SYNTHESIS OF TITANIUM DIOXIDE/ZEOLITE CATALYST AND TREATMENT OF SULFAMETHOXAZOLE

TAN LING CHI

SCHOOL OF CIVIL ENGINEERING
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By

TAN LING CHI

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Name of Student: Tan Ling Chi

I hereby declare that all corrections and comments made by the supervisor(s) and examiner have been taken into consideration and rectified accordingly.

Signature:

Date : 12/8/2022

Approved by:

(Signature of Supervisor)

Name of Supervisor : Assoc. Prof. Dr. Puganeshwary Palaniandy

Date : 12/8/2022

Approved by:

Professor Dr. Hamidi Abdul Aziz
Pusat Pengajian Kejuruteraan Awam, Kampus Kejuruteraan
Universiti Sains Malaysia,
14300 Nibong Tebal, Pulau Pinang, MALAYSIA
Tel: +604-5996215 Fax: +604-5996906
Email:cehamidi@usm.my, cehamidi2013@gmail.com

(Signature of Examiner)

Name of Examiner : HAMIDI ABDUL AZIZ

Date : 11 AUGUST 2022

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ABSTRAK

Kehadiran SMX yang stabil dan mudah alih dalam tanah dan kerap dikesan dalam pelbagai petak akuatik. Pecahan bahan cemar ini adalah lemah di loji rawatan air sisa. Pembangunan strategi penyingkiran SMX yang berkesan adalah penting. Photocatalysis heterogen adalah salah satu AOP yang dianggap paling menjanjikan untuk merawat SMX semasa berfungsi pada suhu dan tekanan bilik. Tindak balas kimia fotokatalisis adalah kompleks, mangkin komposit boleh meningkatkan fotokatalisis. TiO_2/Zeolit dicadangkan untuk degradasi SMX. Dalam kajian ini, spektroskopi SEM, XRD, UV-VIS, FTIR, dan BET digunakan dalam pencirian mangkin. Nanokomposit digunakan dalam fotokatalisis untuk merendahkan SMX di bawah penyinaran suria simulasi. Faktor operasi termasuk dos mangkin, telah dibandingkan dengan kajian terdahulu untuk mendapatkan keadaan optimum yang diperlukan untuk kadar degradasi maksimum. Masa penyinaran untuk keadaan optimum menggariskan kecekapan penyingkiran SMX dengan menggunakan TiO_2/Zeolit dengan cahaya, tanpa cahaya dan zeolit (untuk larian kawalan) sebagai mangkin. Keputusan pencirian menunjukkan bahawa penggunaan TiO_2 kepada zeolit menstabilkan fasa anatase TiO_2, meningkatkan kedua-dua luas permukaan dan isipadu liang bahan TiO_2/zeolit. Dos pemangkin optimum ialah 0.20g dengan kepekatan awal SMX ialah 20mg/L dengan 14.67% kecekapan penyingkiran. Masa penyinaran selama 6 jam dengan menggunakan TiO_2/Zeolit dengan cahaya telah menunjukkan bahawa ia adalah cara yang berkesan untuk memecahkan SMX dalam keadaan optimum.

ABSTRACT

The presence of SMX, that is stable and mobile in soils and is regularly detected in various aquatic compartments. The breakdown of these contaminants is poor in wastewater treatment plants. The development of effective SMX removal strategies is essential. Heterogeneous photocatalysis is one of the AOP that is thought to have the most promise for treating SMX while functioning at room temperature and pressure. As photocatalysis chemical reactions are complex, the composite catalyst could improve photocatalysis. TiO_2/Zeolite is proposed for the degradation of SMX because of the good performance of composites in the photodegradation of propane based on previous study. In this study, SEM, XRD, UV-VIS spectroscopy, FTIR, and BET were used in catalyst characterization. The nanocomposite was used in photocatalysis to degrade SMX under simulated solar irradiation. The operating factor including the catalyst dosage, was compared with previous studies to obtain the optimum conditions required for the maximum degradation rate. The irradiation time for optimum conditions outlined the removal efficiency of SMX by using TiO_2/Zeolite with light, without light and zeolite (for the control run) as catalyst. Characterization results showed that application of TiO_2 to zeolite stabilised anatase phase of TiO_2, enhanced both surface area and the pore volume of the TiO_2/zeolite material. The optimum catalyst dosage is 0.20g with the initial concentration of SMX being 20mg/L with 14.67% of removal efficiency. The 6 hours of irradiation time by using TiO_2/Zeolite with light had shown that it's an effective way to break down SMX under optimum condition.

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LIST OF ABBREVIATIONS

3H5M	3-hydroxy-5-methylisoxazole
AOP	Advanced Oxidation Process
BET	Brunauer-Emmett-Teller
DDD	Defined Daily Doses
DRS	Diffuse Reflectance Spectroscopy
EC	Emerging Contaminants
FTIR	Fourier Transform Infrared
GDP	Gross Domestic Product
HPLC	High Performance Liquid Chromatography
IUPAC	International Union of Pure and Applied Chemistry
OTC	Oxytetracycline
PhAC	Pharmaceutically Active Chemical
POP	Persistent Organic Pollutant
PW6	Pigment White 6
SA	Sulfanilamide
SEM	Scanning Electron Microscope
SMT	Sulfamethazine
SMX	Sulfamethoxazole
SNA	Sulfanilic Acid
STP	Sewage Treatment Plant
TIPT	Tetraisopropoxide
UN	United Nation
UV	Ultraviolet

UV-Vis	Ultraviolet-Visible
WWTP	Wastewater Treatment Plant
XRD	X-Ray Diffraction

LIST OF SYMBOLS

%	Percentage
H_2O_2	Hydrogen Peroxide
$[SMX]^-$	Anion form of Sulfamethoxazole
$[SMX]^+$	Cation form of Sulfamethoxazole
°C	Degree Celcius
Al_2O_3	Aluminium Oxide
AlO_4	Oxidoperoxy(oxo)alumane
$C_{10}H_{11}N_3O_3S$	Sulfamethoxazole
cm	Centimetre
cm^{-1}	Per Centimetre
cm^3/g	Centimetre cube per gram
C_o	Initial Concentration
C_t	Final Concentration
eV	Electronvolt
Fe_2O_3	Hematite
g	Gram
g/L	Gram per Litre
hr	Hour
L	Litre
m^2/g	Meter square per gram
mg	Milligram
mg/L	Milligram per Litre
min	Minutes

mL	Millilitre
ng/L	Nanogram per Litre
nm	Nanometer
º	Degree
O_2	Oxygen
OH	Hydroxide
pg/L	Picogram per Litre
rpm	Revolutions per Minute
SiO_4	Monosilicate
TiO_2	Titanium Dioxide
V	Volt
W	Watt
ZnO	Zinc Oxide
θ	Theta
µg/L	Microgram per Litre
µM	Micromole

CHAPTER 1

INTRODUCTION

1.1. Background

The presence of persistent organic pollutants (POPs) in the aquatic environment, such as sulfamethoxazole (SMX), a pharmaceutical residue that is stable and mobile in soils and is regularly detected in various aquatic compartments. POPs also can be found in water intended for human consumption at very low amounts. The breakdown of these contaminants is poor in wastewater treatment plants. As a result, the development of long-term and effective SMX removal strategies is essential. There are a lot of methods in order to remove SMX in the wastewater which are coagulation, adsorption, advance oxidation process (AOP), ozonation, nanofiltration and others. For the removal of pharmaceuticals from wastewater, AOP based on the production of very reactive hydroxyl radicals (OH) have recently attracted a lot of interest. Heterogeneous photocatalysis is one of the AOP that is thought to have the most promise for treating pharmaceutical active components while functioning at room temperature and pressure (Ahmed et al., 2014).

Photocatalysis is a reaction that takes place by utilizing light and a semiconductor. It is a phenomenon, in which an electron-hole pair is generated on exposure of a semiconducting material to light (Ameta, 2018). This process is important for pharmaceutical wastewater treatment. Pharmaceutical wastewater treatment is a complicated process due to the presence of various kinds of toxic chemicals and antibiotics that are harmful to any living organisms (Azimi et al., 2017). Sulfamethoxazole, $C_{10}H_{11}N_3O_3S$ (SMX) is a popular bacteriostatic antibiotic used in the pharmaceutical field. It is employed in the treatment of numerous bacterial illnesses (such as middle ear, urine, respiratory, and intestinal infections). Another purpose for it is to both prevent and treat a specific kind of pneumonia (pneumocystis-type). Effluents from wastewater treatment plants (WWTPs) have been found to frequently contain SMX (da Silva Rodrigues et al., 2020). Because of the toxicity that they cause and the possibility that they will cause bacteria to become resistant to treatment, SMX is capable of being classified as environmental pollutants, especially in the water bodies, with the concentration ranging from 141-190 ng/L (Wang & Wang, 2018). Hence, their presence in the aquatic compartment becomes a threat to human health (Rodrigues et al., 2020). The presence of SMX in the effluent is due to the traditional wastewater treatment plants were mainly used to reduce levels of conventional pollutants from domestic and industrial sewage. Many studies have shown that the treatment plants cannot fully remove all antibiotics in wastewater. Therefore, AOP have been suggested as tertiary treatments in effluent wastewaters due to their versatility and ability to minimize undesirable effects into the environment (Konstas et al., 2019).

The removal of SMX in wastewater required the application of catalysts to increase the rate of the photocatalysis process. Generally, the application of catalysts is widely used in modern industries. It is the material used to accelerate the chemical process without itself being consumed. The catalyzed process is benefited the major field of industrial process by saving time and cost to obtain the final products. However, some catalysts are difficult to be used directly in the chemical reaction. For example, titanium dioxide (TiO_2) is difficult to be used for the photocatalysis process due to its large bandgap. Composite catalysts, which have two or more components combined together, are widely investigated and used because most practical catalytic processes are so complicated that single component catalysts cannot easily meet the requirements for high performance such as high activity, remarkable selectivity, and good resistance to deactivation. As a result of this, composite catalysts, which have two or more components combined together, are much more popular (Xie et al., 2010).

There are many types of catalysts, including homogeneous, heterogeneous, or enzymes based. Nanoparticles have several important applications, but one of the most important is catalysis. The use of nanocatalysts makes it possible to quickly convert chemicals while simultaneously increasing product yield and simplifying the separation of the catalyst. In a homogeneous nano catalysis reaction, the nanosized catalysts remain in maximum contact with reactants; however, in the case of heterogeneous nanocatalysts, the reactive solvents are insoluble. As catalysts, several nanomaterials consisting of aluminium, iron, titanium dioxide, and silica are utilised. Nanomaterials have a high surface-to-volume ratio, a small size, and a wide variety of forms, all of which are extremely helpful to catalytic processes (Bose, 2021). Apart from that, nanocatalysts are widely used in water and wastewater treatment. The removal of organic and inorganic pollutants from water using photocatalysts provides more efficient, economic, and as well as pollution-free processes to some extent.

In order to investigate the performance of the proposed composite catalyst, catalyst characterization is required for the ongoing quality control during laboratory testing. The catalyst characterization could help to understand the composition, the physical micro or nano-structure, porosity, and surface properties for the better performance of the composite catalyst. There are several methods for the characterization of catalysts. A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning across the surface of the sample with a focused beam of electrons.

In addition, the technique of X-ray diffraction (XRD) is widely utilized in research and industry. In spite of the fact that XRD is most commonly used for qualitative and quantitative analyses of crystalline phases in materials, a careful examination of the diffraction patterns or the use of specific XRD settings can yield a great deal more information. This includes the characterization of solid solutions, crystallite size and shape, crystal orientation, internal elastic strains/stresses at various levels, temperature effect, close surface characterization, and so on (Gonon, 2021).

Besides, Ultraviolet-visible (UV-VIS) spectroscopy is also one of the methods of catalyst characterization. UV-VIS spectroscopy is the measurement of the number of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference or blank sample (Tom, 2021).

Apart from that, for surface characterization of nanoparticles, Fourier transform infrared (FTIR) is a very versatile tool. The surface chemical composition of nanoparticles can be determined under particular conditions, as well as the reactive surface sites responsible for surface reactivity.

Lastly, the Brunauer-Emmett-Teller (BET) theory defined as the physical adsorption of gas molecules on a solid surface and serves as the foundation for a critical analysis technique for calculating the specific surface area of materials.

1.2. Problem Statement

According to Borneo Post Online, public funds and resources go down the drain when medicines prescribed by government health facilities remain unused or are discarded in the trash bin every year. The improper disposal of excess or unused medicines can over the long-term lead to environmental degradation, including the contamination of valuable water resources that can cause harm to aquatic life. According to Dr. Nurfaizah Abu Tahrim, a senior lecturer at Universiti Kebangsaan Malaysia's Department of Chemical Sciences, even the excreted waste from medicines ingested by humans as well as a good portion of drugs will eventually end up in sewage treatment ponds before being channelled into rivers (Borneo Post Online, 2021). However, conventional treatment plants for sewage and raw water are not designed to treat medical waste in Malaysia. As a result, the occurrence of pharmaceutical substances in the final effluent will discharge into the river and cause environmental contaminants. Even though the amount of damage to the environment that is created by pharmaceutical waste is negligible in comparison to the contamination that is caused by chemical effluents, it is imperative that the relevant authorities continue to monitor it. Sulfamethoxazole, $C_{10}H_{11}N_3O_3S$ (SMX) is one of the common bacteriostatic antibiotics used in the pharmaceutical field for the application of bacterial infection had been detected in the final effluent of wastewater samples. The treatment of SMX is investigated by a lot of researchers to increase the efficiency of the removal of SMX from the effluent through various methods including photocatalysis. Its concentration can range from 10 to 1500 ng/L in wastewater treatment plant (WWTP) effluents, from 0.2 to 1100 ng/L in groundwater, and from approximately 100 pg/L to a few ng/L in water that is intended for human consumption (Bizi, 2020).

Although sulfamethoxazole was not listed as a top consumed compound in Malaysia, it was detected at 75% in STP influent and effluent. The mean concentration for sulfamethoxazole ranged between 52 and 650 ng/L in STP influent and effluent according to Fouad et al, 2018. This is because not all medications are entirely digested in the human body. After being consumed and subjected to human metabolism, around 15 percent of the unmetabolized fraction is excreted in the sewage. The improper disposal of excess or unused medicines can over the long-term lead repetitive to environmental degradation, including the contamination of valuable water resources that can cause harm to aquatic life, and cause environmental contaminants.

The application of the composite catalyst could increase the capability of catalysis in photocatalysis as the chemical reactions are complicated. In this project, a composite catalyst, TiO_2/Zeolite is proposed to increase the capability of catalysis in photocatalysis. According to Javier Fernández-Catalá and his co-researcher, it was observed that the composites prepared by incorporating the zeolite in the TiO_2 medium synthesis displayed better results toward the photodegradation of propene than those composites in which presynthesized TiO_2 was incorporated in the synthesis medium of ZSM-5 or the physical mixture of both components (Fernández-Catalá et al., 2020). The effectiveness of the synthesized catalyst will be investigated through laboratory works for the treatment of SMX from the sample.

1.3. Objectives

As this project depends on the experimental data from the laboratory work, it mainly focused on the synthesis of composite catalysts and the treatment of sulfamethoxazole. In this research, the objectives are:

1. To synthesize the composite catalyst TiO_2/Zeolite for the photocatalysis process.
2. To evaluate the effectiveness of composite catalyst TiO_2/Zeolite to degrade sulfamethoxazole from the synthetic sample.

1.4. Scope of Research

This research study on the synthesis of the composite catalyst TiO_2/Zeolite by using a modified sol-gel method. The performance of the composite catalyst will be validated by characterization of UV-vis spectroscopy, XRD, SEM, FTIR and BET.

The concentration of SMX will be evaluated by using UV-vis spectroscopy. The wavelength of SMX in previous studies will be compared to our research. After the synthesis of the composite catalyst, the photocatalytic activity and performance of the composite catalysts will be evaluated through UV-vis spectroscopy to obtain the residuals of SMX from the sample. From here, the efficiency of composite catalysts in the removal of SMX can be obtained.

1.5. Organization of Thesis

This thesis had been organized into five chapters. A summary of each chapter is presented below:

Chapter 1 describes the background of the research topic. The introduction of the treatment for sulfamethoxazole by photocatalysis and the synthesis of composite catalyst is briefly described. Apart from that, it also focuses on the problem statement, the objectives, and the scope of research for this paper.

Chapter 2 provides an extensive literature review that reviews the fundamental theories related to the photocatalysis process. In addition, it provides basic knowledge of the sol-gel method, an overview of the treatment of pharmaceutical compounds, and special highlights on sulfamethoxazole.

Chapter 3 involves the laboratory works in this research study that included the preparation of the synthetic pharmaceutical wastewater, synthesis of composite catalyst, TiO_2/Zeolite, characterization of the catalyst and concentration of SMX using UV-vis spectroscopy, XRD, SEM, FTIR and BET, treatment of sulfamethoxazole in the synthetic wastewater through photocatalysis, and explain how UV-vis spectrometry function to obtain the efficiency of the proposed composite catalyst in the removal of SMX from synthetic wastewater.

Chapter 4 presents the result and discussion of the study. This chapter focus on the photocatalytic performance of TiO_2/Zeolite in the degradation of sulfamethoxazole. The results are visualized, analyzed, and tabulated with a detailed explanation.

Chapter 5 conclude the lab work and recommendations for future research work.

CHAPTER 2

LITERATURE REVIEW

2.1. Overview

The occurrence of pharmaceutical chemicals in the aquatic environment and water bodies is briefly described in this chapter. The sulfamethoxazole is focused on this study and investigated ways of removing medicinal substances. Furthermore, the theoretical description of the heterogeneous photocatalysis process and mechanism also been focused in this chapter. This chapter also entails a thorough examination of the semiconductor catalysts used in this work, such as TiO_2 and natural zeolite. It also covers the history of TiO_2/zeolite nanocomposite synthesis approaches and the concept of adsorption. The final section of this chapter delves into the sol-gel method for the synthesis of the composite photocatalyst.

2.2. Pharmaceutical Wastes

The pharmaceutical industry act as one of the important industries all around the world and has played a significant role in developed and producing medicines, and drugs for medicinal purposes. As new treatments are produced to cure an increasing number of previously untreatable ailments, the pharmaceutical market continues to expand. New biotechnology-based products passing through clinical trials and entering the market are sustaining or even accelerating this trend (Judd & Jefferson, 2003). This trend also obviously happened in Malaysia. As of December 2019, there were 263 licensed manufacturers, with 69.2 percent, or 182 of these manufacturers, classified as producers of traditional medicine, 26.6 percent, or 70, being producers of pharmaceuticals, and 4.2

percent, or 11 companies, being producers of veterinary products (Malaysia Investment Performance Report, 2019).

With rising income and consumer awareness, the demand for high-quality healthcare in Malaysia is on the rise. Currently, healthcare is estimated to consume 7.25% of the country's GDP. With a growing population and higher life expectancy, as well as the government's increased expenditures on better healthcare facilities and services, this is likely to rise (Guide on Pharmaceutical Industry in Malaysia, 2020). Based on Malaysian Statistics on Medicines 2015-2016, the total estimation of medicine utilization in 2015 and 2016 are 624.90 and 632.32 defined daily doses (DDD) /1,000 inhabitants/day respectively. (Fong & Shanizza, 2020). Hence, the increase in the demand for pharmaceutical compounds in various industries has produced more pharmaceutical wastes. The improper way of handling pharmaceutical waste could cause serious environmental pollution which harms aquatic lives. There are several types of pharmaceutical wastes, and this literature review will focus on persistent organic pollutants (POPs), especially sulfamethoxazole (SMX). POPs are a group of hazardous substances that can linger in the environment for a number of years before decomposing. POPs travel around the planet, and chemicals that are released in one area of the earth might be repeatedly deposited far from the source of their release.

The rise of POPs, such as SMX in the aquatic environment has caused widespread concern in recent years. Thousands of synthetic compounds were introduced into commercial usage during the post-World War II industrial boom, and several POPs were widely employed. Pest and disease control, crop production, and industry all benefited from several of these compounds. However, these same compounds have had unintended consequences for human health and the environment (Persistent Organic Pollutants: A Global Issue, A Global Response, 2009). One of the major problems with these compounds is that they are usually found in low concentrations in water bodies, and each of these molecules has a different chemical composition, making identification, analysis, and even removal from drinking water difficult. Therefore, the disposal of pharmaceutical wastes should be controlled to ensure the aquatic life is free from contaminants and preserve the environment.

2.2.1. Occurrence of Pharmaceutical Compound

A pharmaceutical compound is a pharmaceutical that can only be obtained with a medical prescription. It can be found in drinking water, including antibiotics, anti-convulsant, mood stabilizers, and sex hormones. Pharmaceutically active chemicals (PhACs) and their metabolites discarded from human therapy have been identified in low concentrations in surface waters downstream of sewage treatment facilities, despite the fact that they are not removed by sewage treatment plants. Continuously discarding partially treated water may mix with other substances in the environment, resulting in unknown ecological impacts. Fish and other aquatic species are vulnerable to the effects of most medicines because they are very soluble. Pharmaceuticals' long-term impacts on the environment may have an impact on these creatures' survival and reproduction. As a result, pharmaceutical pollution is a global hazard to the environment and human health, as well as the UN's Sustainable Development Goals (Wilkinson et al., 2022).

Due to the constant entry of emerging contaminants (ECs) into aquatic systems, the effluents released from wastewater treatment plants (WWTPs) are the principal source of PhACs. Apart from the effluents from commercial, hospital, and industrial WWTPs, landfill leachate, illegal disposal, and surface runoff from urban and agricultural areas are also sources of pharmaceutical wastes to be founded in the surface water (Alkimin et al., 2019, Barbosa et al., 2016, Tran et al., 2018, Xie et al., 2019).

WWTPs are particularly highest among these sources since they discharge drugs into the aquatic compartments on a regular basis (Tran et al., 2018).

Pharmaceutical pollutants have also been discovered in Malaysian drinking water. However, because pharmaceutical waste is considered non-priority pollution, there is no formal rule governing the issue of pharmaceutical-safe source water (Al-Odaini et al., 2011; Al-Odaini, Zakaria, Yaziz, & Surif, 2016). For example, sulfamethoxazole, carbamazepine, diclofenac, etc. are found in the river Malaysia. According to Praveena and the co-researchers, SMX which belongs to the same therapeutical classes (antibiotics), is found to be in the range of 19.26 to 75.48 ng/L and 96.81 to 109.34 ng/L and 84.31 ng/L to 114.24 ng/L respectively in the Lui, Gombak, and Selangor rivers. Apart from that, SMX was the most common antibiotic, followed by lincomycin and sulfathiazole. In sewage or substantially sewage-impacted waterways, the average concentration of SMX was 1720 ng/L in Vietnam, 802 ng/L in the Philippines, 538ng/L in India, 282 ng/L in Indonesia, and 76 ng/L in Malaysia. These levels were higher than in Japan, China, Europe, the United States, and Canada. In these tropical countries, sulfonamides, particularly SMX, are prevalent. The reduced cost of the antibiotics can be attributed to the greater average concentrations and preponderance of SMX. Antibiotic concentrations and composition in livestock and aquaculture effluent differed significantly. Sulfamethazine (SMT), oxytetracycline (OTC), lincomycin, and SMX were found in abundance in livestock and aquaculture wastewater in numerous situations. Antibiotics for humans and animals were widely disseminated in the receiving waters (Shimizu et al., 2013). Table 2.1 had summarized the average concentration of SMX in various countries.

Table 2.1: Average Concentration of sulfamethoxazole in Different Countries (Shimizu et al., 2013)

Country	Average Concentration
Malaysia	76 ng/L
Vietnam	1720 ng/L
Philippines	802 ng/L
India	538ng/L
Indonesia	282 ng/L

2.2.2. Sulfamethoxazole

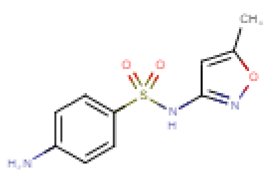
Sulfamethoxazole (SMX) is a bacteriostatic sulfonamide antibiotic that prevents susceptible bacteria from taking folic acid. These agents work together to block two consecutive steps in the biosynthesis of nucleic acids and proteins that are required for bacterial growth and division, and using them together slows the development of bacterial resistance. In most cases, it is given in conjunction with trimethoprim, which inhibits a sequential step in the synthesis of folic acid by bacteria; however, trimethoprim is the one that inhibits the step-in question. When used in conjunction with this other medication, SMX is a successful treatment for a wide variety of bacterial infections, including those that affect the urinary, respiratory, and gastrointestinal systems.

The chemical formula of SMX is $C_{10}H_{11}N_3O_3S$ and its structure is shown in Table 2.2. The melting point of SMX is 167 °C based on PhysProp. It is readily absorbed and has a bioavailability of 85-90 % after oral dosing. The volume of SMX dispersion after a single oral dose was determined to be 13 L. It is found in sputum, vaginal fluid, middle ear fluid, breast milk, and the placenta, among other places. Moreover, the kidneys' glomerular filtration and tubular secretion are the primary routes of elimination, with urine concentrations typically much greater than plasma concentrations. Within 72 hours, approximately 84.5% of a single oral dose of SMX is recovered in the urine, with 30% being free SMX and the rest being the N4-acetylated metabolite (Drug Bank Online, 2005).

SMX is toxic to the human body if over-consume. Anorexia, colic, nausea, vomiting, dizziness, headache, sleepiness, and unconsciousness are all signs or symptoms of a sulphonamide overdose. Pyrexia, haematuria, and crystalluria are some of the less prevalent symptoms. Blood dyscrasias and jaundice are possible side effects of an overdose. Treatment should be symptomatic and supportive and, if necessary, may include gastric lavage or forced emesis (Sulfamethoxazole, 2022).

Although SMX was not listed as a top consumed compound in Malaysia, it was detected with 75% in STP influent and effluent. The mean concentration for sulfamethoxazole ranged between 52 and 650 ng/L in STP influent and effluent according to Fouad et al., 2018. This is because not all medications are entirely digested in the human body. After being consumed and subjected to human metabolism, around 15 percent of the unmetabolized fraction is excreted in the sewage.

Table 2.2: Summarized Properties of SMX (Drug Bank Online, 2005)

Category	Detail
Structure	
Chemical Formula	$C_{10}H_{11}N_3O_3S$
IUPAC Name	4-amino-N-(5-methyl-1,2-oxazol-3-yl) benzene-1-sulfonamide
Melting point	167 °C
Water solubility	610 mg/L

2.2.3. Removal of Sulfamethoxazole

Antibiotics are developing toxins that have a negative impact on human health, livestock, and aquatic life, as well as being resistant to biological wastewater treatment. Antibiotics penetrate surface waters, groundwaters, and eventually drinking water if they are not degraded or removed during sewage treatment (Kümmerer, 2003; Sponza & Demirden 2007). The elimination of low-concentration antibiotics is difficult but necessary. As a result, removing them from wastewaters is critical. SMX can be removed from wastewater using a variety of ways such as adsorption (Adams et al. 2002), UV light (Gonz'alez et al. 2007), anaerobic biological processes (Sponza & Demirden 2007).

In this study, the removal of SMX is mainly focused on the adsorption and photocatalysis process. This is because other methods had their own drawbacks such as required high cost for the disposal of sludge and required the specific temperature and pH. For example, the biological anaerobic method is very sluggish and contributes to the disposal of vast amounts of sludge. Furthermore, they necessitate precise temperature and pH control in the system (Ollis and Al-Ekabi, 1993; Kumar and Pandey, 2017). Hence, the biological anaerobic method is not chosen in our study concern.

2.3. Adsorption

The process of transferring a molecule from a fluid bulk to a solid surface is known as adsorption. Adsorption is a surface process. This can be brought about by either the interaction of physical forces or chemical bonds. It is typically possible to reverse the process, which is known as desorption, and it is ultimately responsible for both the removal of the chemical and its subsequent release. This process is characterized at equilibrium using equations that quantify the amount of substance adhered to the surface depending on the concentration of the fluid in the majority of cases. These equations are known as isotherms due to the fact that the values of their parameters are determined by temperature, which is one of the most significant environmental factors that have an effect on adsorption (the most renowned of which are the Langmuir and Freundlich equations). Because it controls the exchanges that occur between the geosphere, hydrosphere, and atmosphere, is responsible for the movement of substances through ecosystems, and stimulates other important processes such as ionic exchange and enzymatic activities, adsorption is an important concept in the field of ecology (Artioli, 2008). According to Motwani et al. 2011, activated carbon outperformed activated alumina in the adsorption of SMX. When compared to UV treatment and UV treatment with H_2O_2, adsorption has been proven to be more effective.

2.4. Photocatalysis

Photocatalysis is a reaction that occurs when light and a semiconductor are combined. It's a phenomenon in which an electron-hole pair is formed when a semiconducting substance is exposed to light (Ameta, 2018). This procedure is critical for the treatment of pharmaceutical wastewater. The AOP-based photocatalytic process is a green technique for treating polluted water containing hazardous bacteria. In this method, a semiconductor can operate as a photocatalytic substrate by creating highly reactive radicals that can decompose indiscriminately micropollutants, such as dangerous microorganisms found in wastewater, when absorbed by a photon of adequate energy (band gap energy) (Pillai et al., 2017). However, before being transported to the adsorbate species, the majority of the generated charges recombinant inside the bulk/surface of the photocatalyst, releasing heat as a byproduct, resulting in a drop in photocatalytic efficiency of up to 90%. As a result, impurity substitution, lattice defects, and vacancy development on the semiconductor can provide alternate paths for the amplification of photogenerated electrons and holes, preventing recombination. When a semiconductor photocatalyst is exposed to light with an energy level equal to or more than its bandgap energy, the oxidative and reductive entity is formed. In the first step, holes and electrons that are photogenically generated are created in the valence band and the conduction band, respectively. As a consequence of this, the photogenerated charge carriers mix with the water or the oxygen that is dissolved in the water to produce reactive oxidizing species such as OH and O_2, which break down the pollutants into smaller molecules while also rendering the bacteria inactive (Regmi et al., 2018).

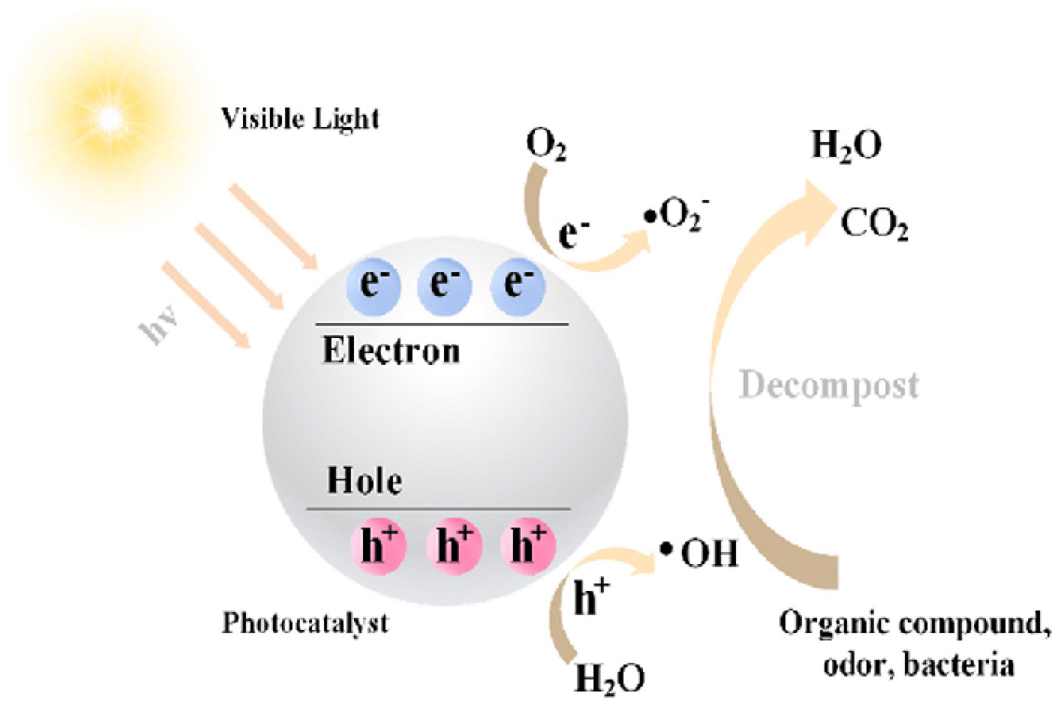


Figure 2.1: Photocatalytic Degradation Mechanism

2.4.1. Photocatalyst

A photocatalyst is a substrate that absorbs light and functions as a catalyst for chemical reactions. Photocatalysts are all made out of semiconductors. When a semiconducting substance is exposed to light, photocatalysis occurs, resulting in the formation of an electron-hole pair (Ameta, 2018). On the basis of the appearance of the physical state of reactants, photocatalytic reactions can be divided into two types such as homogenous and heterogeneous photocatalysts. Homogeneous photocatalysis refers to photocatalytic reactions in which both the semiconductor and the reactant are in the same phase, such as gas, solid, or liquid. Meanwhile, heterogeneous photocatalysis refers to photocatalytic reactions in which the semiconductor and reactant are in distinct stages. The bandgap is the energy difference between the valence band (HOMO) and the conduction band (LUMO) (Ameta, 2018). The materials are divided into three categories based on their band gap:

- metal or conductor: bandgap <1.0 eV

- semiconductor: bandgap <1.5–3.0 eV
- insulator: bandgap >5.0 eV

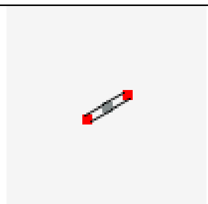
Semiconductors can conduct electricity in the presence of light even at ambient temperature, making them photocatalysts. When a photocatalyst is subjected to light with the desired wavelength and enough amount of energy, photon energy is absorbed by an electron (e) in the valence band, which then causes the electron to be stimulated into the conduction band. During this process, a hole, denoted by the symbol h+, is produced in the valence band. This mechanism causes the establishment of a photo-excitation state as well as the generation of e and h+ pair electrons and protons. This excited electron is put to use in the process of reducing an acceptor, which is then put to use in the process of oxidising donor molecules with a hole. The fact that photocatalysis offers an environment that is conducive to both oxidation and reduction at the same time is one of the primary reasons for its widespread application. The relative positions of the semiconductor's conduction and valence bands, as well as the redox levels of the substrate, determine the fate of the excited electron and hole. Photocatalysts have the potential to be utilized in a variety of applications, including those dealing with antifouling, antifogging, energy savings and storage, deodorization, sterilisation, self-cleaning, air purification, wastewater treatment, and others. Semiconductors, by virtue of their electrical properties, can function as photoredox sensitizers. Photocatalysis has the potential to completely mineralize a wide variety of organic pollutants, including aromatics, halo hydrocarbons, pesticides, herbicides, dyes, and surfactants, amongst others (Xiong et al., 2022).

Heterogeneous binary metal oxides photocatalysts such as TiO_2, ZnO, Fe_2O_3, and Al_2O_3 (Karunakaran and Senthilvelan, 2005) have been extensively studied for the removal of organic-coloured pollutants such as azo dye, acid orange 7 (Vinodgopal et al., 1996a, b), methylene blue (Fabiyi and Skelton (Sivalingam et al., 2003). Therefore, in this research, TiO_2 becomes one of the considerations for the photocatalyst used in lab works.

2.4.2. Titanium Dioxide (TiO_2)

Titanium dioxide is a white powder with no odor, tasteless and pH 7.5. It comes in three different crystalline forms (NTP, 1992). It's a naturally occurring oxide that comes from ilmenite, rutile, and anatase, and it's used for a variety of things. It is used as a food colorant. Apart from that, it's known as titanium white, Pigment White 6 (PW6), or CI 77891 as a pigment. Ilmenite, rutile, and anatase are the most common sources extracted from TiO_2. The physical and chemical properties of TiO_2 are summarized in Table 2.3.

Table 2.3: Summarized Properties of Titanium Dioxide (PubChem Compound Summary for CID 26042, Titanium dioxide, 2022)

Category	Detail
Structure	
Chemical Formula	TiO_2
IUPAC Name	dioxotitanium
Boiling Point	2500-3000 °C
Melting Point	1855 °C
Solubility	Not soluble
Density	3.9-4.3 g/cm^3
pH	7.5

2.4.3. Natural Zeolite

Natural zeolites of sedimentary origin, notably zeolitic tuffs, have been used by mankind in agriculture and building since the dawn of civilization and have found widespread use since the 1950s. These are based on a number of features, including physical adsorption, cation exchange, alkali reactivity, thermal expansion and insulating tendency, and suitable compressive strengths and durability in the form of stone-like materials.

The majority of current applications are in the sphere of environmental protection. On the contrary, only a few industrial applications have been recorded, owing to the fact that natural zeolites are less appealing than synthetic goods in this sector for a variety of reasons. The most common applications of zeolitic tuffs that have recently been evaluated include pozzolanic addition to cement, water and soil purification, soil amendment, animal feeding and husbandry, manufacturing dimension stone, and lightweight aggregates for concrete. Other applications include depuration of soil and water, amendment of soil, animal feeding, and animal husbandry.

However, zeolites, particularly natural zeolites, have intriguing surface features that allow them to interact with large organic molecules and cations that are unable to pass through their microporous structure. Surface activity has been thoroughly investigated in recent years, with a variety of appealing applications in the environment and healthcare domains being tested (Colella, 2007).

2.4.4. TiO_2/Zeolite Photocatalyst

Natural minerals like montmorillonite, kaolinite, diatomite, and zeolite have frequently been employed to make adsorption-photocatalyst composite function materials. The photocatalytic capabilities of these composites have been thoroughly researched. In general, zeolite has a number of benefits, including a large surface area, and chemical and thermal resilience. As a result, our study has concentrated on creating TiO_2/Zeolite composites through adsorption.

Zeolite with a high hydrophobicity can enhance the photocatalytic activity of the TiO_2/Zeolite photocatalyst (Kuwahara et al., 2012). Natural zeolite, on the other hand, has a reduced surface area and pore volume, which makes it difficult to significantly improve adsorption and photocatalytic activity. To our knowledge, the majority of studies have used artificial zeolites such as HZSM-11, ZSM-5, zeolite-4A, and Y-zeolite to support TiO_2. However, natural zeolite support TiO_2 nanoparticles have been documented in fewer works. The photodegradation of SMX by the natural zeolite-supported TiO_2 composite has not been documented as far as we are aware. As a result, we created a TiO_2/Zeolite composite with increased photocatalytic activity to remove contaminants including SMX, efficiently (Zhang et al., 2018).

2.5. Sol-gel Method

The sol-gel process is defined as the chemical conversion or transformation of a solution of precursors into an inorganic solid (Niederberger, 2007). The sol-gel technique is regarded as one of the most cutting-edge methods for the synthesis and production of metal oxide nanoparticles and nanocomposites. Sol-gel is also regarded as one of the most efficient ways of creating nanosized metallic oxides with strong photocatalytic activity (Su et al., 2004). The sol-gel process has a number of characteristics that set it apart from other procedures for solidifying materials from a solution, including crystallization from melts, precipitation and deposition-precipitation, microemulsion, and others. However, there are two primary characteristics that set the sol-gel approach apart from other similar procedures.

The development of colloidal suspension, which is generated by the condensation of dissolved precursors, is the key feature that distinguishes the sol-gel approach. The second advantage is the integration and merging of colloidal particles into a polymeric matrix during the gelation phase by chemical processes that connect the local reactive groups at their surface (de Jong, 2009). The sol-gel approach can be categorized into two methods based on the kind of solvent used in the synthesis of oxide nanoparticles: the aqueous sol-gel route and the nonaqueous sol-gel route (Rao et al., 2017).

In the sol-gel process, the aqueous sol-gel method refers to using an aqueous solution (water) as the reaction media. However, for the synthesis of metal oxides, using the aqueous sol-gel approach is not recommended due to some issues with this process (Rao et al., 2017). Controlling the shape of particles during the sol-gel process is a challenge (Corriu and Leclercq, 1996). However, whereas the aforementioned problem has little impact on the synthesis of metal oxides in bulk, it has a significant impact on the creation of nanoscale oxides (Niederberger, 2007).

The nonaqueous approach is often referred to as the nonhydrolytic sol-gel method. A nonaqueous solution is used as the reaction media in this approach (solvent). In contrast to the aqueous sol-gel method, where the oxygen required for the formation of metal nanoparticles is provided by either organic solvents such as alcohols and aldehydes or metal precursors, the oxygen required for the formation of metal nanoparticles is provided by organic solvents such as alcohols and aldehydes. The nonhydrolytic sol-gel technique is favoured over the aqueous route because it allows for better control of the produced catalyst's shape, surface characteristics, composition, and particle size (Rao et al., 2017). The crystal structure of the produced particles can also be influenced by the nonaqueous sol-gel process. The slow reaction rates that occur during the sol-gel process, together with the stabilizing effect of the organic compounds, lead to the development and production of highly crystalline particle morphologies and nanoscale particles, which has an impact on the crystal structure (Niederberger, 2007).

The sol-gel method is regarded as a chemical procedure. It is started by a three-dimensional network formed by an ion or a chemical molecule. The three-dimensional network matrix is often formed after the creation of oxygen bonds between ions and the release of water or other small molecules in the solution (Guglielmi et al., 2014). The sol-gel method, in general, goes through three key processes to get the final metal oxides or metal oxide composites: hydrolysis, condensation, and drying. Metal hydroxide solution is formed in the first step of the sol-gel process, hydrolysis. The hydrolysis reaction of metal precursors in the presence of water is depicted in Chemical Equation 2.1 (Guglielmi et al., 2014; Rao et al., 2017).

Due to some metal precursors, such as silicon alkoxides, having a slow hydrolysis rate, it is necessary to speed up the reaction rate during the hydrolysis step. The inclusion of a catalyst is frequently used to accomplish this problem. The catalyst used to speed up the sol-gel process might be either an acid or a basic catalyst.

The unstable M-OH group condenses with additional M-OH or M-OR groups (if metal alkoxides were employed as precursors in the sol-gel method) to create M-O-M bonds under the liberation of water or alcohol in the second step of the sol-gel process, condensation (Equation 2.2, 2.3). As a result, three-dimensional gels are created (Guglielmi et al., 2014).

$$M(OR)_n + H_2O \rightarrow M(OR)_{n-1}(OH) + ROH \tag{2.1}$$

$$M(OR)_{n-1}(OH) + (HO)M(OR)_{n-1} \rightarrow M(OR)_{n-1}M\text{-}O\text{-}M(OR)_{n-1} + H_2O \tag{2.2}$$

$$M(OR)_{n-1}(OH) + M(OR)_n \rightarrow M(OR)_{n-1}M\text{-}O\text{-}M(OR)_{n-1} + ROH \tag{2.3}$$

The overall chemical reaction can be stated as (Equation 2.4).