RECOVERY OF TITANIUM DIOXIDE (TIO_2) FROM THE PHOTOCATALYSIS PROCESS

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SCHOOL OF CIVIL ENGINEERING
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RECOVERY OF TITANIUM DIOXIDE (TIO_2) FROM THE PHOTOCATALYSIS PROCESS

By

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ABSTRAK

Titanium dioksida, dikenali sebagai TiO_2, telah dihasilkan secara komersial sejak awal abad ke-20. Perkembangan kegunaan TiO_2 yang cepat telah menjadi pelbagai jenis aplikasi baharu seperti industri seramik, pengawet kayu, gentian tekstil dan elektronik bercetak. Pada tahun 2021, harga titanium dioksida telah meningkat sebanyak lapan kali ganda disebabkan oleh peningkatan kos bahan mentah dan permintaan yang besar. Tambahan pula, pembuatan TiO_2 akan menghasilkan sejumlah besar produk sampingan dan bahan buangan toksik daripada proses klorida dan sulfat. Oleh itu, kebolehgunaan semula TiO_2 yang dipulihkan dan dijana semula dicadangkan dalam kajian penyelidikan ini. Kromatografi cecair berprestasi tinggi (HPLC) telah digunakan dalam kajian ini untuk menyemak kecekapan penyingkiran pemangkin yang telah merawat air sisa sintetik yang mengandungi atenolol, karbamazepin, dan diklofenak. Eksperimen awal telah dijalankan untuk menentukan kesan penjerapan dan fotolisis langsung. Dos optimum pemuatan mangkin 100 mg telah dilaksanakan untuk eksperimen fotokatalisis yang dipulihkan dan dijana semula. Daripada keputusan, TiO_2 yang pulih mencapai fotodegradasi sebanyak 43.8 % (atenolol), 42.1 % (diklofenak) dan 39.5 % (carbamazepine) selepas larian kelima. Penggunaan semula TiO_2 yang dijana semula mempunyai kecekapan penyingkiran yang lebih tinggi daripada TiO_2 pulih selepas empat kitaran berturut-turut. Penggunaan semula pemangkin TiO_2 boleh digunakan untuk kelestarian alam sekitar.

ABSTRACT

Titanium dioxide, often known as TiO_2, has been manufactured commercially since the early 20th century. TiO_2 is quickly developing into a vast variety of new applications such as ceramic industry, wood preservatives, textile fibre, and printed electronics. In 2021, the price of titanium dioxide has multiplied by eight due to the rising cost of raw materials and huge demand. Furthermore, the manufacture of TiO_2 will generate a substantial volume of toxic by-products and waste materials from chloride and sulphate process. Thus, reusability of recovered and regenerated TiO_2 is proposed in this research study. The photodegradation efficiency is determined by treating synthetic wastewater sample containing atenolol, carbamazepine, and diclofenac. High-performance liquid chromatography (HPLC) is used in this study for checking the removal efficiency of photocatalyst. Preliminary experiments were conducted to determine effect of adsorption and direct photolysis on fresh TiO_2 photocatalyst. Optimum dosage of 0.2 mg/L catalyst loading was implemented for recovered and regenerated photocatalyst experiments. From the results, recovered TiO_2 achieve photodegradation of 43.8 % (atenolol), 42.1 % (diclofenac) and 39.5 % (carbamazepine) after the fifth run. Reusing of regenerated TiO_2 has higher removal efficiency than recovered TiO_2 after four successive cycles. Reuse of photocatalyst TiO_2 is applicable for sustainable of environment.

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LIST OF ABBREVIATIONS

ECs	Emerging Contaminants
EU	European Union
HCl	Hydrochloric Acid
HPLC	High Performance Liquid Chromatography
IUPAC	International Union of Pure and Applied Chemistry
NSAID	Nonsteroidal Anti-Inflammatory Drug
PhACs	Pharmaceutically Active Compounds
STP	Sewage Treatment Plant
UV	Ultraviolet
WWTP	Wastewater Treatment Plant

LIST OF SYMBOLS

%	Percentage
H_2O_2	Hydrogen Peroxide
°C	Degree Celsius
µL	Microlitre
µm	Micrometre
$C_{14}H_{11}Cl_2NO_2$	Diclofenac
$C_{14}H_{22}N_2O_3$	Atenolol
$C_{15}H_{12}N_2O$	Carbamazepine
CH_3OH	Methanol
cm	Centimetre
C_o	Initial Concentration
C_t	Final Concentration
eV	Electron Volt
g/L	Gram per Litre
H_2	Hydrogen
H_2O	Water
hr	Hour
L	Litre
lx	Lux
m^2/g	Meter square per Gram
mg	Milligram
mg/L	Milligram per Litre
mg/mL	Milligram per Millilitre

mins	Minutes
mL	Millilitre
mL min^{-1}	Millilitre per Minute
mL/min	Millilitre per minute
mm	Millilitre
nm	Nanometre
NO_x	Nitrous Oxides
O_2	Oxygen
OH	Hydroxide
rpm	Revolutions per Minute
TiO_2	Titanium Dioxide
V	Volt
W	Watt
µg/L	Microgram per Litre

CHAPTER 1

INTRODUCTION

1.1. Background

Titanium dioxide, often known as TiO_2, has been produced commercially since the early part of the twentieth century and has since found widespread application as a pigment in a variety of products, including sunscreens, paints, ointments, toothpaste, and many more (Chen & Mao, 2007). The expanding use of titanium dioxide in the ceramics sector is one of the primary factors contributing to the expansion of the worldwide market for titanium dioxide (TiO_2). TiO_2 is a common component that may be found in a wide range of goods, including plastic, paper, paints, medicines, sunscreen, and food items. It is also used in certain cosmetics. In addition to this, the use of TiO_2 is rapidly expanding into a wide variety of new fields. Titanium oxide is widely utilised in the ceramic industry as a popular white pigment and as a glaze opacifier. This is due to titanium oxide's dual function. Ceramic glazes get their crystallisation and variegation in colour and texture from the use of titanium dioxide. It has a propensity to crystallise, which gives ceramic glazes their characteristic whiteness. Additionally, it offers durable surfaces, powerful melts, and rich visual textures. Ceramic goods are protected against the damaging effects of pollutants such as nitrogen oxide, sulphur oxide, and carbon monoxide by the presence of TiO_2. Because of these qualities, ceramic producers choose to employ titanium dioxide, or TiO_2, as an opacifier rather than other compounds, such as tin oxide or zircopax (Technavio, 2019).

TiO_2 nanoparticles are gaining immense popularity and are being widely used in high-factor sun protection creams, wood preservatives, and textile fibres. They have the potential to use the energy in light to catalyse reactions with other molecules at reduced temperatures. TiO_2 nanoparticles are also being used for new applications such as printed electronics. TiO_2 has a novel property that has potential applications as a medium for room-temperature sensors of mechanical stress at the nanoscale. This property makes it useful in several sensing applications, ranging from biosciences to metrology (Technavio, 2019).

Titanium dioxide prices have been going up almost every month since the beginning of the year, and Lomon Billions Group, the market leader in the titanium dioxide industry, has just announced the eighth round of price increases for this year. The cumulative price increase has now reached 7,000 yuan/ton, and current prices have been raised by $1093/tonne. According to the price rising notice from main TiO_2 suppliers in China, the rising cost is the primary factor that is pushing up the price of titanium dioxide, and the prices of major raw materials such as titanium concentrate and sulfuric acid have increased greatly. In addition, the rising cost is the leading factor that is pushing up the price of titanium dioxide. Second, the demand on the home market continues to increase, whilst the demand on international markets is still being hampered by the pandemic. Despite the fact that manufacturing capacity has not yet recovered to normal levels, a growing number of items are being sent overseas (Wong, 2021).

There are two main production methods to manufacture titanium dioxide which are sulphate process and chloride process. The chloride method has a number of drawbacks, the most notable of which are high initial investment, sophisticated equipment construction, high material needs, resistance to high temperatures and corrosion, difficulty in repairing the device, and difficulty in research and development. Furthermore, the disadvantage of the sulphate process is that it takes a long time, and it can only be based on intermittent operation, wet operation, high consumption of sulfuric acid and water, and the production of a large number of wastes and by-products that are hazardous to the environment (Industry, 2022).

Improper disposal of titanium dioxide might expose people to danger of exposure, which could have negative health impacts. Exposure to excessive concentration of titanium dioxide can irritate the eyes, nose, and throat. Repeated exposure of titanium dioxide may result in bronchitis, phlegm production, coughing, and shortness of breath, as well as lung cancer (Health, 2016).

Photocatalysis based on nano-catalysts is a very promising method for the treatment of contaminated water. Solar photocatalysis and photocatalytic systems with artificial ultraviolet (UV) light are two separate forms of photocatalytic applications in water treatment. Both methods can be used to break down various chemical and microbiological contaminants in water and air at room temperature. Solar photocatalysis technology is affordable, environmentally beneficial, and universally accessible because it uses sunshine. The required equipment is modest, making it ideal for impoverished countries or distant locations without access to electricity.

Photocatalysis works on a very basic principle: A photocatalyst collects ultraviolet (UV) radiation from the sun and uses it to break down various compounds. Photocatalysis can be used to break down a wide range of organic materials, organic acids, oestrogens, pesticides, dyes, crude oil, microbes (including viruses and chlorine resistant organisms), and inorganic molecules such as nitrous oxides (NO_x), and metals when combined with precipitation or filtration. Photocatalysis with nanoparticles as catalysts is utilized to reduce air pollution, in building materials for self-cleaning surfaces, and in water purification because of its universal application (Kumari & Tripathi, 2019).

There are various potential photocatalysts, however, titanium dioxide (TiO_2) nanoparticles are the most promising and widely used. Nanosized particles are chosen over bulk TiO_2 because their increased surface area makes them substantially more reactive than bigger particles. TiO_2 is chemically stable, however, it has a high proclivity for breaking molecular bonds, which leads to deterioration. It is also plentiful and so affordable. For decades, TiO_2 has been employed in commercial products, such as a pigment in white paint and as a UV absorber in sunscreens. Hence, TiO_2 is chosen as the catalyst of photocatalysis for this project (Patchaiyappan, et al., 2016).

In addition, TiO_2 is used to explore the possibilities for recovery and reuse after it is collected from the photocatalysis process. The removal efficiency of recovered and regenerated TiO_2 will be evaluated through characterizations of catalysts such as High-performance liquid chromatography (HPLC).

1.2. Problem Statement

The use of titanium dioxide is quickly spreading into an increasingly extensive range of new applications. Titanium dioxide prices have been rising up virtually every month since the beginning of the year, and Lomon Billions Group, the global leader in the titanium dioxide business, has just announced the eighth round of price hikes for this year (Wong et al., 2021). The prosperity of titanium dioxide keeps becoming better despite many price hikes over the course of the year. Titanium dioxide welcomes the "price boom" once again; nonetheless, the demand is higher than the supply. Furthermore, the manufacturing of titanium dioxide using the sulphate process will have a number of negative effects on the surrounding ecosystem. These effects include the generation of vast quantities of waste materials, the need for costly pollution management, and the formation of anatase and rutile pigments (Industry, 2022). When titanium dioxide is not disposed of properly, it is exposed to humans at high levels, which can have harmful effects including coughing, breathlessness, and lung disorders (Health, 2016).

Hence in this project, the probability of the recovery of TiO_2 from photocatalysis are carried out to investigate the efficiency of the reused TiO_2. The filtration method is used for collecting the used TiO_2 from the effluent. Recovery of titanium dioxide is hoped to reduce the demand and usage of fresh titanium dioxide for sustainable environment. The regenerated TiO_2 is hoped to increase the efficiency of photocatalysis in the treatment of pharmaceutical wastewater.

1.3. Objectives

This study will use recovered and regenerated TiO_2 as the photocatalyst to test the photodegradation efficiency of 3 pharmaceutical compounds (carbamazepine, atenolol, and diclofenac) by treating synthetic wastewater using photocatalysis process in a laboratory scale. The following is a list of the research's goals:

1. To determine the regeneration process for recovered TiO_2 and its application in the removal efficiency of atenolol, carbamazepine and diclofenac, the pharmaceutical compounds.
2. To evaluate the effectiveness of recovered and regenerated TiO_2 photocatalyst by using HPLC technique.

1.4. Scope of Research

This research work focuses on the performance of TiO_2 as the photocatalyst in synthetic wastewater for the removal of carbamazepine, atenolol, and diclofenac. The recovered TiO_2 is collected after the photocatalysis process and undergoes regeneration.

The regenerated TiO_2 will be used to determine the efficiency of the removal of 3 pharmaceutical compounds (carbamazepine, atenolol, and diclofenac). The collected aliquot samples during the photocatalysis process will be sent for high-performance liquid chromatography (HPLC) test. This test could determine the concentration of the pharmaceutical compound that remained in the synthetic wastewater. Hence, the efficiency of the recovered TiO_2 can be determined at the optimum concentration of synthetic wastewater.

1.5. Organization of Thesis

This thesis is divided into five chapters, with a summary of each chapter provided below:

Chapter 1 provides a brief background on the research issue and emphasizes the importance of this investigation. It also includes a description of the problem statement, the research scope, and the study's objectives.

Chapter 2 covers the literature review of the core concepts and theories connected to photocatalysis. Furthermore, it covers the fundamentals of TiO_2 as well as a brief overview of the treatment of pharmaceutical compounds, with a focus on the pharmaceutical pollutants (carbamazepine, atenolol, and diclofenac).

Chapter 3 provides the methodology for the laboratory works in this study that included the preparation of the synthetic pharmaceutical wastewater, recovery, and regeneration of photocatalyst, TiO_2, and concentration of pharmaceutical compounds (carbamazepine, atenolol, and diclofenac) using HPLC, photocatalysis, and explain how HPLC test function to obtain the efficiency of the recovered TiO_2 in the removal of carbamazepine, atenolol, and diclofenac from synthetic wastewater.

Chapter 4 compare and focuses the performance between the recovered TiO_2 and regenerated TiO_2 in photocatalysis process. Apart from that, this Chapter also investigates the photocatalytic performance of TiO_2 in the removal of carbamazepine, atenolol, and diclofenac from synthetic wastewater in the lab-scale work.

Chapter 5 concludes the outcome of this research and highlights the recommendations for future research work.

CHAPTER 2

LITERATURE REVIEW

2.1. Overview

The incidence, fate, and retention of pharmaceutical chemicals such as carbamazepine, atenolol, diclofenac in the aquatic environment and water bodies are briefly described in this Chapter. The most modern techniques for removing pharmaceutical substances were then studied. Additionally, the emphasis of this Chapter is on the theoretical explanation of the mechanism and process of photocatalysis. Lastly, a thorough analysis of the nano photocatalyst employed in this work, including TiO_2, and recovered TiO_2 is involved.

2.2. Emergence of Titanium Dioxide Nanoparticles

Titanium dioxide's increasing usage in the ceramics sector is a significant driver driving the expansion of the worldwide titanium dioxide (TiO_2) market. TiO_2 is a prominent component found in several goods, including plastic, paper, paints, medications, sunscreen, and food. Additionally, the utilization of TiO_2 is expanding to several new applications. As a prominent white pigment and glaze opacifier, titanium oxide is widely used in the ceramics industry. TiO_2 gives ceramic glazes crystallization and variation in colour and texture. It lends whiteness to ceramic glazes and produces durable surfaces, powerful melts, and rich visual textures due to its inclination to crystallized. TiO_2 also protects ceramic items against contaminants such as nitrogen oxide, sulphur oxide, and carbon monoxide. These properties urge ceramic producers to choose TiO_2 as an opacifier rather than tin oxide or zircopax (Technavio, 2019).

The usage of TiO_2 nanoparticles in high-factor sun protection lotions, wood preservatives, and textile fibers is gaining great appeal. They could harness the energy in light to catalyze low-temperature reactions with other molecules. Nanoparticles of TiO_2 are being employed in innovative applications, such as printed electronics. TiO_2 has a new characteristic that has potential uses as a nanoscale mechanical stress sensor medium at ambient temperature. Several sensing applications, spanning from biosciences to metrology, may benefit from this characteristic. Consequently, the diverse applications of TiO_2 nanoparticles are anticipated to drive market expansion throughout the projected period (Technavio, 2019).

2.2.1. Price of Titanium Dioxide Rising

Titanium dioxide is unquestionably the brightest "titanium white" Venus since the beginning of the year, as the chemical industry has risen steadily since the start of the year. Titanium dioxide prices have increased nearly every month since the beginning of the year, and Lomon billions Group, the titanium dioxide market leader, has ushered in the eighth round of price increases this year, with the cumulative price increase reaching 7,000 yuan/ton, increased by $1093/tonne currently.

According to a price increase notice from the top TiO_2 suppliers in China, the growing cost is the primary cause driving up the price of titanium dioxide, and the costs of key raw materials such as titanium concentrate and sulfuric acid have risen significantly. Second, the demand on the local market continues to increase, while the pandemic continues to impact overseas markets. The manufacturing capacity has not yet restored to normal, and exports are rising (Wong, 2021).

Table 2.1: Price of Titanium Dioxide in Year 2021 (Wong, 2021)

Material	2021/9/15 (¥/ton)	Beginning price this year	Increase this year
Titanium dioxide (TiO_2)	21000	16695	125.79 %

2.2.2. Process Generate TiO_2 Produce Waste

Titanium, one of the ninth most prevalent elements in the Earth's crust (0.63 % by weight), is a crucial element for several industrial uses. This paper examines the various mining and industrial processes involved in the manufacturing of titanium dioxide. First, the beneficiation mining process of titanium mineral will be examined, followed by a discussion of the two primary TiO_2 production methods (sulphate and chloride routes).

The wastes created by the chloride process consist mostly of unreacted coke and ore solids during the chlorination process. When the combined stream of unreacted coke and ore particles, metal chloride solids, is acidified with water or waste hydrochloric acid (HCl) from the reaction scrubber, a waste acid solution, often known as iron chloride waste acid, is also produced. Metal chloride impurities are often detrimental to the environment, particularly iron chloride, which is removed, neutralized with lime or limestone, and disposed of in a landfill. In one chlorine facility in the United States, the chlorine salts are not neutralized, but are instead poured into a deep, depleted oil well (Gázquez et al., 2014). The disadvantage of the sulphate process is that it is lengthy and can only be based on intermittent operation, wet operation, high consumption of sulfuric acid and water, and the production of several pollutants and byproducts that are damaging to the environment (Industry, 2022).

2.3. Pharmaceutical Wastes

Pharmaceutical drug use continues to rise as the healthcare system improves and people's hopes for a longer life rise. Human beings use roughly 1 lakh tons of pharmaceutical medications each year on a global scale. This information demonstrates that the global average intake is 15 grams per capita per year (Ternes & Joss, 2006). The rise of micropollutants in the aquatic environment has caused widespread concern in recent years. Micropollutants, also known as emerging contaminants (ECs), are made up of a variety of synthetic and natural substances, such as medications, personal care items, agrochemicals, and steroid hormones, in varying amounts.

The concentration of this material, however, will be on medicinal substances (PhACs). Pharmaceuticals are chemical compounds that are used to identify, treat, and prevent diseases (Quesada et al., 2019). Pharmaceuticals can also be defined as over-the-counter prescriptions and veterinary drugs that are used to treat humans and animals (Ebele et al., 2017). Antibiotics, synthetic hormones, statins, anti-inflammatories, and cytotoxins are among the many types of human medicines that are continuously created and consumed in vast quantities, amounting to thousands of tons per year (Quesada et al., 2019). Pharmaceutical compounds are a significant category of developing pollutants (ECs). Furthermore, their existence in water has sparked widespread worry due to the possible danger they pose to humans and the aquatic environment (Quesada et al., 2019). Furthermore, the widespread and intense use of pharmaceuticals increased the concentration and prevalence of these chemicals in water bodies, wastewater, and stormwater runoff.

Several studies have looked into the routes and fates of pharmacological chemicals in the environment (Rosman et al., 2018; Lee et al., 2017b; Quesada et al., 2019). PhACs are typically delivered into the aquatic environment in either their parent form or as metabolites via a variety of mechanisms.

Essentially, the principal pathway for the occurrence of these medical compounds is through their disposal as municipal sewage following consumption, metabolism, and excretion in the human body. These medical chemicals are administered to the environment via animal excretion in addition to human use. In typical wastewater treatment plants, these pharmaceutical chemicals are not biodegraded. As a result, they are dumped into water bodies, such as rivers and lakes, along with the treated effluent. Furthermore, even after typical water treatment, these medications can still be found in drinking water, according to research (Rosman et al., 2018; Quesada et al., 2019).

The presence of pharmaceutical substances in water bodies is causing widespread worry, and it is quickly becoming a global problem. Determining the global consumption of pharmaceutical items is quite challenging. This is because the amount of compounds utilized locally varies according to lifestyles, accessibility, geography, and population (Quesada et al., 2019).

2.3.1. Occurrence and Fate of Pharmaceuticals

Pharmaceuticals are essential to the practise of contemporary medicine. The use of medicines has significantly increased over the past few decades due to factors like an expanding worldwide population, rising health care spending, technological advancements, widespread global market accessibility, and ageing societies in developed nations (Beek, et al., 2015).

Due to their continued introduction into the environment primarily through hospital effluents, agricultural activities, and waste-water treatment plants, the increased consumption, disposal, and presence of human pharmaceuticals in the environment, particularly in aquatic systems, has raised concerns worldwide (WWTP). Surface water, groundwater, and treated drinking water are all contaminated as a result of insufficient pharmaceutical removal efficiency in WWTPs (Ngqwala & Muchesa, 2020).

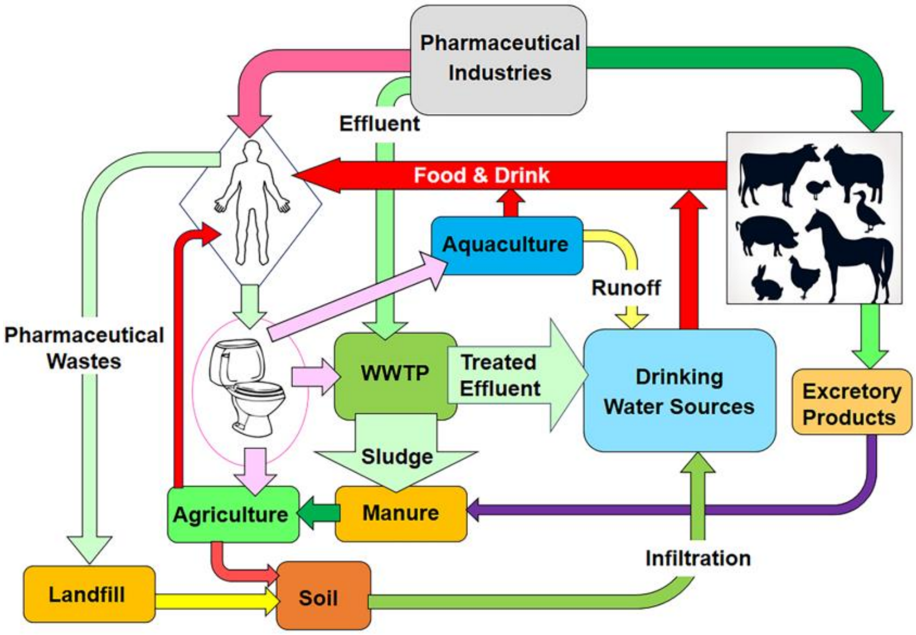


Figure 2.1: Occurrence and Fate of Pharmaceuticals in the Environment (Majumdar & Pal, 2019)

Pharmaceuticals get up in the environment as a result of releases from many locations, including homes, hospitals, farms, and areas used for agriculture, aquaculture, and livestock. Both people and animals excrete the medications that have been taken in both their unaltered (parent pharmaceuticals) and altered (transformation products) forms because they have not been completely digested. Pharmaceuticals are primarily received by wastewater treatment facilities (WWTPs) through human excretion, medication rejection, and untreated pharmaceutical industrial effluent (Majumdar & Pal, 2019).

2.3.2. Carbamazepine

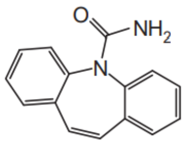
Carbamazepine is a kind white or crystalline white powder in appearance. The IUPAC name of carbamazepine is 5H-dibenzo[b,f]azepine-5-carboxamide.

Carbamazepine has melting point range 189 – 193 °C. The molecular weight of carbamazepine is 236.27. Some of the trade name of carbamazepine is Biston, Finlepsin, Stazepine, Tegretal, Telesmin, and Timonil. Carbamazepine is very slightly soluble in water, freely soluble in methylene chloride, sparingly soluble in acetone and in ethanol (96%). It shows polymorphism. The acceptable crystalline form corresponds to carbamazepine CRS. The properties of carbamazepine are summarized in Table 2.1 (Alrashood, 2016).

Carbamazepine is a kind of anticonvulsant. It functions by reducing the nerve impulses responsible for conditions like trigeminal neuralgia and diabetic neuropathy that led to seizures and nerve pain. Bipolar disorder is also treated with carbamazepine. Other uses for carbamazepine not included in this pharmaceutical guide are possible (Entringer, 2022).

Carbamazepine as a widely prescribed antiepileptic drug, has regularly been found in aquatic environment. It has raising concerns about its potential effects on aquatic creatures. The behaviour and molecular reactions of carbamazepine has an effect on zebrafish embryos. Existence of carbamazepine had disturbed normal growth and development of exposed zebrafish embryos and larvae. Upon exposure to carbamazepine at 1 μg/L, the hatching rate, body length, swim bladder appearance and yolk sac absorption rate were significantly increased (Qiang et al., 2016). Exposed to chronic contamination by carbamazepine, aquatic invertebrates might be disadvantaged in front of predators or competitive neighbour species, and less able to compete for resources. They might thus have somewhat reduced life expectancy and reproduction rates (Cammaerts, et al., 2015).

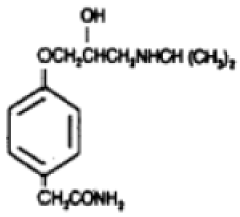
Table 2.2: Properties of Carbamazepine (Alrashood, 2016)

Categories	Details
IUPAC name	5H-dibenzo[b,f]azepine-5-carboxamide
Structure	
Chemical formula	$C_{15}H_{12}N_2O$
Melting point	189 – 193 °C
Molecular weight	236.27
Proprietary name	Biston; Finlepsin; Stazepine; Tegretal; Telesmin; Timonil

2.3.3. Atenolol

Atenolol a synthetic, beta$_1$-selective (cardioselective) adrenoreceptor blocking agent, may be chemically described as benzeneacetamide, 4-[2'-hydroxy-3'- [(1 methylethyl)amino]propoxy]-. The molecular formula of atenolol is $C_{14}H_{22}N_2O_3$. Atenolol (free base) has a molecular weight of 266. It is a relatively polar hydrophilic compound with a water solubility of 26.5 mg/mL at 37°C and a log partition coefficient (octanol/water) of 0.23. It is freely soluble in 1N HCl (300 mg/mL at 25°C) and less soluble in chloroform (3 mg/mL at 25°C). The pH of the solution is 5.5-6.5. The properties of atenolol were summarized in Table 2.2 (Cunha et al ., 2022). Atenolol is a adrenergic receptor antagonist (‘-blocker’) regularly used for the treatment of angina, glaucoma, high blood pressure and other related conditions (Winter, et al., 2008).

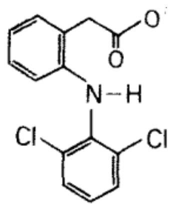
Table 2.3: Properties of Atenolol (Cunha et al., 2022)

Categories	Details
IUPAC name	4-[2'-hydroxy-3'- [(1 methylethyl)amino]propoxy]-, benzeneacetamide
Structure	
Chemical formula	$C_{14}H_{22}N_2O_3$
Melting point	508 °C
Molecular weight	266
Proprietary name	Tenormin

2.3.4. Diclofenac

Diclofenac is a nonsteroidal anti-inflammatory drug (NSAID). This medicine works by reducing substances in the body that cause pain and inflammation. Diclofenac is used to treat mild to moderate pain, or signs and symptoms of osteoarthritis or rheumatoid arthritis. Voltaren is also indicated for the treatment of ankylosing spondylitis. The Cataflam brand of this medicine is also used to treat menstrual cramps. Diclofenac powder (Cambia) is used to treat a migraine headache attack. Cambia will only treat a headache that has already begun. It will not prevent headaches or reduce the number of attacks (Kaci Durbin, 2022).

Table 2.4: Properties of Diclofenac (Menassé, et al., 1978)

Categories	Details
IUPAC name	2-[2-(2,6-dichloroanilino)phenyl]acetic acid
Structure	
Chemical formula	$C_{14}H_{11}Cl_2NO_2$
Melting point	302-310 °C
Molecular weight	296
Proprietary name	Cataflam, Voltaren-XR, Dyloject, Cambia, Zipsor, and Zorvolex

2.3.5. Concentration of Pharmaceutical Compound in Water Source

In recent years, both manufacturing and consumption of pharmaceutical products have increased rapidly with the development of medicine. Nearly 3,000 pharmaceutical compounds are used to make medicine, and hundreds of tonnes are produced annually (Carvalho and Santos, 2016; Grenni et al., 2018). The most widely used pharmaceuticals in the world are analgesics, antibiotics, and anti-inflammatory medications. As a result, the development of water-soluble and pharmacologically active organic micropollutants, also known as pharmaceutical active compounds (PhACs), has attracted considerable attention on a global scale.

Pharmaceutical substances that end up in water bodies, including groundwater and surface water, come from a variety of sources. The first of them is urban wastewater, which has a high concentration of pharmaceuticals from human waste and insufficiently disposes of unused or expired medications because of the lack of management oversight.

Agricultural and livestock waste, particularly the latter, is a significant source of pharmaceuticals. Large farms with extensive livestock frequently enhance the grain they eat with medications, and they frequently employ animal excreta as soil amendments, which leach into the groundwater. Another significant source is pharmaceutical sector effluents. Despite stringent control, pharmaceuticals are discovered in high amounts in factory emissions from Asia, Europe, and America (Ortúzar et al., 2022).

Table 2.5: Types of Pharmaceutical Compounds

Types of Pharmaceutical Compounds	Studies	Average Concentration (ng/L)	References
Carbamazepine	Groundwater in Japan, USA, Canada, and Germany	1 - 100	(B., T., & J, 2008)
Carbamazepine	Groundwater	610	(Drewes et al., 2002)
Carbamazepine	Groundwater	20 - 135	(T.Heberer et al., 2001)
Carbamazepine	Drinking water in Mediterranean region	13.9 - 43.2	(Rabiet, et al., 2006)
Carbamazepine	WWTP effluent	90 - 155	(J.E.Drewes et al., 2002)
Diclofenac	49 WWTP effluents	1600	(Ternes T. , 1998)

Diclofenac	22 rivers	800	(Ternes T. , 1998)
Diclofenac	10 WWTP effluents in EU countries	140 - 1480	(Paxéus, 2004)
Diclofenac	WWTP in Switzerland	10 - 29	(H.-R.Buser et al., 1998)
Diclofenac	Stream in Ohio, USA	24.5	(H.-R.Buser et al., 1998)
Diclofenac	Estuaries in UK	195	(K.V.Thomas & M.J.Hilton, 2004)
Diclofenac	Estuary at North Sea	6.2	(S.Weigel et al., 2002)
Diclofenac	Surface water in Berlin	1030	(Heberer et al., 2002)
Atenolol	Main hospital in Fossvogur	20.8 - 12700	(Huber, et al., 2013)
Atenolol	Hvarageroi	20.8 - 1730	(Huber, et al., 2013)
Atenolol	Surface water of South Korea	690	(Chander, et al., 2016)

2.4. Photocatalysis

An electron-hole pair is produced when a semiconducting substance is exposed to light, a process known as photocatalysis. On the basis of the appearance of the physical state of the reactants, two types of photocatalytic reactions may be distinguished.

- Homogeneous photocatalysis: This type of photocatalytic reaction occurs when the semiconductor and reactant are both in the same phase, such as a gas, solid, or liquid.
- Heterogeneous photocatalysis: These photocatalytic processes are referred to as heterogeneous photocatalysis when the semiconductor and reactant are in distinct stages. (Ameta R. , 2018)

2.4.1. Principles and Mechanism of Photocatalysis

Numerous literatures have extensively explored the photocatalytic process' reaction processes (Fujishima et al., 2008; Hoffmann et al., 1995; Chong et al., 2010). The most often used photocatalyst for causing a number of reductive and oxidative processes on its surface is the semiconductor TiO_2. The lone electron will be photoexcited and jump to the conduction band when a photon energy (hv) equal to or greater than the bandgap energy of titania (3.2 eV for anatase and 3.0 eV for rutile) illuminates its surface.

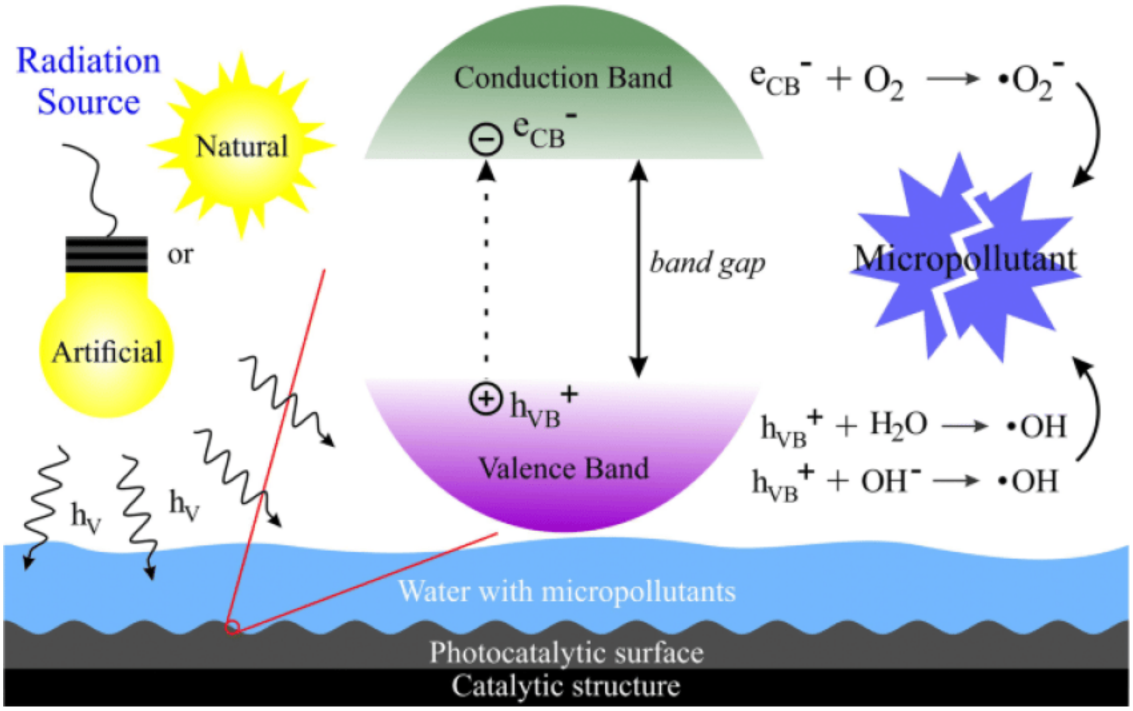


Figure 2.2: Principles and Mechanisms of Photocatalysis Process

As time has gone on, new and varied approaches have been used. In order to improve and boost the photocatalytic properties, for instance, surface and interface modification by controlling particle size and shape, composite or coupling materials, doping of transition metal, doping of nonmetal, application of co-doping (like; metal–metal, metal–nonmetal, nonmetal–nonmetal), deposition of noble metal, and by the use of organic dye and metal complexes sensitization of surface. In our studies, TiO_2 is used as our photocatalyst, and the recovery study is reviewed at section 2.3.2.

In an electrolytic cell with ultraviolet (UV) light irradiation, Boddy discovered in 1968 that O_2 was generated on TiO_2. By exposing the TiO_2 electrode to UV light, Fujishima and Honda discovered that photoelectrochemical water (H_2O) splitting could create O_2 on a TiO_2 electrode and H_2 on a platinum black electrode. Rapid growth in TiO_2 heterogeneous photocatalysis has been accompanied by a number of energy and environmental challenges, such as the direct solar H_2O splitting into H_2 and the breakdown of air pollutants and H_2O at low concentrations. TiO_2 heterogeneous photocatalysis has advanced greatly, but there is still more to learn. This presents an intriguing challenge for both engineers and fundamental scientists. The formation of charge carriers, their separation, relaxation, trapping, transfer, recombination and transportation, and bond breaking, and forming are just a few of the fundamental processes that are typically present in a typical photocatalytic reaction in TiO_2 photocatalysis. These processes require careful investigation.

The ideal method for gaining profound understanding of TiO_2 photocatalysis is to investigate the basic mechanisms of the reaction in actual environmental circumstances. Currently, the single charge transfer step in TiO_2 photocatalysis as well as charge carrier formation, separation, relaxation, trapping, recombination, and transportation have all been thoroughly studied by a variety of techniques with the aid of suitable electron acceptors or donors in actual environmental settings. But in TiO_2 photocatalysis, the entire reaction is often carried out in a series of charge transfer and bond breaking/forming phases. Additionally, the majority of reactants are neither excellent electron donors nor acceptors of electrons. Due to this, it is exceedingly challenging to pinpoint the mechanistic investigations of TiO_2 photocatalysis in actual environmental settings.

2.4.2. Photocatalyst

The terms photo, which has to do with photons, and catalyst, which is a chemical that affects the pace of a process when it is present, are combined to form the phrase "photocatalyst." As a result, photocatalysts are substances that, when exposed to light, alter the pace of a chemical process. Photocatalysis is the term for this phenomenon. Reactions that use light and a semiconductor are referred to as photocatalysis. A photocatalyst is a substance that absorbs light and serves as a catalyst for chemical processes. In essence, all photocatalysts are semiconductors (Ameta R. , 2018).

Semiconductors function as photocatalysts because they can conduct electricity even at ambient temperature in the presence of light. The energy of photons is absorbed by an electron (e^-) in the valence band of a photocatalyst when it is exposed to light of the desired wavelength (enough energy). This electron is then stimulated to the conduction band. A hole (h^+) is made in the valence band during this operation. This procedure creates the photoexcitation state and produces the e^- and h^+ pair. An acceptor is reduced using this excited electron, while donor molecules are oxidised using the acceptor's hole. The significance of photocatalysis resides in the fact that a photocatalyst simultaneously creates an oxidation and a reduction environment (Ameta R. , 2018).

Photocatalysts can be utilised for a variety of purposes, including antifouling, antifogging, energy storage and conservation, deodorization, sterilisation, self-cleaning, air purification, wastewater treatment, and more. Due to their electrical composition, semiconductors serve as photo redox process sensitizers. Many organic contaminants, including aromatics, halo hydrocarbons, insecticides, herbicides, dyes, and surfactants, can be completely mineralized by certain semiconductors (Ameta R. , 2018).

2.5. Nano-catalyst

The catalytic activity of transition metal oxide structures, such as spherical nanoparticles, nanowires, nanorods, and nanocubes, with or without support, is based on the size of the material with the maximum feasible surface area (Gadipelly & Mannepalli, 2019).

2.5.1. Titanium Dioxide

Titanium dioxide (TiO_2), often known as titanium, has a wide range of uses in the textile, pharmaceutical, culinary, electronics, polymer, and biomedical and biological fields of study. Its employment as a potent photocatalyst and top-notch support material to carry out a number of ecologically friendly transformations is its most significant application. The procedures for production and processing have a significant impact on the physical and chemical characteristics of titania nanocrystals. There have been several published synthetic processes with exact control over the phase development and shape of TiO_2 nanoparticles. The hydrolysis of titania salts is all that is required to produce nano-TiO_2.

Because of its exceptional activity, non-toxicity, ease of availability, reusability, high oxidising power, acidity, and long-term stability, nano-TiO_2 has been demonstrated to be an effective catalyst in synthetic chemistry. Additionally, compared to commercial TiO_2 (SA: 10.69 m^2/g), nano TiO_2 has a greater surface area (500 m^2/g) and higher porosity, both of which may improve its chemical reactivity. TiO_2 has three primary crystallographic types: anatase, rutile, and brookite, each of which has a unique chemical reactivity and photochemical activity as well as a range of refractive indices. This wide range of options makes it possible to tailor the right material to a variety of needs and applications (Gadipelly & Mannepalli, 2019).