers over the last few decades because of their potential negative effects on the ecosystem (Fawzi Suleiman Khasawneh and Palaniandy, 2019). Antibiotics, synthetic hormones, statins, anti-inflammatories, and cytotoxins are among many types of human medications that are consistently created and consumed in large. quantities, amounting to thousands of tonnes per year (Quesada *et al.*, 2019). The incomplete removal of pharmaceutical compounds can be found from the discharge of wastewater treatment plants that enters the receiving streams and sewage sludge that is used as fertilizer.

Although Municipal WWTPs using tertiary processes are more effective at removing pharmaceuticals, researchers found that numerous pharmaceuticals can still be found in the final effluent following tertiary treatment (Fawzi Suleiman Khasawneh and Palaniandy, 2021). Pharmaceutical compounds are chemical substance that is produced and manufactured by the pharmacy industry to maintain healthcare and provide medication purposes to human and animal life. Pharmaceuticals are often thought to have insignificant effects because they appear at low concentrations (ng/L) below their prescribed dose (Fawzi Suleiman Khasawneh and Palaniandy, 2021). However, the consumption of pharmaceuticals by humans and animals is known to be the cause of the increase in pharmaceutical pollution in various water sources (Cardoso, Porcher and Sanchez, 2014). Researchers reported that psychiatric medicines (such as Carbamazepine and Diazepam) can influence reproduction, endocrine function, and photosynthesis in aquatic creatures (Subedi and Kannan, 2015).

Based on a review on Advanced Treatment of Pharmaceutical Wastewater, studies show that without advanced treatment of pharmaceutical wastewater, the potential of increase of PhCs in treated effluent is high due to the complexity of pharmaceutical processes, poor biodegradability, and high concentration (Fawzi Suleiman Khasawneh and Palaniandy, 2019). Advanced oxidation processes (AOPs) are the most effective treatment technologies for removing non-biodegradable substances such as pharmaceuticals and dyes because can address a wide range of developing pollutants (Fawzi Suleiman Khasawneh and Palaniandy, 2019). Heterogeneous photocatalysis is a potential low-temperature and pressure method with applications such as solar energy, green chemistry, and environmental remediation (Bellardita *et al.*, 2018). Photocatalysis is known as an acceleration of a photoreaction in the presence of a catalyst (Fawzi Suleiman Khasawneh and Palaniandy, 2019). Hazardous and non-hazardous contaminants, as well as persistent organic micro-pollutants, can be removed in water and wastewater via heterogeneous photocatalysis oxidation (Qu, Alvarez and Li, 2013).

1.2 Problem Statement

Pharmaceutical compounds were designed to be biologically active and persistent to maintain therapeutic activity in humans and fauna (Fawzi Suleiman Khasawneh and Palaniandy, 2021). Present conventional wastewater treatment cannot fully remove the pharmaceutical compounds due to their insufficiency of treatment processes applied and non-available advanced oxidation technologies implemented in WWTPs. Besides, the difficulties in pharmaceutical compounds removal are generally because of their low biodegradability and physicochemical properties such as high polarity, volatility, persistence, and adsorption during the treatment processes in WWTPs (Fawzi Suleiman Khasawneh and Palaniandy, 2019). Municipal WWTPs are not designed to remove persistent micro-pollutants like pharmaceuticals (Khan, Rehman and Malik, 2020). As a result, pharmaceuticals are not eliminated in M-WWTPs and are constantly discharged into the aquatic environment via WWTP effluents (Fawzi Suleiman Khasawneh and Palaniandy, 2019). Studies found that six out of ten pharmaceutical residues are detected in sewage samples that were discharged from the inefficiency of current biological treatment systems(Yacob *et al.*, 2017). Furthermore, the fast development of various pharmaceutical products using high technology and different scale and chemical processes are causing pharmaceutical pollution to increase with more complexity than ever(Guo, Qi and Liu, 2017).

Previous study has discovered that heterogeneous photocatalysis is the most effective and suitable approach for the degradation and remediation of pharmaceutical compounds and some other developing pollutants (Lee *et al.*, 2017). Many studies have been conducted on pharmaceutical compounds degradation adopting heterogeneous photo-catalysts centered on titanium dioxide (TiO_2) as a semiconductor catalyst base (Amalraj Appavoo *et al.*, 2014; Djouadi *et al.*, 2018; Mugunthan, Saidutta and Jagadeeshbabu, 2019). However, there are several drawbacks using TiO_2 as a bare catalyst. It is mostly due to its activation being limited to light in the UV region, making the process less efficient (Lee *et al.*, 2017). As a result, various studies have been conducted to improve the photocatalytic activity of TiO_2 photocatalysts by doping and (or) combining it with other substances, such as TiO_2-SnO_2 (Mugunthan, Saidutta and Jagadeeshbabu, 2019) and Fe-TiO_2 (Moradi *et al.*, 2016) core shells, as well as to shift its photo-activity to the visible region.

However, the preparation conditions for the doped TiO_2 nanocomposite catalyst were complicated, and there are few studies on improving the operating parameters affecting pharmaceutical compounds degradation via photo-catalysis. A review study is being carried out to examine the effect of photocatalytic degradation of pharmaceutical compounds (Atenolol, Carbamazepine, and Diclofenac) using Fe_2O_3-TiO_2 with different dose loading that affects the final concentrations of Atenolol, Carbamazepine, and Diclofenac after three hours of solar exposure. Furthermore, the research aims to investigate the efficiency of recovered nanocomposite catalyst Fe_2O_3-TiO_2 using different method after photocatalysis treatment. The comparison between the efficiency of the recovered nanocomposite catalyst Fe_2O_3-TiO_2 using different method is made at the end of this study.

1.3 Aims and Objectives

This study will use Fe_2O_3-TiO_2 nanocomposites as a photocatalyst to investigate the degradation efficiency of ATL, CBZ, and DIC in synthetic wastewater on a laboratory scale. The following is a list of the research's goals:

1) To examine the effect of photocatalytic degradation of pharmaceutical compounds (ATL, CBZ, and DIC) using Fe_2O_3-TiO_2 with different dose loading.
2) To investigate the efficiency of recovered nanocomposite catalyst Fe_2O_3-TiO_2 using different method after photocatalysis treatment.

1.4 Scope of Research

The first part of research comprised of the photocatalysis treatment on the synthetic sample. The preparation of stock solution is required before the photocatalysis process. The operating parameter that will be considered during photo-catalysis process are classified into variable and fixed parameters. The variable parameter use in this study is the dose of catalyst (0.1, 0.2 and 0.3 g/L). The fixed parameter employed in this study are the initial concentration of PhCs (5 mg/L), the pH value of sample solution (Neutral = 7), the light intensity (20,000 Lux) and irradiation duration (3 hours), and the distance between batch reactor and solar lamps (75 cm). Sample solutions will be mixed and stirred until three hours of irradiation under solar exposure. Sample collection will be carried out at every 30 minutes interval. Solutions were filtered using 0.45 micrometer membrane filter paper. The treated solution collected are stored in amber bottle and kept in dark place with fixed cold temperature (4° Celsius). HPLC Analysis to compare and find the removal efficiency from using two different synthesized photo-catalyst via SPE method (Solid-phase extraction). The photo-catalysis process will take place in the Chemical Lab at the School of Chemical Engineering. The HPLC analysis will be carried out in the School of Pharmacy at the main campus of USM. For the second part of this study is the recovery study of nanocomposite catalyst Fe_2O_3-TiO_2 by different method for five consecutive cycles with solar exposure in three hours of photocatalysis treatment. The optimum dose loading of photocatalyst are use in the recovery study after it was determined from the results obtained in the first part of this study. The same photocatalyst use at first run of the experiment were collected, weighed, recorded, and reuse again for the next consecutive runs up to five runs to assess the efficiency of re-using Fe_2O_3-TiO_2 after 5 runs (cycles).

1.5 Dissertation Outline

This study has five chapters. In Chapter 1, a brief introduction on the research study, research problem, research aims and objectives, and scope of the research were discussed. Chapter 2 provides a literature review based on the research topic. Chapter 3 discusses the methodology in obtaining and analyzing the samples. Chapter 4 provides the results and discussion of the findings. Finally in Chapter 5, a conclusion based on the analysis in Chapter 4 and suggestions for future research are discussed.

CHAPTER TWO

LITERATURE REVIEW

2.1 Overview

The occurrence, origin, and persistence of pharmaceutical compounds in the aqueous resources and environmental bodies are briefly described in this chapter. Then there are the recently studied ways for removing medicinal substances. Furthermore, the theoretical explanation of the heterogeneous photocatalysis process and mechanism is the highlight of this Chapter. Furthermore, it entails a thorough examination of the semiconductor catalysts employed in this work, such as TiO_2 and Fe_2O_3-TiO_2. It also covers the history of Fe_2O_3-TiO_2 nanocomposite synthesis approaches, the factors that impact the nanocomposite catalyst's features, and the science behind the sol-gel method, as well as the factors that influence the nanocomposite's manufacture using the sol-gel method. The final part of the Chapter focuses into the operational factors that have a significant impact on the photocatalysis process.

2.2 Pharmaceutical Compounds

The presence of micropollutants in the aquatic environment has caused significant concern in recent years. Micropollutants, also known as emerging contaminants (ECs), are made up of a variety of synthetic and natural compounds, such as medications, personal care items, agrochemicals, and steroid hormones, in varying amounts. One of the major concerns with these compounds is that they are usually found in low concentrations in water bodies, and each of these substances vary in its toxicity. The concentration of this material, however, will be on medicinal substances (PhCs). Pharmaceuticals are chemical substances that are used to identify, treat, and prevent illnesses (Quesada *et al.*, 2019). Pharmaceuticals may also be described as over-the-counter medications and veterinary medicines that are used to treat humans and animals (Ebele, Abou-Elwafa Abdallah and Harrad, 2017). Antibiotics, synthetic hormones, statins, anti-inflammatories, and cytotoxins are among the many types of human medications that are continually created and used in massive quantities, totaling to thousands of tones each year (Quesada *et al.*, 2019).

2.2.1 Occurrence of Pharmaceuticals

The difficulties in the removal of PhCs are due to their low biodegradability and physicochemical properties such as high polarity, volatility, persistence, and adsorption (Fawzi Suleiman Khasawneh and Palaniandy, 2021). Pharmaceutical compounds are chemical substance that is produced and manufactured by the pharmacy industry to maintain healthcare and provide medication purposes to human and animal life. The presence of PhCs like antibiotics and NSAIDs in aquatic compartments and wastewater treatment plants (WWTPs) are giving negative impacts on the ecosystem. Researchers reported that PhCs such as Carbamazepine and Diazepam can influence reproduction, endocrine function, and photosynthesis in aquatic creatures. The potential of increasing quantity of pharmaceutical compounds in treated effluent is due to the complexity of PhCs processes, poor biodegradability, and high concentration.

2.2.2 Atenolol

Atenolol, ATL, ($C_{14}H_{22}N_2O_3$) is commonly known as Tenormin is a medication from the beta blocker class that is frequently prescribed to treat cardiac problems, migraines, and high blood pressure. ATL (4-[2-hydroxy-3-[(1-methyl) amino) propoxyl] benzeacemide) is a constituent of the beta-blocker class of medications, which are mostly used to treat cardiovascular disorders. The hepatic glands in the human body only slightly process the medication. In less than 24 hours, the renal system excretes between 50 and 85 percent of the substance. Because only a small portion of this substance is metabolized by humans, there is a constant release into the environment a beta blocker medication used to treat high blood pressure and chest discomfort caused by the heart. This medicine able to lower the blood pressure including the risk of strokes, heart attacks, and renal disease. Because of its widespread use and the slow rate at which humans metabolize it, ATL was found in high concentrations in the effluents of sewage treatment plants and in surface waters. The mean ATL concentration detected in Saudi Arabia is range from 1 ng/L to 4 ng/L (Al Qarni *et al.*, 2016). Previous studies have shown that common wastewater treatment methods, such as activated sludge, granular activated carbon filtration, and ozonation, are unable to efficiently eliminate ATL from the water (Fawzi Suleiman Khasawneh and Palaniandy, 2021) .Therefore, the development of improved treatment methods is very necessary in order to guarantee the efficient removal of ATL from wastewaters prior to their disposal into water sources.

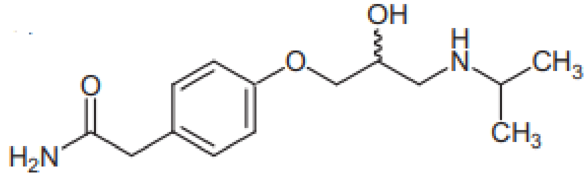

Figure 2.1: Chemical structure of Atenolol (Hapeshi *et al.*, 2010)

2.2.3 Carbamazepine

Carbamazepine, CBZ, ($C_{15}H_{12}N_2O$) or also known as Tegretol is a seizure medicine that is used to prevent and treat seizures. This medicine helps by preventing seizure activity from spreading across the brain and restoring normal nerve activity balance. The main purposes of using carbamazepine are for the treatment of epilepsy and bipolar disorder (Esquerdo *et al.*, 2021). Effluent coming from wastewater treatment facilities is the primary source of CBZ in open rivers (WWTPs) (Al Aukidy *et al.*, 2012). A tricyclic compound containing anticonvulsant and analgesic characteristics, carbamazepine is chemically linked to tricyclic antidepressants (TCA). Reduced polysynaptic responses and a block on post-tetanic potentiation allow carbamazepine to work as an anticonvulsant. A carbamoyl substituent is found at the azepine nitrogen in the dibenzoazepine carbamazepine, which is seen as an anticonvulsant. It has a mean concentration (ng/L) of 3.3 in France according to (Zhang, Geißen and Gal, 2008). In addition to this, CBZ is said to be potentially hazardous to aquatic life in lower concentration. Therefore, it is of the extreme significance to get eliminate of CBZ in an environment containing water.

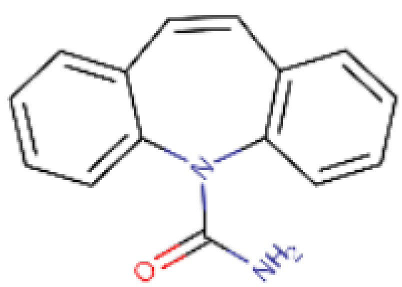

Figure 2.2: Chemical structure of Carbamazepine (Décima *et al.*, 2021)

2.2.4 Diclofenac

Diclofenac, DIC, ($C_{14}H_{11}Cl_2NO_2$) is a non-steroidal anti-inflammatory drug (NSAID). Diclofenac is also known as Voltaren can treat arthritis-related pain, swelling (inflammation), and joint stiffness. Full-dose diclofenac therapy is generally linked with moderate serum aminotransferase concentrations and, in rare circumstances, can result in significant clinically evident, acute, or chronic liver damage. A monocarboxylic acid called diclofenac is constituted of phenylacetic acid with a (2,6-dichlorophenyl) amino group at the 2-position. It comprises an aromatic amine, an amino acid, a dichlorobenzene, a monocarboxylic acid, and a secondary amino compound. It originates from a diphenylamine and phenylacetic acid. Following ingestion, the majority of DIC is converted into hydroxyl metabolites by the human metabolism, which are then eliminated from the body into the aquatic environment. Additionally, higher DIC metabolites are present in aqueous environments because of biological activities that take place in WWTPs and converted DIC to hydroxy diclofenac; the same process occurs through a photochemical mechanism, which is referred to as photolysis. DIC is one of the most frequently found PhCs in the water environment, and it is vulnerable to being removed by most wastewater treatment plants. According to the finding (Shamsudin, Azha and Ismail, 2022), the mean concentration of DIC found in Malaysia is in range of 32 to 5049 ng/L.

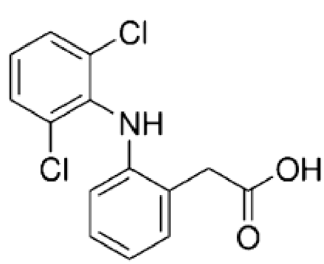

Figure 23: Chemical structure of Diclofenac (Martínez *et al.*, 2011)

2.2.5 Occurrence of Carbamazepine, Atenolol and Diclofenac in Water Resources

Since these three pharmaceuticals are persistent in the environment and cannot be efficiently biodegraded by conventional biological oxidation water or wastewater treatment facilities, it has become an issue on a worldwide scale, along with other pharmaceutical compounds. Due to the possible health dangers it causes to both humans and the aquatic environment, the presence of the pharmaceutical chemical like carbamazepine, atenolol and diclofenac in drinking water has been documented in several literatures (Ebele, Abou-Elwafa Abdallah and Harrad, 2017). Pharmaceutical contaminants from pharmaceutical industries, the dumping of unwanted pharmaceutical wastes in hospitals and homes, and urban wastewater contaminated with active compounds have all been considered as critical sources of pharmaceutical hazards (Massima Mouele *et al.*, 2021).

2.3 Removal of Pharmaceutical Compounds

The most popular treatment methods for removing emerging contaminants (ECs), mostly pharmaceutical compounds through the process of biodegradation, including biological treatment technologies such as activated sludge, designed wetlands, trickling filter, and aerobic bioreactor (Ahmed *et al.*, 2017). By converting organic material into nutrients that other creatures may consume, biodegradation is nature's way of recycling trash. Some forms of environmental toxins can be decreased and entirely eliminated by employing these organic bio-degradational factors (B. Eskander and M. Saleh, 2017).

2.3.1 Advanced Oxidation Processes for the Removal of Pharmaceuticals

Advanced oxidation processes (AOPs) are thought to be the most efficient technologies since they provide a large potential for the removal of a number of new contaminants (Fawzi Suleiman Khasawneh and Palaniandy, 2019). In the sector of removing organic pollutants, advanced oxidation processes (AOPs) are becoming increasingly popular. AOPs are recognized by their high oxidation effectiveness and minimal of secondary pollutants as compared to other chemical processes (Ma *et al.*, 2021).

2.3.2 Photocatalysis as an Advanced Oxidation Process

The method of photocatalysis is regarded as one of the most potentially beneficial advanced oxidation processes (AOPs). The oxidation of contaminants usually starts in AOPs through the production of the hydroxyl radical (•OH), and this is the foundation of what the term "AOPs" refers to. Following this, advanced oxidation processes (AOPs) may be separated into homogeneous and heterogenous processes according to the phase of the catalysts that are used and the reaction mixture (Fawzi Suleiman Khasawneh and Palaniandy, 2019). However, the use of photocatalysis may be separated into two distinct processes, which are known as homogeneous photocatalysis and heterogenous photocatalysis. The recovery and reusability of the utilized catalyst is more difficult in homogeneous photocatalysis, which is the primary difference in both the homogeneous and heterogeneous photocatalysis methods. Heterogeneous photocatalysis with the use of semiconductor (nano) particles provides advantages in commercial product, such as inexpensive and more durable catalysts, simpler re-use, and removal from the reaction media. On the other hand, in contrast to homogeneous catalysis, heterogeneous photocatalysis is a straightforward procedure that is also a simplified and low-cost method.

2.4 Heterogenous Photocatalysis

Heterogeneous photocatalysis is an interesting method for its potential applications in various fields of solar energy, green chemistry, and environmental remediation since it can operate at low temperatures and under low pressures (Bellardita *et al.*, 2018). (Finegold and Cude, 1972) were the ones who first encountered the potential of utilizing photocatalysis for the treatment of water. Their research was founded on the photo-electrochemical water splitting process, which utilized titania as the semiconductor catalyst. (Finegold and Cude, 1972) discoveries were made in 1972. One definition of photocatalysis is "the acceleration of a photoreaction in the presence of a catalyst," which refers to a process well. The term "semiconductor photocatalysis" is used to refer to heterogeneous photocatalysis (Singh *et al.*, 2020).

Photocatalytic oxidation is regarded as one of the advanced oxidation processes (AOPs), and it is definitely one of the AOPs that has the most potential for the treatment of wastewater that contains harmful and non-biodegradable components such pharmaceutical compounds (PhCs) and dyes. It is effective to use heterogeneous photocatalysis oxidation for the removal of harmful and non-hazardous chemical contaminants and persistent organic contaminants in water and wastewater. Numerous studies have been conducted to investigate the use of heterogeneous photocatalysis for the degradation and removal of various persistent pollutants and emerging new pollutants (ENPs). The photocatalytic activity and the effectiveness at which the contaminants were degraded lead to a bright future for the application of heterogeneous photocatalysis as an advanced oxidation process (AOP) for the treatment of water and wastewater.

When compared to other advanced oxidation technologies (AOTs) including biological treatment, chemical oxidation, activated carbon adsorption, ozonation, and so on, the heterogeneous photocatalysis process offers a number of benefits that set it apart from the competition (Kumar, 2017; Miklos *et al.*, 2018). The method of chemical oxidation is only useful for the degradation of contaminants that are available in significant concentrations; also, this procedure does not completely remove organic compounds from the environment. The removal rates of biologically methods of treatment are quite slow; these methods also produce a significant quantity of sludge that must be disposed of, and they need for careful regulation of both the pH and the temperature. The adsorption of pollutants by activated carbon is quite efficient; nevertheless, the primary drawback of this method is that even the pollutants are moved from one location to another without being degraded, which results in the formation of yet another contaminant.

On the other hand, the photocatalytic oxidation process is effective in the removal contaminants even at small concentrations and obtaining complete oxidation of pollutants in a short period of time even at low concentrations. In addition, this process can degrade pollutants without releasing harmful byproducts into the environment (ppb). In addition, the photooxidation process may be carried out without the production of secondary pollutants by making use of a catalyst that is both inexpensive and extremely active (Kumar, 2017).

2.4.1 Principles of Heterogenous Photocatalysis

Under the effect of UV irradiation, the photocatalytic process can be activated when a catalyst is present in the reaction mixture. According to (Herrmann and Puzenat, 2015), in order for the heterogeneous photocatalysis project to proceed, there are basically three components that need to be present:

(j) Photons that have been emitted, at the right wavelength.

(ii) Chemical catalyst; semiconductor, i.e., titanium dioxide.

(iii) Powerful oxidizing agent; oxygen is the most common example.

The heterogeneous photocatalysis, also called semiconductor photocatalysis, is categorized into 3 primary steps that occur simultaneously throughout the photocatalytic process (Lim *et al.*, 2010):

(j) The photocatalyst is activated by UV light, which results in the production of electrons (e-) and holes (h+).

(ii) The generated holes (h+) oxidize water to form hydroxyl radicals (•OH), while at the same time the generated electrons (e-) decrease oxygen molecules to create extra oxidizing agents that include hydroxyl radicals (•OH).

(iii) The pollutants are oxidized by the hydroxyl radicals (•OH), which results in the formation of water, carbon dioxide, and basic mineral acids.

2.4.2 Photocatalytic Mechanism

The reaction mechanisms of the photocatalytic process have been investigated extensively in many different literatures (Hoffmann *et al.*, 1995; Chong *et al.*, 2010). The semiconducting material TiO_2 has shown to be the most successful photocatalyst in terms of initiating a sequence of oxidative and reductive processes on the surface of its atoms. TiO_2 becomes active when a photon with an energy (hv) that is either equal to or larger than the band - gap energy of titania (3.2 eV for anatase and 3.0 eV for rutile) is irradiated on its surface. This causes the lone electron to become photoexcited and move towards the conduction band. When a particle of titania is bombarded with a photon energy that is high enough, an electron-hole pair will occur. The necessary light wavelength required to generate TiO_2 particles in the instance of titanium dioxide equals to = 400 nm.

2.5 Semiconductor Catalyst

Semiconductors are a significant group of substances that display a conductivity that is across that of conductors and insulators. This placed them in the middle of the conductivity spectrum. Inorganic and organic semiconductors can be identified from one another according to the chemical build of the semiconductors. While it is necessary to classify them as crystalline, amorphous, or liquid depending on their structure, the most common form is liquid. According to (Fawzi Suleiman Khasawneh and Palaniandy, 2019) over than 130 inorganic semiconductor materials, such as metal oxides, nitrides, and sulphides, have been explored in this area. These materials were tested and the results to function as semiconductors. When it comes to photocatalytic activities, the metal oxides that are recognized to be the most effective are thought to be semiconductors that comprise of a conduction band of d_0 or d_{10}, such as Ti, V, Ga, Zr, Ge, etc. Because of their conduction band and valence band, these metal oxides discover broad acceptance.

A semiconductor material, such as titanium dioxide (TiO2), has a valence band and a conduction band. These two bands are distinguished from an energy band (or bandgap

Eg). The molecules of the semiconductor material absorb the photons when the semiconductor is exposed to UV light. If the energy of the photons (hv) is greater than or equal to the energy of the band gap of the semiconductor, the electrons in the valence band get to be excited and are bound up to the conduction band, which results in the generation of charge carriers. According to (Akpan and Hameed, 2009), the processes that are involved when a molecule of a semiconductor absorbs photons that have a large amount of energy. Despite this, several of the metal-semiconductor catalysts that are used in the photocatalytic activity for the degradation of contaminants have very few limitations like high price of catalyst.

2.5.1 Titanium Dioxide (TiO_2)

Titanium dioxide (TiO_2), also known as titania, is the catalyst that has garnered the most recognition and is the main topic among the most research. This is primarily due to the fact that it possesses a high level of stability, a high level of photocatalytic activity, nontoxicity, as well as physical and optical characteristics (Akpan and Hameed, 2009). Titania's photocatalytic activity and chemical structure have been the subject of a substantial amount of research, as well as several articles and reviews. In the next section, the chemical composition and the physical-chemical features of titania nanoparticles will be described. This will allow the reader to get a better understanding of the role that titanium dioxide plays in the treatment and degradation of contaminants

2.5.1.1 TiO_2 Properties

Titanium dioxide, in its most fundamental form, is a kind of semiconductor that belongs to the category of transition metal oxides. The crystalline structures of the three most frequent forms of titania's polymorphs, brookite, anatase, and rutile. In addition to the four polymorphs that have already been mentioned, Simons and (Simons and Dachille, 1967) have reported the synthesis of following two forms of TiO_2 that have been derived from titania. As a consequence of this, TiO_2 has a composition that is composed of 60 percent titanium and 40 percent oxygen. Titania has a density of 4.23 g cm^-3, a bulk density of 0.85 g cm^-3, and a molecular weight of 79.87 g mol^-1. These values may be found in the table below (Lim *et al.*, 2010).

Calcination temperature, duration, and heating rate all have a significant impact on the crystalline state phase creation and growth of TiO_2 nanosized powder. It has been shown that the surface area of TiO_2 particles reduces as the calcination duration and heating rate rise (Fawzi Suleiman Khasawneh and Palaniandy, 2019). The change from amorphous to crystalline phase may be responsible for the disintegration and collapse of pores in the TiO_2 powder, which resulted in the reduction in surface area. According to (Ibrahim et al., 2018) research, the transition from anatase to rutile occurs more frequently when calcination temperatures are adjusted from 400 to 800 degrees Celsius. Titanium dioxide's photocatalytic activity is affected not only by its chemical structural attributes but also by its bandgap (Eg), which is a significant optical property of titanium dioxide.

Titania, in general, displays a band gap that is 3.0 eV for rutile and 3.2 eV for anatase, however this value can change depending on the phase structure. The redox potential of the charge carriers is generally considered to be the primary criterion for determining whether a semiconductor photocatalyst is optimal. For example, the domain of the band gap should be where the electron-hole recombination occurs in the catalyst. The conductive band, or CB, energy of TiO_2 (ECB = -0.51 V), which is slightly higher than the reduction reaction of oxygen (EO = -0.33 V), makes it easier for electrons to go from the conductive band to the conduction band of oxygen. The valence band (VB) level of

TiO_2, on the other hand, is significantly lower than the oxidation potentials of the majority of the electron donors. According to (Khaki *et al.*, 2017), the location of the bands in TiO_2 makes it possible for it to encourage the redox transformation of pollutants.

According to the finding (Khaki *et al.*, 2017), the anatase phase of titania possesses increased photocatalytic activity. This is because anatase has a larger conduction band energy of (0.2 eV), which can be related to the fact that it has more electrons in its ECB. Because of anatase's increased specific surface area (SSA), the electron transfer rate and, as a result, the charge recombination rate might be affected. This is due to the high electron cofactor binding site (ECB) of anatase as well as the location of the ECB. On the other hand, this might lead to a greater rate of recombination. Because of this, having rutile phase present is highly recommended, as it can reduce and even eliminate the amount of electron-hole recombination, leading to increased photocatalytic activity (Hoffmann *et al.*, 1995). However, it is possible to draw the conclusion that it is not a necessity that the anatase phase have a higher photocatalytic activity than the rutile phase. It is important to point out that the rutile structure, in comparison to the anatase structure, has a narrower band gap, which, as a result, has the potential to boost the photocatalytic activity of the catalyst.

2.5.1.2 Usage of TiO_2 as a Photocatalyst in Pharmaceuticals

In general, an ideal photocatalyst should have a few features, including stability, non-toxicity, low cost, photoactivity, and abundant. These are the primary requirement. Although there are a number of different semi-conductor photocatalysts, such as CeO, Fe_2O_3, WO_3, TiO_2, ZnO, and SnO_2, that match all of the requirements of an ideal photocatalyst, TiO_2 is the semiconductor photocatalyst that has been the main topic of the most research and is the catalyst that has been selected the most frequently for the degradation of pharmaceutical compounds (PhCs) (Kanakaraju, Glass and Oelgemöller, 2014). The use of heterogeneous photocatalysis with titanium dioxide semiconductors has shown to be particularly successful for the degradation of a variety of micro-pollutants. Titania is affordable, plentiful, photoreactive, non-toxic, chemically, and physiologically harmless, which places it in an advantageous position when compared to other photocatalysts. This places TiO_2 in a favourable position (Friedmann, Mendive and Bahnemann, 2010).

In general, the majority of the research that utilizing TiO_2 as a photocatalyst for the degradation of pharmaceutical compounds concentrated on establishing the best-operating parameters to create the highest degradation rate. This was the case for the majority of the investigations (Kanakaraju, Glass and Oelgemöller, 2014). Researcher have looked at operational characteristics such the pH of the pollutant solution, the amount of catalyst loading, the length of time the pollutant is exposed to sunlight, and the initial concentration of the contaminant (Lee *et al.*, 2017). However, we have determined that more research is necessary to improve the combination of operating factors that will lead to the highest amount of paracetamol degradation. Because these pharmaceutical compounds are relevant to the environment (Kanakaraju, Glass and Oelgemöller, 2014), the photocatalytic activity of non-steroidal anti-inflammatory drugs (NSAIDs), analgesics, antibiotics, and antiepileptics has been the main topic of the most explanation. Such pharmaceutical compounds can be found in drinking water and river water.

2.5.1.3 Characteristics of TiO_2 Photocatalyst

Even though titanium dioxide is an effective photocatalyst for the degradation of pharmaceutical compounds (PhCs) and other types of contaminants, the utilization of a single undoped photocatalyst, on the other hand, is connected to a few restrictions and disadvantages. A number of publications (Gupta and Tripathi, 2011; Singh *et al.*, 2020) have identified the primary downsides of utilizing a bare catalyst, and those shortcomings are summarized in the following points. Titania, in general, has several drawbacks, including the following: (i) a rapid recombination rate for the photo-induced e^-/h^+ pairs; (ii) the absorption of only a small amount of visible light photons; (iii) low stability; (iv) agglomeration of particles; and (v) a low photocatalytic activity when present in the presence of visible solar radiations.

In general, titania as a result of these disadvantages, a significant amount of research has been done to seek solutions to those challenges, improve the qualities of the catalyst, and, as a result, improve its photocatalytic activity for the removal of contaminants. The large band gap of 3.2 eV in the case of anatase is the primary reason why utilizing a bare TiO_2 photocatalyst is considered to be one of the most significant disadvantages of this method. This indicates that the TiO_2 particles can only successfully absorbed wavelengths shorter than 395 nm to form electron-hole pairs. In other words, this suggests that only shorter wavelengths. As a direct consequence of this, a variety of strategies have been designed to improve the photocatalytic activity of TiO_2 by enhancing its characteristics.

2.5.2 Ferric Oxide (Fe_2O_3)

Compounds containing iron oxide may be found frequently and widely distributed throughout the natural world, and it is simple to produce such compounds in the laboratory. Iron oxides are considered to be members of the family of transition metal oxides. Hematite (α-Fe_2O_3), magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and wüstite (FeO) are all examples of different types of iron oxide minerals, and they each have their own distinct crystalline structures (Fawzi Suleiman Khasawneh and Palaniandy, 2019). This is obvious to see that the crystallization of hematite is hexagonal. This structure is made up of iron atoms which are circled by six oxygen atoms. Because of its low cost, minimum of toxicity, chemical stability, and availability, α -Fe_2O_3 is a potential resource for the photocatalytic degradation of a wide number of contaminants and applications including the water treatment process.

2.5.3 Fe_2O_3-TiO_2 Photocatalyst

Extensive research has been conducted on the bonding of titanium dioxide with hematite in order to improve the structural and optical properties of titania, transition the ultraviolet region of titanium dioxide to the visible light region, and, as a result, improve the photocatalytic performance of titanium dioxide for the degradation of contaminants. In addition, the presence of iron can have a direct impact on the properties of TiO_2, such as the nanoparticles and photocatalytic reaction when exposed to ultra-violet light irradiation (Elghniji *et al.*, 2012). In a brief, minimizing the electron hole recombination process may be accomplished by connecting TiO_2 with the other transition metals like Fe. This is due to the fact that the energy level of Fe^{3+}/Fe^{2+} is below the conduction band edge of TiO_2, which allows Fe^{3+} to trap photo-generated electrons. This significant