TREATMENT OF PHARMACEUTICAL ANTIBIOTIC WASTEWATER USING PHOTOCATALYTIC PROCESSES WITH COMMERCIAL TiO$_2$ POWDER

MASTER’S THESIS
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TREATMENT OF PHARMACEUTICAL ANTIBIOTIC WASTEWATER USING PHOTOCATALYTIC PROCESSES WITH COMMERCIAL TiO$_2$ POWDER

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Oladele Honour Adedayo

Hanoi, August 2020.
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<td>Advanced Oxidation Processes</td>
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<tr>
<td>APIs</td>
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<td>AS</td>
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INTRODUCTION

Antibiotics were developed to restrain and destroy certain microorganisms, nonetheless, based on the chemical structures, antibiotics are commonly categorized into macrolides, quinolone, sulfonamides, aminoglycosides, and tetracycline (TC) (Binh et al., 2018). Antibiotics have long been widely used for the prevention of human and animal diseases. Although most antibiotics cannot be fully absorbed, approximately 90% (Halling-Sørensen et al., 1998) were discharged into the environment with the fecal matter of patients and livestock in an unaltered form and as metabolites when utilized as manure, results in certain levels of contaminants, thereby infiltrating the aquatic ecosystem even at low concentration. As shown in the Figure below, antibiotics exist in the environment primarily from pharmaceutical intake by human and through animal breeding. The pathway for both animal and human antibiotic deposits existence in the environment comprises of expired antibiotics discarded from hospitals; antibiotic remains in medical appliances and vials utilized in the hospital; prescribed antibiotic drugs discharged through the patient’s feces and urine. Likewise, the route of antibiotic existence in the environment through animal/ livestock breeding may involve low doses of antibiotic residues which have accumulated over a relatively long term ingestion.

The route of the existence of pharmaceutical deposits in the water environment (Haller et al., 2002). Several studies in recent years have implied that the pervasiveness
of pharmacological and personal care products (PPCPs) and their metabolites are typically found in the sewage treatment plants (STPs) effluent, also in water environment owing to the heavy load from pharmaceutical companies which are discharged into rivers, lakes and other superficial waters. The occurrence of these pollutants in water could be largely attributed to the incapability of most STPs to achieve complete degradation with only the biological oxidation process, which is a contributory factor to the prevalence of Eco toxicological implications for the aquatic microorganisms (Richards & Cole, 2006).

Presently, in several developed countries such as the United States and the European Union, the challenges from antibiotic pollution have become an important environmental issue and related researches are evolving rapidly. Every human life activity generates wastes, more directly related to the country or citizen’s standard of living and the quantity of wastes produced over time. Around 23% of the global population lives in developed nations and expend 78% of the available resources; however, 82% of waste materials are yielded (Halling-Sorensen et al., 1998). Furthermore, it should also be noted that the amount of accumulated waste tends to increase remarkably in direct contrast to the level of industrialization of a country. Presently, approximately 5,000,000 identified substances have been reported, with roughly 70,000 usages worldwide, and a recent estimate of 1,000 new chemicals are reportedly incorporated in the list each year (Kumar & Vyas, 2013). The problems associated with appropriate water treatment and resources cannot be handled objectively but have to be managed by a wide range of procedures. Issues associated with toxic effects of organic compounds that are very active in water even at trace levels must be eradicated through the disinfection of water utilized by the general populace especially in the rural communities.

In order to tackle this wider range of issues, advanced processes that vary due to complexity levels of these problems and their scales for application are required. Formerly, waste products have been disposed of and eliminated by discharging them directly into the environment without treatment, not until the depleting self- purifying efficacy of the environment has been exhausted and the permissible standards were
significantly exceeded, thereby resulting in environmental contamination.

Subsequently, Advanced Oxidation Processes (AOPs) which are currently used as an alternative treatment for a wide variety of recalcitrant micro pollutants includes UV/O3 process, UV-H₂O₂, heterogeneous photocatalysis, Fenton and photo-Fenton reaction, sonolysis, non-thermal plasma, electrolysis, etc. (Goslan et al., 2006). Photocatalysis, a branch of advanced oxidation processes (AOPs) is a promising technique for the removal of these organics from water/wastewater, due to the in-situ generation of strong oxidants which possess the ability to degrade these pollutants. In this study, the photocatalytic activity of Titanium dioxide (TiO₂) powder was investigated by checking the degradation efficiency of tetracycline. The characteristics of TiO₂ powder were characterized by Scanning Electron Microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR). Different dosage of the photo-catalyst as well as different concentrations of pollutants, were varied in the degradation processes under UV light conditions.
**Research Objectives**

This work was carried out with the following objectives:

1. **Survey on the behavior and awareness of residents concerning pharmaceutical products and wastewater pollutants in Hanoi** which was achieved by questionnaires about pharmaceutical wastewater concerning the use of antibiotics for their wellbeing.

2. **Treat model pharmaceutical wastewater using the photocatalytic treatment method.**

3. **Characterization of the TiO\(_2\) photocatalyst**

4. **Study on the effects of some experimental variables on the photodegradation ability of the TiO\(_2\) photocatalyst to obtain the optimal condition.**
Structure of thesis

The thesis includes 4 chapters which is categorized into literature review, materials and methodology, results and discussions, and finally conclusions.

Chapter 1: Literature Review

The literature review discusses the conventional methods of wastewater treatment, the challenges and disadvantages involved with the conventional treatment methods, advanced oxidation processes focusing on the application of photocatalysis to the treatment of wastewater, mechanism of photocatalysis and photocatalytic degradation of pharmaceutical effluent.

Chapter 2: Materials and methodology

This section focuses on the materials, equipment, experimental design and methods used for this research. The characterization of the photocatalyst, survey process, and analytical method are also stated.

Chapter 3: Results and discussions

The results of the calibration process, adsorption capacity, photocatalytic activity of TiO₂, and optimization of experimental conditions are presented in this section. The effects of various experimental conditions such as temperature, pH, and catalyst load, etc. on the optimized condition of tetracycline treatment by TiO₂ are discussed. Analysis of the data obtained from survey activities is also included.

Chapter 4: Conclusions sums up the key findings from the study.

Appendices comprise some photos of the study’s research activities.
CHAPTER 1. LITERATURE REVIEW

1.1. Antibiotics pollution in the environment.

The consistent use of antibiotics in humans and veterinarians has become so widespread that their existence is now very prevalent in the environment and virtually, the entire world recognizes their emergence in the biotic and abiotic environment such as surface water, soils, wastewater, aquatic life, groundwater, etc. (Gothwal & Shashidhar, 2015). Antibiotics are detectable globally at different concentrations. According to other reports in USA, 6 classes of antibiotics were discovered in raw effluent. Amongst which the concentration of sulfamethazine in the influent was detected to decrease from 0.21 \( \mu g/L \) to a negligible value below the detection limit in the effluent, the others include sulfamethoxazole with its influent concentrations of 1.25 \( \mu g/L \) which was decreased to 0.37 \( \mu g/L \), the other antibiotics including tetracycline, trimethozin, ciprofloxacin and erythromycin has influent concentration ranging between 0.25 \( \mu g/L \) -1.25 \( \mu g/L \), which reduces to 0.21 \( \mu g/L \)-1.30 \( \mu g/L \) in the effluent concentration respectively (Karthikeyan & Meyer, 2006). Furthermore, in a wastewater treatment plant in china, 20 antibiotics were found in the raw influent while 17 were detected in the effluent wastewater. The total concentration of antibiotics per capita was approximately 500 – 900 \( \mu g \) per person in the samples of influents obtained and mean value of 175 \( \mu g \) per person in the effluent (Zhou et al., 2013). Non-detectable range – 7.3 \( \mu g/L \) was reported for macrolides, sulfonamides and trimethoprim from 37 rivers in Japan (Alidina et al., 2014). Other studies have also reported on the adverse impacts of the existence of antibiotics in aquatic life, for example, distortion of the fish’s immune system has been reported to be one of the implication of Tetracycline prevalence (0.1 – 50 \( \mu g/L \)) in the aquatic environment (Grondel et al., 1985), harmful effects on the population growth rate and breeding rate of zebra fish due to the 200 \( \mu g/L \) concentration of sulfamethoxazole and norfloxacin was reported (Yan et al., 2016). Thus, the emergence and perseverance of antibiotics in the environment has to be controlled and managed.

1.2. Recent methods of water and wastewater treatment.

The increasing demand for clean water alongside its decreasing resources caused by the expansion of industries, human population swelling, and long-term droughts have
become an intense problem everywhere on the planet. It leads to the demand for development of the newly, practically and economically attractive technologies enabling reasonable water use. It is estimated that over 4 billion individuals have really limited access to clean water and millions of people die per annum due to diseases caused by bacteriologically damaged water (Malato et al., 2009). It should be expected that in future those numbers will increase consistent with rising environmental pollution caused by the deposition of hazardous substances to the natural water cycle (Chong et al., 2010). Improvement of cheap and efficient water and wastewater treatment technologies is necessary, due to the low quality of remaining natural water and lack of clean water.

The conventional methods of water treatment, which include membrane filtration, sedimentation, coagulation, activated carbon adsorption, flocculation, chlorination and either used in single or combined processes, cannot eradicate from drinking water, the microorganisms, organic and inorganic toxic compounds. Hence, the emergence of modern water and wastewater treatment processes such as membrane processing, UV disinfection and the advanced phase of the oxidation process are therefore studied (Bodzek & Rajca, 2012). Moreover, these methods only facilitate the reformation of pollutants transport or concentration from one stage to the other; meanwhile, achieving complete removal or degradation is unlikely. Although, chlorination is widely used to disinfect but this process is a vast contributory to the development of mutagenic toxins, immunotoxin and carcinogenic byproduct (Matilainen & Sillanpää, 2010). Chemical and membrane applications, which include Nano filtration, microfiltration, reverse osmosis, and ultrafiltration, distinguished by high operational and maintenance costs, which may further influence the effects of secondary environmental toxic pollutants. Although membranes have become an ideal replacement for conventional technologies, their treatment approaches are considerably restricted partly because these techniques only ensure the complete isolation of microbes, inorganic and organic substances. So, the highly concentrated stream (10% volume of effluent) containing active harmful microbes poses a significant threat to the receiving aquatic environment where these effluents are deposited (Bodzek & Rajca, 2012).
1.2.1. Treatment by activated sludge

Activated sludge is a process that enhances the production of bacteria and microbes by feeding on the organic component yielded by the wastewater aeration process (El-Gohary et al., 1995). Activated sludge process is typically more ecofriendly than other chemical processes including chlorination, this treatment requires minimal operational procedures and cheaper cost of initial startup, which are some of the benefits of activated sludge treatment (New et al., 2000). Despite its advantages, the challenges of utilizing activated sludge methods of treatment include the excessive production of sludge, pigmented colors, froth formation in the secondary clarifiers and a huge demand for energy usage and output (Oz et al., 2004).

1.2.2. Membrane Filtration

The efficacy of membrane filtration in the removal of pharmaceuticals and APIs is intrinsically linked to the features of the membrane including the pore depth, solubility ability, specific surface area/structure, molecular mass of the pollutant and surface loading (Bellona et al., 2004). A selection of prototypes and full-scale membrane models such as sequence membrane, reverse electro dialysis, microfiltration, membrane bioreactors, Nano filtration, reverse osmosis, and ultrafiltration have been investigated and tested (Snyder et al., 2007). The elimination of the substantial proportion of toxic organic pollutants by the microfiltration and ultrafiltration has no relative influence because the pores range from 100-1,000 times the size of the micro contaminants such that there is no apparent physical retention. They demonstrated some removal ability when run as MBRs and retention are vastly greater than secondary clarifier levels. MF/UF can yield economic solution and sustainability when vulnerable surface waters warranted the advanced mode of treatment with the use of limited space. However, the enormous energy demand and expensive cost are some of the constraints in the utilization of micro and ultra-filtration (Larsen et al., 2004).

1.2.3. Chlorination

The degradation of some pharmaceutical products, such as sulfonamides (Qiang et al., 2006), 17 α-ethinylestradiol, and 17 β-estradiol (Alum et al., 2004) through the
chlorination process has been detected to be efficient and effective. Chlorine dioxide is likewise used to eliminate sulfamethoxazole, 17α-ethinylestradiol, and diclofenac (Khetan & Collins, 2007a). The degradation of bisphenol A, 17α-ethinylestradiol, and 17β-estradiol and estrogenicity byproduct from purified water through the combination of chlorination and ozonation process have demonstrated consistent result in comparison with ozonation process culminating in a 75-99% removal rate (Alum et al., 2004). Amidst the process of chlorination, Sulfamethoxazole, diclofenac, fluoroquinolone, and acetaminophen become oxidized, all other compounds will also be metabolized. These pharmaceuticals, including acetaminophen, generate toxic by-products such as N-acetyl-p-benzoquinone imine and 1,4-benzoquinone, while chloramines, one of the oxidizing compounds are released as a toxic by-product of sulfamethoxazole and metoprolol (Pinkston & Sedlak, 2004). Chloramines are commonly considered carcinogenic compounds.

1.2.4. Adsorption method

This method involves the collection and removal of organic pollutants from wastewater using the absorbent solids to evacuate toxic contaminants, thus disinfecting the effluent (Li & Li, 2015). This separation technique enhances the further removal of foul stench, discoloration from organic matter and toxic substances by transferring contaminants from the dissolved liquid phase to the adsorbent surface and allowing them to accumulate for elimination to occur (Ikehata et al., 2006). Hence, the activated carbon adsorption is extensively utilized for the treatment of wastewater, often applied as a granular or powdered activated feed. TC adsorption on silica was investigated and the study indicated that the adsorption enthalpy and entropy were nearly -16 and -25 J/mol accordingly (Turku et al., 2007).

Fe-incorporated SBA15 (Fe-SBA15) of varying Fe content (III) was fabricated to improve the adsorption efficiency of TC and the study demonstrated that Fe-SBA15 had higher adsorption capability of TC than SBA15, however, tetracycline was not completely removed (Zhang et al., 2015).
1.2.5. **Photolysis**

Solar radiation photolysis has been acknowledged to be among the most effective method to degrade antibiotics in the aquatic ecosystems (Andreozzi et al., 2003). Photolysis is simply the direct disintegration of chemical compounds through light absorption (Legrini et al., 1993), however, some pharmaceutical products have been found to be highly resistant to photolytic alterations, in particular APIs which are not prone to absorb light at wavelengths greater than 290 nm (Khetan & Collins, 2007b). In general, the existence of organic contaminants in the water habitats is ascertained by various physicochemical (abiotic) and biological processes. Abiotic transitions of any pollutant as well as pharmaceutical substances in the aquatic environment occurs through hydrolysis and even photolysis. As the norm, pharmaceuticals, typically intended for oral ingestion are hydrolysis-resistant, thereby signifying the techniques of indirect photolysis as a default route to their inorganic form in surface water environs.

Whilst, organic compounds which absorb solar light directly become photolyzed (Richard G. Zepp & Cline, 1977), indirect photolysis process incorporates nitrate and humic acid photosensitizers which occurs naturally in the environment, however when the sun is irradiated, naturally occurring strong oxidants such as hydroxyl radicals are produced (R. G. Zepp et al., 1981).

1.2.6. **Electrochemical oxidation**

Electrochemical oxidation has been tested on a lab-scale and pilot plant scale to degrade organic compounds in aqueous solutions, however, due to its relatively high operational cost, this process is not being used commercially. The transmission of electrons within the electrodes which provides a clean reactor system is among the major benefits of this process because it restricts the surge in the number of organic molecules involved (Martínez-Huitte & Ferro, 2006). However, they have certain limitations including the fact that in cost comparison with several other processes, the electrochemical oxidation process is rather expensive and the water mechanism is even more complex. Therefore, if the effluents do not have sufficient conductivity, salt has to be incorporated into the flux to be processed. There are three phases for the mechanism of electrochemical
oxidation process to be completed namely; Electrocoagulation, Electro-flotation and Electro-oxidation (O’Shea & Dionysiou, 2012)

\[ \text{RH}^{\text{-e}} \rightarrow \text{RH}^+ \quad (1) \]

\[ \text{RH}^+ \rightarrow \text{H}^+ + \text{R}^* \quad (2) \]

\[ \text{R}^* + \text{R}^* \rightarrow \text{R} - \text{R} \quad (3) \]

The anodizing reaction is usually regarded as a precise process that implies the exact transition to the electrode by an electron from the organic compound thereby emitting a cationic radical. The cationic radical products generated are significantly impacted by the existence and pH of the electrodes. Studies involving the anodic oxidation process using a boron-doped diamond electrode and a graphite cathode to treat acetaminophen on a small scale have been shown to be effective (Brillas et al., 2005). This is due to the production of high amounts of hydroxyl radicals (\(\text{OH}^\bullet\)) from the electrodes which allows a total solubilization of the acetaminophen to be achieved at lower concentrations. The properties of the BDD included optical clarity, good electrical conductivity, and inertness (G. Chen, 2004).

This literature review summarized the biological, physical, and chemical methods utilized for the elimination of pharmaceuticals stating their advantages and limitation as listed in Table 1.1.
### Table 1.1. The advantages and limitations of various methods utilized for the treatment of wastewater

<table>
<thead>
<tr>
<th>Methods</th>
<th>Functions</th>
<th>Advantages</th>
<th>Limitations</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS</td>
<td>Processes large volume of organic matter</td>
<td>Cost-efficient and widely utilized</td>
<td>Bulk load affects its durability and efficiency</td>
<td>(New et al., 2000)</td>
</tr>
<tr>
<td>MF</td>
<td>Filtration</td>
<td>Well combined with membrane-based treatment technologies</td>
<td>Biofouling Quite ineffective for the degradation of many APIs</td>
<td>(Snyder et al., 2007)</td>
</tr>
<tr>
<td>Chlorination</td>
<td>Use of chlorine primarily for disinfection</td>
<td>Highly effective for disinfecting water</td>
<td>Releases carcinogenic disinfection end products</td>
<td>(Alum et al., 2004)</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Adsorb and separate</td>
<td>Economical</td>
<td>PAC: mainly for low organic wastewater</td>
<td>(Ikehata et al., 2006)</td>
</tr>
<tr>
<td>Photolysis</td>
<td>Disintegration of recalcitrant compounds into biodegradable matter by light absorption</td>
<td>Cheap and reasonably efficient for APIs biodegradation</td>
<td>The efficiency could vary based on the geographical area with a lower supply of sunlight</td>
<td>(Legrini et al., 1993)</td>
</tr>
<tr>
<td>Electrochemical Oxidation</td>
<td>Anodic oxidation process which generates $\text{OH}^*$ which allows mineralization of APIs</td>
<td>More effective for breaking down APIs to non-toxic compounds</td>
<td>Expensive and effluent has to be highly conductive</td>
<td>(O’Shea &amp; Dionysiou, 2012)</td>
</tr>
</tbody>
</table>

Difficulties observed within the discussed treatment methods have resulted in the rapid development of AOPs as the ideal technology for water and wastewater treatment.
1.3. Advanced oxidation processes

AOPs are a treatment alternative for a wide variety of recalcitrant micro pollutants. AOPs generate a sufficient quantity of highly reactive radicals (in particular hydroxyl radicals) which have an especially important reactive effect on organic molecules. These technologies for the rehabilitation of soil, air and wastewater comprising of recalcitrant contaminants are considered to be highly promising methods (Glaze et al., 1987). AOPs degrade contaminants in rudimentary, biodegradable form, rendering their treatments in traditional processes more cost-effective.

Besides, AOPs can be in homogenous and heterogeneous phases. Homogeneous processes usually involve the use of certain chemicals called homogeneous advanced oxidation whilst, heterogeneous processes utilized some catalysts known as heterogeneous advanced processes of oxidation or catalytic processes, to increase the rate of degradation reaction. Some of the most frequently AOPs studied for water treatment applications are UV/O₃ process, UV-H₂O₂, heterogeneous photocatalysis, Fenton and Photo-Fenton reaction, supercritical water oxidation, etc.

1.3.1. UV/O₃ method

The UV / O₃ method provides a valuable means of oxidizing and destroying organic pollutants in water. Specifically, UV radiation of 253.7 nm irradiates aqueous conditions with ozone saturation. The coefficient of extinction at O₃ is 3,300 L.mol⁻¹.cm⁻¹ at 253.7 nm, much greater than the coefficient of hydrogen peroxide (18.6 L.mol⁻¹.cm⁻¹). The ozone depletion level is nearly 1,000 times higher than H₂O₂ (Duguet et al., 1992). Photolysis of ozone is necessary for the AOP with UV and ozone radiation to occur. The ozone-based photodecomposition creates two hydroxyl radicals that do not recombine to create hydrogen peroxide (Glaze et al., 1982)

\[
H_2O_2 + O_3 \rightarrow 2HO^* + O_2 \quad (4)
\]

\[
2HO^* \rightarrow H_2O_2 \quad (5)
\]

This treatment method entails hydrogen peroxide, UV radiation and ozone for the
formation of hydroxyl radicals and oxidation of pollutants during corresponding reactions to occur. Hence, the most common treatment methods such as biological degradation do not have to be substituted, wherever possible.

1.3.2. *UV/O$_3$/H$_2$O$_2$ method*

This method is a very effective technique of drastically reducing TOC by accelerating the ozone breakdown thereby increasing the generation rate of HO$^\bullet$ radicals. (Mokrini et al., 1997) showed that the optimal H$_2$O$_2$ concentration and at varying pH values, a 40% reduction in TOCs were demonstrated. The integration of UV radiated ozone and peroxide proved higher efficiency than single ozone in degrading nitrophenols, enhancing reaction rate, and reduce the consumption of ozone by using low pH levels (Trapido et al., 2001).

1.3.3. *Fenton method*

Fenton’s method entails the formation of hydroxyl radicals due to the chemical reaction of hydrogen peroxide in the presence of iron (Carey et al., 1976). The UV light greatly improves the production of hydroxyl radicals by reducing ferric ions (Fe (III)) to ferrous ions (Fe (II)) as shown in equation 6. Moreover, given the vast availability and non–toxic nature of iron, Fenton’s chemical reaction would seem to be feasible for the treatment of wastewater (Ruppert et al., 1993).

\[
Fe^{3+} + H_2O \xrightarrow{hv} Fe^{3+} + HO^\bullet
\]  

(6)

Fenton process was reportedly used to degrade nitrobenzene, phenol, 2,4-dichlorophenol and 4- chlorophenol, this process was observed to improve biological degradation and reduce toxic compounds (Chamarro et al., 2001). The UV-Vis/ferrioxalate / H$_2$O$_2$ method has reportedly been modified and observed to be more effective for the removal of organic pollutants than the photo–assisted Fenton processes (Richard G. Zepp et al., 1992).

1.3.4. *Heterogeneous Photocatalysis process*

This process involves the photoexcitation of the semiconductor photocatalyst in the presence of oxygen under UV radiation thereby oxidation occurs which then produces
hydroxyl radicals and free holes are generated. There are two stages involved, the solid and liquid phase, so this process can be termed to be heterogeneous. The wavelength shorter than 380nm along the solar spectrum makes this system ideal to be utilized on a large scale (Kositzi et al., 2004). Although several catalysts had been tested however the anatase form of TiO$_2$ has the most advantageous properties including relatively great stability, high efficiency with lower cost, subsequently, the disadvantage is that its fouling with organic substances (Andreozzi et al., 1999). Azeez et al investigated the photocatalytic degradation of MB with Nano titania and a complete mineralization of MB with TiO$_2$ NPs was observed (Azeez et al., 2018). Tsai et al also reported that in the presence of UV-A, the number of antibiotic-sensitive and antibiotic-resistant microbes were reduced effectively by TiO$_2$ photocatalysis (Tsai et al., 2010). In recent years, the trend has been to initiate photocatalytic degradation in the presence of the catalyst in order to create hydroxyl radicals, and thus, it is not mandatory to add an oxidizer to the medium. The photocatalysis process has been shown in industrial effluent and potable drinking water to be a potential approach for the disintegration of toxic and recalcitrant organic substances. A total oxidative degradation of pollutants was ascertained in most cases and the byproducts comprise of CO$_2$, H$_2$O, and other inorganic molecules. Nonetheless, due to its economic viability, it's simple operation at massive scale and process efficiency, solar illumination for photocatalysis process has been such a tremendous booming advancement.

**Table 1.1.** The removal efficiencies of various target pollutants using different kinds of photocatalyst

<table>
<thead>
<tr>
<th>Name of photocatalyst</th>
<th>Light condition</th>
<th>Target pollutant</th>
<th>% of removal</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ – SBR process</td>
<td>UV</td>
<td>Antibiotic wastewater containing amoxicillin and cloxacillin</td>
<td>57</td>
<td>(Elmolla &amp; Chaudhuri, 2011)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>UV and solarium lamp</td>
<td>Tetracycline</td>
<td>50</td>
<td>(Reyes et al., 2006)</td>
</tr>
<tr>
<td>Natural zeolite heulandite/polyaniline @nickel oxide</td>
<td>Natural Sunlight</td>
<td>Safranin-T dye</td>
<td>84.5</td>
<td>(Abukhadra et al., 2018)</td>
</tr>
</tbody>
</table>
1.4. Mechanism of photocatalysis

The aim of the heterogeneous photocatalysis with the utilization of semi conductive catalyst TiO$_2$ is to perform a series of redox reactions on the catalyst surface (Haque & Muneer, 2007). The mechanism of photocatalysis is the process associated with the formation of holes and electrons by the absorption of photons by a semiconductor. The valence band (VB) consists of the highest occupying (h-bonding) band entailing the semi-conductor energy levels and the conduction band (CB) is the lower unoccupied band. Both VB and CB are partitioned by the bandgap energy. As shown in Figure 1.1,
when photon energy (hv) of greater than or adequate to the bandgap energy of TiO₂ illuminated onto the catalyst surface (usually 3.2 eV - anatase or 3.0 eV - rutile) (Huang et al., 2016), free electrons are transferred from the VB to the CB. Thus, pairs of “electron hole” are formed (e⁻ - h⁺) as seen in equation (6).

\[
TiO₂ + hv \rightarrow TiO₂(e_{CB}^- + h_{VB}^+) \tag{6}
\]

If electron scavengers are not present, the photo-excited electron is recombined with the valence band within a few nano-second with simultaneous heat dispersion. Therefore, for efficient photocatalytic reaction and elongation of recombination, the inclusion of electron acceptors such as oxygen is highly essential.

![Schematic diagram of detailed mechanism of photocatalytic reaction](image)

**Figure 1.1.** Schematic diagram of detailed mechanism of photocatalytic reaction

Chain redox reactions which occur on the surface of the photocatalyst are clearly described by the following equations (7) – (15):
• The oxidation reaction of the formed holes with adsorbed water molecules to generate hydroxyl radicals

\[ h^+ + OH \rightarrow OH^* \]  
(7)

\[ h^+_{(VB)} + H_2O_{(adsorbed)} \rightarrow OH^* + H^+ \]  
(8)

• Dissolved oxygen with excited electrons undergoes the reduction reaction to create radical superoxide anions which will in turn through various series of redox reactions produce H₂O₂

\[ O_2(\text{adsorbed}) + e^- \rightarrow O_2^- \]  
(9)

\[ O_2^- + H^+ \rightarrow HO_2^* \]  
(10)

\[ HO_2^* + HO_2^* \rightarrow H_2O_2 + O_2 \]  
(11)

\[ *O_2^- + HO_2^* \rightarrow HO_2^- + O_2 \]  
(12)

\[ HO_2^- + H^+ \rightarrow H_2O_2 \]  
(13)

• The photo excited hydrogen peroxide is then further disintegrated to produce hydroxyl radicals

\[ H_2O_2 + O_2^- \rightarrow OH^* + OH^- + O_2 \]  
(14)

\[ H_2O_2 + e^- \rightarrow OH^* + OH^- \]  
(15)

The major oxidants which include H₂O₂, OH* and radical superoxide anion can trigger a series of chemical degradation reactions. They are known to be resilient, non-selective oxidants. The chemical degradation of organic compounds continues through various redox processes which creates a substantial number of intermediates, eventually leading to the production of CO₂, H₂O, and inorganic ions as the final degradation products.
CHAPTER 2. MATERIALS AND METHODS

2.1. Materials

Commercial Titanium dioxide, Anatase with a purity of 99.7% was purchased from Aldrich and used throughout the experimental study. The hydrochloric acid and sodium hydroxide solution used to adjust the pH of the model pharmaceutical pollutants were of analytical standard. Tetracycline crystalline powder was obtained from Alfa Aesar by Thermo Fisher Scientific and its chemical structure with other properties was listed in Table 2.1.

Table 2.1. Chemical Structure and the properties of Tetracycline (TC)

<table>
<thead>
<tr>
<th>Chemical Structure of Tetracycline</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Chemical Structure of Tetracycline" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Formula</td>
<td>C_{22}H_{24}N_{2}O_{8}</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>444.4 g/mol</td>
</tr>
<tr>
<td>Melting Point</td>
<td>172-174°</td>
</tr>
<tr>
<td>Solubility</td>
<td>Limited solubility in water, Soluble in 1M HCl with heating</td>
</tr>
<tr>
<td>Form</td>
<td>Crystalline powder</td>
</tr>
<tr>
<td>Storage and Sensitivity</td>
<td>Keep cold</td>
</tr>
</tbody>
</table>
2.1.1. Preparation of glassware and apparatus

The deionized water used in cleaning all the glass and plastic laboratory wares that were utilized during every experimental process was obtained from the double-distilled water equipment (A4000D, Bibby, England) situated in the MEE laboratory. The handmade dark beaker, as shown in Figure 2.1, was a 500 mL Pyrex griffin volumetric glass beaker which was taped around with black elastic tape to create a dark condition, more so to repel the interference of the surrounding light atmosphere during the chemical reaction, while being stirred with a Magnetic stirrer. The other glassware used includes 200mL graduated measuring glass cylinder, thermometer, 125 mL of volumetric conical flask, 45 mL Centrifuge tubes, 25 mL Terumo syringe, and safety goggles to protect the eyes from UV Light radiation.

2.1.2. Preparation of sample solution

For each experiment conducted, sample solutions were prepared by dissolving appropriate quantities of TC in double-distilled water. Standard solutions with concentrations of 40, 60, 80, and 100 ppm were prepared in the 500 mL volumetric flask and used as samples for optimization of the pollutant’s initial concentration.
2.1.3. Equipment Used

IKA C-Magnetic Stirrer
High Speed

UV Spectrophotometer
(Shimadzu UV-1280)

Thermo scientific
Sorvall legend XTR
Centrifuge

S220-Kit Mettler Toledo
pH meter

JSM – IT 100 Scanning
electron microscope

Jasco FT/IR - 4600typeA
spectroscopy

MS 12002TS/A00
Precision weighing scale

IKA HS 26 0 basic
Horizontal Shaker

UVC TNE Ultraviolet
Light

Figure 2.2. The equipment used during this research
2.2. Methodologies

2.2.1. Survey Methodology

Antibiotic resistance is a significant threat to public health. The general public awareness is considered to be a necessity for the safe and proper use of antibiotics, also to restrict the spread of antibiotic resistance. So as part of the objectives of the research study, a survey was undertaken. The main purpose of the survey was to ascertain the behavior and level of awareness of residents concerning pharmaceutical products and wastewater pollutants in Hanoi, Vietnam. A cross-sectional questionnaire-based study was carried out between students from Vietnam Japan University, Hanoi University of Science, members of Hanoi International Fellowship, and friends from other provinces in Vietnam.

The questionnaire comprised the following 1) personal information including age, educational level (two statements), 2) attitude towards antibiotic use such as practices of using antibiotics with regards to their daily routine and health (three statements), 3) knowledge of antibiotics and treatment of pharmaceutical effluents (five statements). The survey questionnaire was distributed to participants electronically across various social platforms including emails, Facebook, etc., direct face-to-face interviews were also conducted, participation in the survey was voluntary and over a hundred responses were received back. The sample of the questionnaire used for this survey has been included in Appendix A.

2.2.2. Characterization of the TiO₂ material

The SEM images were obtained by using the JSM – IT 100 Scanning electron microscope to evaluate the size and morphological structure of the photocatalyst. The Energy dispersive x-ray spectroscopy (EDX) device which features as an SEM integral function was used to determine the elemental composition of the material. This experiment was conducted at the Nanotechnology laboratory, VNU - Vietnam Japan University, Vietnam. The functional group present in the photocatalyst and their absorption bands were evaluated using Jasco FT-IR-4600typeA spectroscopy. This FTIR analysis was conducted at VNU, Hanoi University of Science, Vietnam.
2.2.3. *Experimental design and set-up*

The adsorption and photocatalysis processes were carried out in a laboratory-scale system with the set-up comprising of UV-C emitting light bulb TNE UV Lamp 20W, (Ho Chi Minh, Vietnam) with a wavelength of 360 nm placed in the center of the photocatalytic reactor at a distance of 18cm from the sample in the handmade beaker positioned on the IKA C-Magnetic Stirrer High speed which was set to a temperature of 25°C and speed of 200 rpm. The photo-reactor system was enclosed with a hard cardboard to keep out any kind of illumination by ambient light. The schematic illustration of the photochemical reactor system is displayed in Figure 2.3.

![Schematic illustration of the set-up of the photocatalytic experiment](image)

*Figure 2.3.* Schematic illustration of the set-up of the photocatalytic experiment
2.2.4. Experimental procedure

The degradation experiment with TC was carried out in a 200 mL aqueous solution containing the antibiotics (40 mg/L, 200 mL) and TiO$_2$ photocatalyst (0.1g/Loading). As shown in Figure 2.4, for photocatalytic degradation to occur, the sample solution was kept in the dark with constant stirring on the magnetic stirrer at a speed of 200 rpm to allow the adsorption of the TC molecules on the surface of the TiO$_2$ photocatalyst, and after 60 minutes, the maximum adsorption equilibrium was achieved. The UV lamp was thereafter turned on after 60 minutes of adsorption in the dark and the photocatalytic process started. The influence of different parameters on the photodegradation process was investigated. The experiments were performed at different initial concentration (40, 60, 80, 100 ppm), different TiO$_2$ dosage (0.1, 0.3, 0.5g/L), pH levels (3, 7, 9), and temperature (25, 35, 45°C). Each photodegradation process during this study was conducted for 3 hours as illustrated in Figure 2.4.
Step 1  
Calibration of TC to different concentration

Step 2  
Adsorption of TiO2 in the dark condition

Step 3  
Photocatalytic activity under the UV light

Step 4  
Aliquot was centrifuge for 20 min at a speed of 10,000 rpm using K Model PLC-012E universal centrifuge

Step 5  
Unico S 2150 UV spectrophotometer was used to measure absorbance

Figure 2.4. Overview of the experimental procedure
2.3. Analytical methods

The aliquot samples were taken after the required irradiation time which is 15 min, afterward centrifuged, the solution was then carefully extracted with a 25 mL Terumo syringe to separate the particles of the photocatalyst and the resulting solution was analyzed by UV spectrophotometer (Shimadzu UV-1280) at the maximum wavelength of 357 nm. The removal efficiency of TC (%R_{TC}) was expressed as

\[
\% R_{TC} = \frac{C_0 - C_e}{C_0} \times 100\%
\]

Where \( C_0 \) is the initial concentration of the TC pollutant, \( C_e \) is the concentration of TC in the photocatalytic reactor at time \( t \) (min).

The standard calibration curve of TC concentrations as shown in Figure 2.5, demonstrated strong linearity of \( R^2 > 0.9963 \). All the experiments were repeated in triplicates to verify and ensure that the data collected were satisfactory. In addition, all the data points represented were the mean values from the three repetitions.

![Figure 2.5](image.png)

**Figure 2.5.** Showing the standard calibration curve of TC
CHAPTER 3. RESULTS AND DISCUSSION

3.1 The analysis of the survey carried out during the study

This study assessed the knowledge and awareness regarding the use of antibiotics and the treatment of pharmaceutical wastewater pollutants in Vietnam. A total of 123 responses were received with most of the participants (92.7%) belonging to 20-30 years’ age group (Figure 3.1), furthermore, a good number of the participants (90%) had higher educational levels (Figure 3.2). Simultaneously, as shown in Table 3.1, more than half of the respondents (55%) ingested antibiotics as a daily routine, which could over time result in overdose, presumably leading to antimicrobial resistance.

Figure 3.1. Distribution based on age groups

Figure 3.2. Distribution based on educational qualifications
Table 3.1. Questions and responses of the survey participants, total number of participants = 123

<table>
<thead>
<tr>
<th>Question</th>
<th>Response Options</th>
<th>Number</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Do you use antibiotics for your daily life (Bạn có sử dụng thuốc kháng sinh trong cuộc sống hàng ngày không)?</td>
<td>Yes / Có</td>
<td>68</td>
<td>55.3%</td>
</tr>
<tr>
<td></td>
<td>No / Không</td>
<td>43</td>
<td>35%</td>
</tr>
<tr>
<td></td>
<td>Not sure / Không rõ</td>
<td>12</td>
<td>9.7%</td>
</tr>
<tr>
<td>When you fall ill, how do you treat the sickness (Bạn sẽ làm gì khi gặp vấn đề về sức khỏe)?</td>
<td>Go to the hospital to seek for doctor’s advice (Đến bệnh viện/phòng khám để đe đọa và nghe lời khuyên của bác sĩ)</td>
<td>55</td>
<td>44.7%</td>
</tr>
<tr>
<td></td>
<td>Go to the pharmacy to buy antibiotic drugs directly</td>
<td>55</td>
<td>44.7%</td>
</tr>
<tr>
<td></td>
<td>Self-medicate with drugs at home without any prescription</td>
<td>13</td>
<td>10.6%</td>
</tr>
<tr>
<td>After you get better, how do you dispose of the remaining unused antibiotics (Nếu bạn sử dụng thuốc kháng sinh còn dư, bạn sẽ)?</td>
<td>Throw away with other domestic waste in the refuse dump (Vứt bỏ cùng với các rác thải sinh hoạt thông thường khác)</td>
<td>104</td>
<td>84.6%</td>
</tr>
<tr>
<td></td>
<td>Flush down the kitchen sink or toilet</td>
<td>3</td>
<td>2.4%</td>
</tr>
<tr>
<td></td>
<td>Specific disposal technique, for example, return unused pack to the pharmacy (Có biện pháp xử lý đặc biệt, ví dụ như đem hoàn trả lại hiệu thuốc/công ty sản xuất thuốc)</td>
<td>16</td>
<td>13%</td>
</tr>
<tr>
<td>Do you know about the side effects of over-using antibiotics without the doctor’s advice, for example, over-use of tetracycline has been known to be the cause of yellow teeth in children? (Bạn có từng nghe qua/có biết về các hậu quả của việc sử dụng thuốc kháng sinh không theo chỉ định của bác sĩ, ví dụ, sử dụng tetracycline có thể gây hư hỏng men răng hoặc vàng răng ở trẻ em)?</td>
<td>Yes, I know / Có biết</td>
<td>61</td>
<td>49.6%</td>
</tr>
<tr>
<td></td>
<td>No, I do not know / Không biết</td>
<td>34</td>
<td>27.6%</td>
</tr>
<tr>
<td></td>
<td>I know, but not sure / Có biết, nhưng không rõ</td>
<td>28</td>
<td>22.8%</td>
</tr>
<tr>
<td>Do you know about the specific rule or of Vietnamese standard guiding pharmaceutical products and industries (Bạn có biết luật/qui định hay tiêu chuẩn nào ở Việt Nam về sản xuất thuốc kháng sinh)?</td>
<td>Yes, I know / Có biết</td>
<td>12</td>
<td>9.8%</td>
</tr>
<tr>
<td></td>
<td>No, I do not know / Không biết</td>
<td>88</td>
<td>71.5%</td>
</tr>
<tr>
<td></td>
<td>Not sure / Có biết, nhưng không rõ</td>
<td>23</td>
<td>18.7%</td>
</tr>
<tr>
<td>Do you know that wastewater generated from pharmaceutical product/industry are needed to be treated in a specific way (Bạn có biết nước thải từ hoạt động sản xuất thuốc kháng sinh cần được xử lý đặc biệt không)?</td>
<td>Yes, I know / Có biết</td>
<td>12</td>
<td>9.8%</td>
</tr>
<tr>
<td></td>
<td>No, I do not know / Không biết</td>
<td>88</td>
<td>71.5%</td>
</tr>
<tr>
<td></td>
<td>Not sure / Có biết, nhưng không rõ</td>
<td>23</td>
<td>18.7%</td>
</tr>
</tbody>
</table>
However, based on the survey result, 45% of respondents took antibiotics from drug stores and pharmacies while some of the participants (45%) sought the medical personnel’s recommendation, which thereafter revealed that the younger generation would usually go directly to the pharmacy rather than consulting the doctor for prescriptions and merely close to 11% of the respondents had actually taken antibiotics without professional advice. The use of antibiotics has been said to be strongly affected by the easy availability of medication and regulatory enforcement, as well as the belief amidst the independent pharmacy owners and distributors in several countries that if antibiotics are not sold without prescriptions, they would incur losses and businesses might be lost, as patients would most likely just go somewhere (Holloway et al., 2017). This result is quite similar to the findings of the survey conducted across the Pan-European region which reported that the issue of self-medication amidst their respondents ranged between 0.1% - 21% (Grigoryan et al., 2007). Besides, majority of the respondents (85%) had attested to disposing of their unfinished pharmaceuticals together with domestic waste, 2.4% dispose by flushing down their toilets together with the human waste, thereby permitting the existence of antibiotic waste in the environment. Moreover, the current study showed that the lack of knowledge and awareness regarding the method of treating pharmaceutical effluent varied between 43-
86%. Similarly, amidst 123 participants, 87% agreed that untreated pharmaceutical effluents deem unsafe and could have adverse effects on the environment and human health.

The problem of antibiotic resistance is an underrated health concern in most developing nations and more attention should be paid to the dispensation of antibiotics. Subsequently, one efficient strategy of combating self-medication could be to avoid left-overs by dispensing only the specific amount prescribed and reduce reusing the same medications for similar ailment. Simultaneously, enhancing the laws and policies regarding the pharmaceutical industry, so also creating higher awareness campaigns to educate the general public on the appropriate use of antibiotics, the possible adverse environmental and human health effects especially an emphasis on resistance to antibiotics may deter the increased existence of antibiotics in the environment.

3.2. The characterization result of the photocatalyst

3.2.1. Morphology analysis using Scanning Electron Microscope (SEM)

The images from the SEM and EDX analysis of the photocatalyst can be seen in Figures 3.3 and 3.4. As shown in Figure 3.3(a), the TiO$_2$ material was observed to be relatively uniform in distribution and size with the particle size found to be within the micrometer scale with a diameter of 1.5 $\mu$m, more so the shape of the particle was found to be spherical. Also, the EDX spectra showed high peaks of Ti and O (Figure 3.3c) in the sample with the elemental composition percentage (Figure 3.3d) as 87.09% and 12.91% respectively, thereby confirming that the photocatalyst is purely TiO$_2$ without other elemental impurities. To further investigate the elemental composition, one area of the sample was selected during SEM analysis, and EDX mapping analysis was conducted. Invariably from Figure 3.4, the two elements Titanium and Oxygen were detected, the images revealed a uniform distribution of these elements and can be attributed to confirm the presence of Ti and O in the sample.
Figure 3.3. The SEM images and EDX spectra of TiO$_2$ particle

<table>
<thead>
<tr>
<th>Formula</th>
<th>Atom</th>
<th>Mass %</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>87.09</td>
<td>2.43</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>12.91</td>
<td>1.08</td>
<td></td>
</tr>
</tbody>
</table>
3.2.2. Fourier Transform Infrared Spectroscopy (FTIR) analysis

Figure 3.5 shows the FTIR spectra of the TiO$_2$ photocatalyst. The functional group and composition of the TiO$_2$ material were analyzed within the infrared (IR) spectra frequency range of 400 - 4000 cm$^{-1}$ with resolution 4 cm$^{-1}$. In transmittance (% T), these IR spectra provides qualitative data on how the adsorbed molecules are bound to the surface. The spectrum displayed several absorption peaks however, the pure TiO$_2$ sample exhibited the Ti – O – Ti bending vibrations at 638 cm$^{-1}$ – 521 cm$^{-1}$ (Mahalingam et al., 2017). While the absorption peaks at 1105 cm$^{-1}$ indicates the characteristics of surface adsorbed water and the peak at 3448 cm$^{-1}$ corresponds to the bending vibrations of the hydroxyl functional groups (Vetrivel et al., 2015).
3.3. Photodegradation of Antibiotic pollutant

3.3.1. Effect of initial concentration on the removal of TC with TiO$_2$

The chemical composition of different organic molecules tends to have an impact on the photocatalytic degradation rate as a result of the chemical reactions of these organic compounds with different photocatalysts. One of the essential aspects to consider in photodegradation processes is the effect of TC initial concentration (Prabha & Lathasree, 2014). The initial concentration of TC varying from 40, 60, 80, and 100 ppm was investigated and as displayed in Figure 3.6, after 180 mins, the decrease in the removal efficiency was observed to range between 98.9, 87.9, 76.4, and 18% with increasing TC concentrations respectively. This is because the increase in the pollutant’s initial concentration causes more molecules to be adsorbed to the surface of TiO$_2$ by the Vanderwaal force, thereby diminishing the adsorption ability of hydroxyl ions which will inhibit the production of hydroxyl radicals (Lu et al., 2013). Furthermore, at higher concentrations, more molecules will be adsorbed until TiO$_2$
particle cannot adsorb anymore which would compel the molecules of the pollutant to block the photons, hence the removal efficiency would decrease. However, at low concentration of 40 ppm, TC was completely degraded and chosen as the optimum pollutant initial concentration.

![Graph showing TC removal efficiency over time with varying concentrations.]

**Figure 3.6.** The effect of initial concentration on TC removal efficiency, Volume of the sample solution = 200 mL; TiO$_2$ dosage = 0.1g/L, TC concentration = 40 ppm, temperature = 25°C, Total reaction time = 180 min, absorbance wavelength for TC = 357 nm

### 3.3.2. Effect of catalyst dose on the degradation efficiency of TC with TiO$_2$

The dosage of photocatalyst highly affects the rate of heterogeneous photodegradation reaction, as significant increases are usually detected. Overall, to prevent wasteful use of the catalyst, the optimum dosage must be estimated so as to achieve maximum absorption of effective photons (Prabha & Lathasree, 2014). For this experiment, varying photocatalyst ranging from 0.1g/L, 0.3g/L, and 0.5g/L were investigated to determine their effects on the removal of 40 ppm TC pollutants. As seen in Fig.3.7, the percentages of TC removal were 98.9%, 92.9%, and 78.7%, thus there was no
significant increase in the degradation rate when the TiO$_2$ dosage was increased, rather it indicated a negative effect. Similarly, (Mozia et al., 2013) reported a decline in the removal efficiency of diclofenac TiO$_2$ loading was increased to 0.3g/L, but no substantial influence on degradation was observed for catalyst dose ranging between 0.05 – 0.2g/L.

![Graph showing the effect of catalyst dose on TC removal efficiency](image)

**Figure 3.7.** The effect of catalyst dose on TC removal efficiency, Volume of the sample solution= 200 mL; TC concentration= 40 ppm, temperature= 25°C, Total reaction time = 180 min, absorbance wavelength for TC = 357 nm

Although, other findings have claimed that “catalyst loading tends to have both benefits and limitations to the process of photodegradation”, however, reducing the catalyst load had shown to decrease both the amount of photons absorbed as well as, increases the rate of degradation process. The reduction in the amount of catalyst loading also enhances the transparency of the sample solution which further enables easy penetration of the light intensity, thus, improving the photochemical reaction (Bagheri et al., 2017). Hence, to avoid unnecessary excess catalyst and also ensure appropriate absorption of light photons for utter degradation, 0.1g>Loading was selected as the optimum catalyst
dose for subsequent experiments.

### 3.3.3. Effect of pH value on the degradation efficiency of TC with TiO$_2$

The most significant parameter in ensuring effective photodegradation is the pH value, as hydroxyl radical formation is greatly dependent on the influence of pH (Jiao et al., 2008), so also alters the surface of the photocatalyst, dissociates the pollutant and changes the structure of the pollutants in the aqueous solution (Etacheri et al., 2012).

The point of zero charge (pHpzc) is commonly used to depict where the pH value of a photocatalyst at the surface charge density is equal to zero. Initial pH is amongst the most crucial parameters in the photodegradation activities due to its influence on the photocatalyst’s surface charge and ionizing nature. As shown in Figure 3.8a, the effect of pH on TC removal efficiency was determined by evaluating different initial pH values ranging from 3-9, whilst other parameters remained constant. After 120 mins of irradiation, 62%, 97%, and 22% of TC were removed at pH 3.0, 7.0, and 9.0, respectively. Evidently, TC in the neutral solution showed quicker degradation than in the acidic and alkaline solution. Similar findings were reported by other study that MWCNT/TiO$_2$ nano-composite were used to study the enhanced photocatalytic degradation of tetracycline and real pharmaceutical wastewater (Ahmadi et al., 2017).

Nevertheless, the effects of pH values on the process of TC photodegradation are quite complex to interpret due to its numerous functions such as influencing the adsorption rate of TC on the surface of the TiO$_2$ catalyst. The pHpzc for anatase TiO$_2$ was evaluated at 6.2 using the salt addition method (Figure 3.6b) which corresponds to the value reported by other researcher (Zeng, 2013). Thus, at pH solution > pHpzc, the charge on the surface of the catalyst is negative, and for pH solution < pHpzc, the charge on the surface of the catalyst is positive as shown in equation (17) and (18) (Zeng, 2013)

\[
\text{Ti-OH} + \text{OH}^- \leftrightarrow \text{TiO}^- + \text{H}_2\text{O} \quad (17)
\]

\[
\text{Ti-OH} + \text{H}^+ \leftrightarrow \text{TiOH}_2^+ \quad (18)
\]

The neutral surface charge will be when pH solution = pHpzc. Thus, in the acidic and neutral pH medium, degradation of TC was more favorable than in the alkaline medium. Therefore, in this study, the neutral pH =7 is the optimal and most favorable medium.
with a removal efficiency of 97%.

Figure 3.8. a) Effect of pH on the removal efficiency of Tc, Volume of the sample solution= 200 mL; TiO₂ dosage = 0.1 g/L, TC concentration = 40 ppm, temperature=...
25°C, Total reaction time = 180 min, absorbance wavelength for TC = 357 nm, b) the pH0 vs pH Δ2 using the salt addition method

3.3.4. Effect of temperature on the degradation efficiency of TC with TiO₂

Temperature has been considered to be a valuable parameter while investigating the conditions that influence the photodegradation of pollutants (Behnajady et al., 2006). This study examined the effects of varying temperatures ranging from 25°C, 35°C, and 45°C with 0.1g/L of TiO₂ on the removal of 40 ppm TC pollutants, and 98.5%, 99.1%, 99.7% of TC were degraded respectively which could be said to show a slight increment as the temperature changes. But, the optimal temperature was observed at 45°C with a removal efficiency of 99.7%. The result as seen in Figure 3.9 showed that as the temperature increased, a significant rise in the reaction rate was observed thereby enabling a faster removal efficiency, which has been the case in numerous findings ascertaining that temperature is directly proportional to the rate of the chemical reaction. However, at a very high temperature, the reaction pathway is hindered, and adsorption capability becomes low thereby weakening the oxidation of the direct hole on the surface of the TiO₂ photocatalyst which may cause desorption to occur (C. Chen et al., 2011).

Figure 3.9. Effect of temperature on the removal efficiency of TC, Volume of the sample solution= 200 mL; TiO₂ dosage = 0.1g/L, TC concentration= 40 ppm,
temperature= 25°C, 35°C, 45°C Total reaction time = 180 min, absorbance wavelength for tetracycline = 357 nm

3.3.5. The removal of TC with the optimized conditions

This study conducted quite several experiments to optimize the following experimental variables; at an initial concentration of 40 ppm, 0.1g/L of TiO₂ photocatalyst, pH =7, and temperature at 25°C. The result obtained as shown in fig.3.10 indicated that under optimum conditions, the removal efficiency was 99.7% after 180 mins in the presence of oxygen. Thus, utter degradation was observed.

**Figure 3.10.** the optimized condition on the removal efficiency of Tc, Volume of the sample solution= 200 mL; TC concentration= 40 ppm, TiO₂ dosage = 0.1g/L, pH = 7, Temperature= 45°C, Total reaction time = 180 min, absorbance wavelength for tetracycline = 357 nm
CHAPTER 4 CONCLUSION

This research provides an overview of the basic concepts and mechanisms of the photocatalytic process, methods, and how experimental variables affect the efficiency of this process.

Firstly, the survey analysis identified the behavior, knowledge, and attitude of the respondents, and it could be speculated that to reduce the spread of antimicrobial resistance, appropriate antibiotic dispensation and increased awareness should be encouraged to educate the general public. Furthermore, this study applied the photocatalytic process in removing tetracycline using commercial TiO$_2$ material and the optimal condition for TC removal: TC concentration 40 ppm, catalyst dose 0.1g/L, pH 7. The optimum degradation efficiency was 99% of TC within 180 minutes. Thus, the results obtained from SEM, EDX, and FTIR analysis confirmed that the purchased commercially produced material was TiO$_2$ with high purity and uniformity.

The result presented in this laboratory-scale study clearly shows the application of the TiO$_2$ photocatalyst to degrade antibiotics-laden wastewater in a sustainable way and would definitely protect the environment as well.
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APPENDICE

Appendix A

Treatment of Antibiotic pharmaceutical wastewater in Hanoi. (KHÁO SÁT VỀ MỨC ĐỘ HIỂU BIẾT VỀ SỬ DỤNG THUỐC KHÁNG SINH VÀ TÌNH TRẠNG XỬ LÝ THUỐC KHÁNG SINH TRONG NƯỚC THẢI TẠI HÀ NỘI.)

We aim to examine the respondent’s opinions about pharmaceutical wastewater with respect to the use of antibiotics for their wellbeing. Please check for the Vietnamese version in the inserted bracket.

1. How old are you (Bạn bao nhiêu tuổi)?
   - 20 - 30 years / tuổi
   - 31 - 40 years / tuổi
   - 41 - 50 years / tuổi
   - 51 - 60 years / tuổi
   - Over 60 years / Trên 60 tuổi

2. What is your highest level of education (Trình độ học vấn cao nhất của bạn)?
   - High School / Trung học phổ thông
   - University / Đại học / Cao đẳng
   - Post Graduate / Sau đại học

3. Do you use antibiotics for your daily life (Bạn có sử dụng thuốc kháng sinh trong cuộc sống)?
   - YES / Có
   - NO / Không
   - NOT SURE / Không rõ