Photocatalytic degradation of caffeine using bismuth titanate under visible light

وَمَن يُؤْتَ الحِكْمَةَ
فَقَد أُوتِيَ خَيرًا كَثِيرًا

QUAID-I-AZAM UNIVERSITY

ISLAMABAD

LAIBA GUL

Registration No. 02312011008

DEPARTMENT OF ENVIRONMENTAL SCIENCES
FACULTY OF BIOLOGICAL SCIENCES
QUAID-I-AZAM UNIVERSITY
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This work is submitted as a dissertation in partial fulfilment for the award of the degree of

Master of Philosophy

in

Environmental Sciences

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By

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To my parents and husband for their faith in me, endless love, support and encouragement.

DECLARATION

I, **"Laiba Gul" (Registration No. 02312011008)** hereby declare that my M.Phil. thesis titled as **"Photocatalytic degradation of caffeine using bismuth titanate under visible light"** is all my own effort done in Renewable Energy Advanced Lab, Department of Environmental Sciences, Quaid-i-Azam University, Islamabad. All the investigations, findings, results, conclusions of this research has neither been previously presented anywhere nor published in any local or international forum.

Laiba Gul

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Laiba Gul

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I am very thankful to my **Allah Almighty**, who is most merciful and beneficent, who blesses me with all of His blessing and gave me strength to finish my work in time.

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I highly indebted to all my friends and family members who helped me out with their experiences and moral support. A special gratitude to my siblings. They have been my constant support system throughout my work.

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Laiba Gul

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LIST OF ACRONYMS

PL	Photoluminescence
UV-Vis	Ultraviolet Visible
XRD	X-Ray Diffraction
AOPs	Advance Oxidation Processes
WWTP	Wastewater Treatment Plant
CB	Conduction Band
VB	Valance Band
EMR	Electromagnetic Radiation
eV	Electron Volte
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
PL	Photoluminescence
Eg	Bandgap Energy
CAF	Caffeine
BIT	Bismuth Titanate
API	Active pharmaceuticals ingredients
NSAID	Non-steroidal anti-inflammatory drug
Ops	Oxidation Products
PPCPS	Pharmaceuticals and personal care products
EPA	Environmental Protection Agency
CSO	Combined Sewer Overflows

Highlights

❖ A novel $Bi_{12}TiO_{20}$ catalyst was prepared through simple alcohol assisted hydrothermal method at different calcination temperatures.

❖ All the studied photocatalysts exhibit good visible light activity

❖ The BIT-500 photocatalyst showed best degradation performance for caffeine.

Graphical Abstract
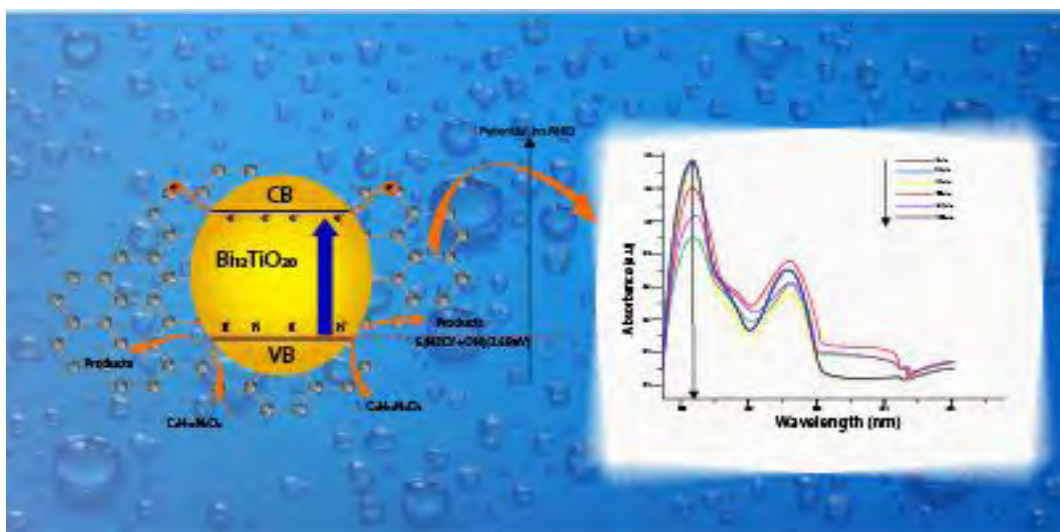
Abstract

Caffeine is ubiquitous in different environmental matrices, usually proposed as a tracer for human pollution since it can be entirely anthropogenic. Caffeine cannot be efficiently treated by simple near UV-Vis irradiation, the treatment of water polluted with emerging contaminants requires visible light active approach. Bismuth titanate with 12:1 has been prepared through simple alcohol assisted hydrothermal synthesis at different calcination temperature. The effect of calcination temperature on surface area and morphology and structure was analyzed by XRD, and TEM. Optical attributes were studied by PL and UV-Vis spectroscopy. During dark reactions, insignificant adsorption of 7.94% and 9% photolysis confirmed that degradation occurs in presence of photocatalyst under visible light. Parametric study including intensity of light, photocatalyst dose, pollutant concentration, pH was also investigated. While testing all prepared samples BIT-500ºC showed 86% degradation at 0.3g/L in 20ppm solution in acidic condition i.e., pH=2.All the reaction followed pseudo-first-order kinetics. Mechanism of photocatalytic degradation has also been studied. This study provides to synthesized more efficient visible light active photocatalyst for the degradation of emerging contaminants in water bodies.

Keywords: Bismuth titanate, calcination temperature, photocatalytic performance, Caffeine CAF.

Introduction

1.1 Background

Pharmaceuticals are biologically active and resistant compounds used in healthcare. They have been widely used in humans, veterinary medicine to cure diseases, husbandry medicines to enhance the production of dairy products, and aquaculture. The quest to live longer has increased the use of pharmaceuticals. Medicinal products have specific mode of action and persistence in human body.[1] Indeed, such compounds have helped and guarantees prolonged life of humans and animals. These lives-saving drugs are widely produced and consumed in large volumes across the globe. Pharmaceuticals have been detected in environment since the late 1990s.[2] At first, even though they were seen, there were very few or no toxicological studies done for both humans and other living things. PCs are now considered as emerging organic pollutants due to their ubiquitous nature in environmental matrices. It is detrimental to humans and ecosystems since a large number of them are unregulated or insufficiently regulated.[3]

'Emerging organic pollutants' is one of the things they are worried about (EOCs). PPCPs, pesticides, and veterinary products are all examples of things made in the environment that haven't been around for a long time.[4] Recently, Pharmaceuticals and Personal Care Products among emerging contaminants– was highlighted as a chemical that is becoming a problem for the environment.[5] Most of the pharmaceuticals are tested before marketing and distribution of the medicines. But, the negative effects of making pharmaceutical products on the nature are well known. The risk assessment of such synthetic chemicals started since the late 1960s.[6] The worse impacts of these medicines are not limited to any specie. A little has been known about the ecotoxicological impacts of these products up to now.[7] These Issues and concerns regarding pharmaceuticals can be complex and difficult to understand. Several medicines which are used for different diseases are continuously discharged into domestic wastewater through sewage systems or runoffs. WWTPs are not designed to remove these contaminants. Thus they found in the environment at significant concentration. Diclofenac was said to be the reason for the decline in the number of vultures in Pakistan. Even the aquatic environment and aquatic organisms are being affected by these chemicals. Many pharmaceuticals have been found in

marine waters. However, this remains mostly unregulated, thus the severely detrimental effects on both animals and humans persist .[8]

Many people around the world are concerned about pharmaceutical pollution, but those who live near manufacturing plants and have drinking water and food sources that are contaminated with waste pharmaceutical products have a more direct and severe impact on their health than people in other parts of the world. Roughly few countries have some sort of collection system on national or local scale. A big chunk of the countries does not have any national policy or system to control or reduce the pollution caused by these drugs. For better and clear understanding an integrated study is essential about pharmaceuticals. These are the bioactive substances which have target specific mode of work.   One of the most troubling aspects of pharmaceuticals is that they are designed to work specifically on known biological targets. They have a high degree of interaction with biological systems and are resistant to deactivation prior to performing the desired function. Discussion about any dimension of these drugs or as environmental contaminants requires a clear understanding about basic terminologies of these products and their active ingredients. There are almost 12000 ranges of pharmaceuticals which are consumed by humans while there are 2500 ranges of veterinary medicines.[9]

1.2. Types of pharmaceuticals

Common types of pharmaceuticals are as follow:

- Analgesics
- Antibiotics
- Psycho-stimulants
- Estrogen and hormonal drugs
- Antiepileptic drugs

1.2.1. Analgesics

Analgesics are a class of medications used to relieve suffering. There are several types of analgesics available, including sedative analgesics, non-sedative analgesics, and non-steroidal anti-inflammatory medicines (NSAID). They exert a variety of effects on the nervous systems and are usually take to relieve discomfort associated with nearly all disorders.[10] Acetaminophen and aspirin are two commonly used non-

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narcotic analgesics. Codeine, methadone, morphine, and oxycodone are all narcotic analgesics. Additionally, nonsteroidal anti-inflammatory drugs (NSAIDs) include diclofenac, ketoprofen, mefenamic acid, naproxen, and ibuprofen.

1.2.2. Antibiotics

Antibiotics are used to treat bacterial infections. There are more than 10 different types of antibiotics used to kill or stop the growth of bacteria. Among the antibiotics available are beta lactams, macrolides, tetracycline and sulfonamides. Several of them, particularly beta lactam antibiotics (amoxicillin and penicillin), are the most often given antibiotics in humans

1.2.3. Psycho-stimulants

Psycho-stimulants are used for the purpose of reducing physical exhaustion and restoring mental alertness. Caffeine is the most often used nonprescription drug as CNS and metabolic stimulant. It is frequently used in different beverages, drugs and food items.[11]. Also, it has been frequently detected in surface water.[12]

1.2.4. Estrogen and hormonal drugs

the most important types of pharmaceuticals because they are used a lot and have a lot of critical effects on humans and other animal mutational changes, feminization of male fishes).[13]

1.2.5. Antiepileptic drugs

Any drug that helps treat epilepsy, which is a long-term condition of the central nervous system that causes seizures that happen quickly and often. carbamazepine is frequently used medicine. Most of the time, one of the PPCPs are reported in waste water effluent.it causes mutational changes in the aquatic fauna.[14]

1.3. Pharmaceuticals in environment

PIE" stands for "Pharmaceuticals in the Environment," and it's a field of study that looks at how pharmaceuticals get into surface and ground waters. The pharmaceutical companies are making more effectual active pharmaceutical ingredients (APIs) by scheming them to be more potent, bioavailable, and resistant to degradation.[8] Pharmaceutical goods come into contact with the environment at several times during

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their life cycle, but most notably during the manufacturing process. Releasing antibiotics in water results in the formation of antibiotic-resistant bacteria that are more difficult to deal. Pollution of the environment by pharmaceutical goods also has a negative effect on animals, notably fish that live in contaminated water.

1.3.1. Sources of pharmaceuticals

There are two ways to look at the source of pharmaceuticals. One type of pollution is referred to as point source pollution, while the other type is referred to as diffuse pollution. Single identifiable sources of pollution originate from industrial effluent, biomedical waste and sewage treatment processes.

Waste disposed of in landfills may contain substances that are harmful to the environment's health. Additionally, municipal landfills may produce leachate containing high levels of dissolved organic matter, heavy metals, and other pollutants.[15]
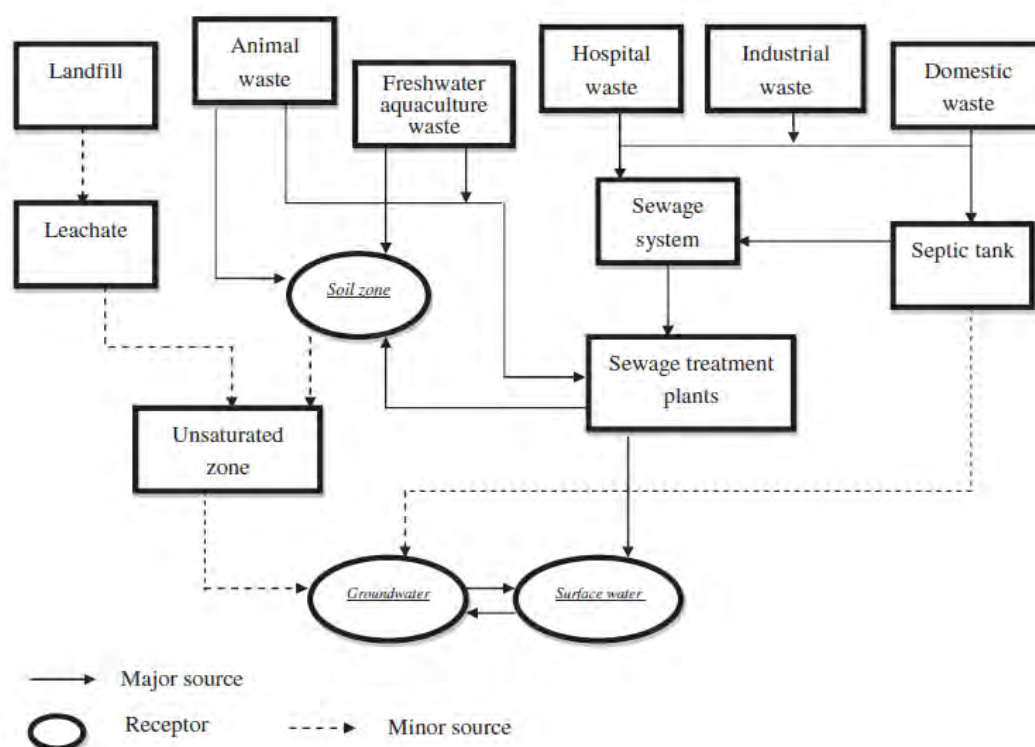
Figure 1.1: Possible sources and routes of pharmaceuticals in environment.[16]

According to the **Figure 1.1** waste water generated is from the different kinds of sources such as hospital, fresh water and aquaculture, industrial and household waste. Most of the pharmaceutical and PPCPs surplus is released in to the environment

directly through WWTPs via sewage systems.[17]Pharmaceutical contamination is mostly caused by incomplete human metabolism and excretion in waste water. Domestic route through waste water treatment plant has been reported as the main source of human pharmaceuticals pollutants into aquatic bodies.[18] Pharmaceuticals are also found in substantial amounts in hospital and industrial waste water. According to many studies conducted identified pharmaceuticals in the effluents and influents of waste water treatment plants due to their incomplete removal.[19]Waste water used for the irrigation purposes contains pharmaceuticals that degrade the soil quality. Leachate from the soil reaches the ground water by infiltration of waste water. Also, Septic tanks and waste water resources are considered to be the primary point sources of contamination for the soil zone and water resources.[20] According to a study conducted regarding septic tanks there were 22 different types of pharmaceuticals 18 of them were present in higher concentration above detection limit caffeine being the most common.[21] Sewage sludge, which is called Biosolid is one of the major sources of diffuse source pollution applied to the land ultimately reaching ground water.[22] Septic tanks and waste water resources are considered to be the primary point sources of contamination for the soil zone and water resource.

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Table 1.1: Notable occurrence of pharmaceuticals in environmental matric

Pharmaceuticals	Remarks
Acetaminophen, salicylic acid, salicylamide, ibuprofen, naproxen, ketoprofen, clarithromycin, trimethoprim, roxithromycin, azithromycin, sulfamethoxazole, sulpiride, thiamphenicol, atenolol, diphenhydramine, and pirenzepine	Thirty-six pharmaceuticals, majority of them were antibiotics and analgesics, had high predicted environmental concentrations in influent. Nine pharmaceuticals in the effluent showed high toxicity based on predicted environmental concentrations/predicted no effect concentration ratio[23]
Caffeine, carbamazepine, azithromycin, bezafibrate, metoprolol, sulfadiazine, sulfamethoxazole, erythromycin, roxithromycin, and trimethoprim	Spatiotemporal distribution of 27 pharmaceuticals in the Chaobai River Agriculture area presented the highest pharmaceutical concentrations The acute toxic pressure in the river was mainly driven by caffeine[24]
Phenazone, ibuprofen, ketoprofen, phenylbutazone, clarithromycin, erythromycin, paroxetine, scopolamine, omeprazole, trimethoprim, atenolol, fenofibrate, gemfibrozil,, metformin, amoxicillin, ampicillin, caffeine, and enoxacin	Trace levels of pharmaceuticals were detected in superficial and drinking water Conventional drinking water treatment plants were not able to remove the pharmaceuticals completely Drier periods were related to the highest concentration of the pharmaceuticals Drinking water treatment plants' removal efficiency shows a great variation over the year[25]
Acetaminophen, caffeine, atorvastatin, lorazepam, cotinine, metformin, metoprolol, paraxanthine, naproxen, quetiapine, ramipril, salbutamol, and warfarin	Twelve of top-used pharmaceuticals and 2 metabolites were assessed. Primary treatment was significantly less efficient than other technologies Removal efficiencies of pharmaceuticals with 9 treatments technologies were tested[26]
Caffeine, theophylline, acetaminophen, lincomycin, sulfamonomethoxine, metoprolol, ofloxacin, ketoprofen, bezafibrate, and roxithromycin	In-stream attenuation of pharmaceuticals was observed by a mass balance approach Source was estimated based on populations for pharmaceuticals conservative in the river Three pharmaceuticals were substantially affected by household septic tanks[27]
Trimethoprim, ofloxacin, metronidazole, ciprofloxacin, sulfamethoxazole, propanolol, ranitidine, omeprazole, fluoxetine, carbamazepine, metamizole, ketoprofen, naproxen, ibuprofen, diclofenac, bezafibrate, gemfibrozil, clofibric acid, nicotine	Twenty-three pharmaceuticals were monitored in sewage from wastewater treatment plants in Gran Canaria (Spain) Removal efficiencies of pharmaceuticals from two different wastewater treatment plants were evaluated Environmental risk assessment of pharmaceuticals was determined[28]
Amoxicillin, erythromycin, clarithromycin, ibuprofen, metoprolol, caffeine, clofibric acid, diclofenac, salicylic acid, and carbamazepine	Caffeine showed the highest influent concentration than other pharmaceuticals Wastewater treatment plants in north China had a higher influent level of total pharmaceuticals Several high-risk pharmaceuticals to the environment were identified[29]

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1.4. An insight on caffeine

Caffeine ($C_8H_{10}N_4O_2$, CAF), the most extensively used alkaloid in the world, is present in a wide variety of natural species, including coffee and cacao seeds, as well as in a wide variety of beverages and edible products (e.g. tea, coffee, and energy drinks).[30] CAF is a core pillar in the pharmaceutical industry, and it is found in a wide range of medicinal product and PPCPs. It enhances the effect of certain analgesics along with cerebral and respiratory stimulant.[30,31] 90% of the adults consumes caffeine with mean daily intake of 227mg.[32] So, a lot of CAF is needed to make a lot of different industrial products, thus it has been included to the US. EPA's list of high production volume chemicals. The overall average intake of CAF per person per day is 70 mg.[30] Drinking coffee or using it as a medicinal or personal care product is a popular way to get your caffeine fix (PPCPs).When ingested caffeine is distributed in all body about 1-10% is not metabolized is excreted in urine and ultimately reached the WWTPs enter the water bodies.[33] Natural watercourse have been found to contain it Surface waterways, groundwater, and wastewater treatment plant effluent (WWTP) influent and effluent are all common places to detect high concentrations of CAF because it is ubiquitous as shown in figure 1.2. A portion of this might be due to the widespread use of coffee, caffeinated drinks, and food goods on a worldwide scale. (11.7 mg CAF/g commercial coffee). CAF's have high solubility in water (21.7 g/L at 20 °C) and negligible volatility are other contributing factors, as are the waste created by coffee shops, pharmaceutical industries, and untreated wastewater discharge (e.g. combine sewer overflows CSOs and unconsumed CAF).[34, 35]

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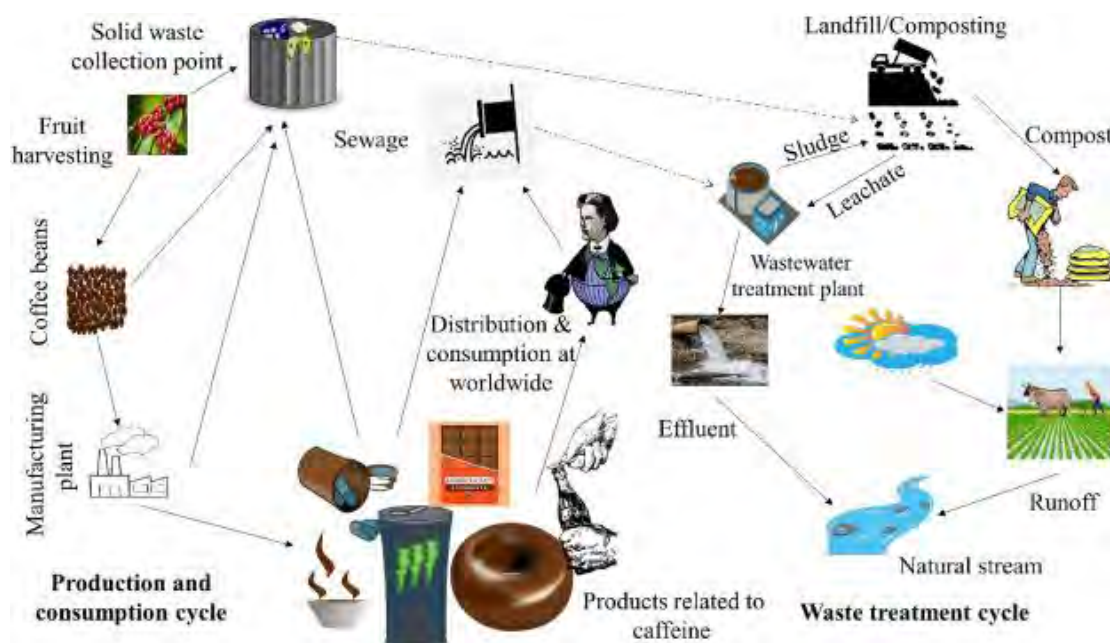
Figure 1.2: Life cycle of caffeine (Rishabh et, al., 2021)

CAF concentrations of up to 230 g/L have been identified in a variety of surface streams and wastewater treatment plant effluents. From 3 to 1440 ng L-1 of CAF have been found in various lakes and rivers across the USA.[36] Table 2 reports the occurrence and concentration of caffeine in different environmental matrices.

For this study's model compound, CAF has been chosen.

Table 1.2: Occurrence and concentration of caffeine in different matrices

Matrix	Sampling country	Maximum Conc.	Minimum Conc.	References
Wastewater	Singapore	3594	4.119	37
Wastewater	Turkey	159.8	20.8	38
Wastewater	India	120	40	39
Wastewater	Greece	96	0.213	40
River	Brazil	0.213	0.0111	41
Drinking water	Korea	0.095	0.034	41

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Caffeine Toxicity:

Caffeine has a median oral LD50 in rats of 192 mg/kg. [MSDS] About 10-14 grams of caffeine (equal to 150-200 mg/kg of body weight) is lethal to humans in a single, short-term overdose. As a central nervous system stimulant, however, coffee in excess can trigger seizures. Those who suffer from epilepsy or any kind of seizure disorder should consume it with great caution. Nausea, vomiting, diarrhea, and gastrointestinal distress are possible signs of overdose. Caffeine toxicity is declared as a medical condition by the WHO and is included in their International Classification of Diseases (ICD-10). Psychomotor agitation, agitation, anxiety, restlessness, rapid heart rate, sweating, and trembling are all symptoms of this condition. Those who don't drink coffee regularly but use energy drinks are at a higher risk of overdosing [42]

1.5. General method and systems for waste water treatment

In the past decades, the removal of pharmaceuticals from water environments has been investigated using a variety of methods, the most common of which include biological treatments in which different enzymes are used to degrade the contaminants. Different chemicals are used in ozonation, chemical oxidation, chlorination for waste water treatment Adsorption, ultrafiltration and reverse osmosis are traditional physical methods. The aqueous contaminants can be removed using these procedures, however most of them have certain drawbacks.[43-44]

1.6. Advance oxidation process

Advanced oxidation processes (AOPs), which combine two or more oxidation procedures, have gained considerable interest in wastewater treatment systems. AOPs are cost effective as they work under ambient temperature and pressure conditions.[45] AOPs are preferred over chemical oxidation procedures utilizing chlorine, hydrogen peroxide, or ozone. In comparison to Advance oxidation processes Chemical oxidation techniques have a limited oxidation potential and are thus incapable of entirely degrading and mineralizing all organic contaminants.[46] AOPs have the potential to mineralize resistant organic pollutants more efficiently and without creating secondary hazardous pollutants. AOPs are characterized by their ability to generate highly reactive hydroxyl radicals ($\cdot$OH) in situ. When compared to chemical oxidation procedures, this has shown to be far more advantageous since the produced hydroxyl radicals are non-selective, resulting in high mineralization efficiency and excellent degradation. Hydroxyl radicals are one of the most powerful oxidants in the

table because they have a lot of power and can react quickly. Hydroxyl radicals prefer electron-dense areas, which results in their addition to an unsaturated bond in aromatic compounds.

AOPs create hydroxyl radicals by pairing chemical or physical processes such as, Fenton system, (H_2O_2 / Fe^2+ or Fe^3+), H_2O_2 / catalyst, H_2O_2 / O_3 (peroxone). All of these techniques include the use of radiation (light), such as ultraviolet (UV) irradiation, vacuum-UV irradiation, ultrasonic or pulse radiolysis, and hydrodynamic generated cavitation.[47] AOPs is regarded as a potential approach for degrading organic waste water contamination that exists in trace amounts.

Heterogeneous photocatalysis is a potentially advantageous approach for degrading emerging organic contaminants by using variety of catalyst under visible light These reactions are dependent on the formation of extremely reactive hydroxyl radicals caused by light, which oxidize the organic materials and results in complete mineralization.

1.6.1. Photocatalysis

Photocatalysis employing heterogeneous photocatalysis is becoming more dynamic as a result of recent developments in light-related technologies (AOTs). Semiconductor-aided photodegradation of wastewater contaminants has been the most prevalent heterogeneous photocatalysis. For water filtration, it is one of the most promising methods. Heterogeneous photocatalysis has a wide variety of uses in water treatment because of a number of essential qualities. Organic compounds may be completely mineralized into CO_2 and H_2O through this process because it can be performed at room temperature and pressure, does not require mass transfer, is inexpensive, and has the potential to lead to total mineralization.

The next paragraphs lay out the fundamentals of heterogeneous photocatalysis. Various redox reactions on the surface of semiconductor photocatalysts have been achieved using semiconductor nanoparticles as an improved photocatalyst. For example, the semiconductor catalyst's electronic band structure (cb/vb) can be explained by the bandgap that separates the conduction and valence bands. To excite the electronic transition from VB to CB and remove the hole and electrons from the vb, a photon with a light energy equal to or greater than the band energy is irradiated onto the semiconductor catalyst's surface. Alternatively, the photon can become stuck

on the catalyst's surface and respond to the species that has been absorbed. The oxidation and reduction of electrons and holes can begin from the excited state.[48] **Figure 1.3** Photoelectrons' reduction potential (cb) and photoholes' oxidation potential (vb) are actually the same energy level. The presence of oxygen acts as electron scavengers resulting in the formation of superoxide and hydroxyl radicals afterwards the H_2O_2 formation.[49] In the following Equations **(1.1)** to **(1.6)**, the sequence of redox processes that occur at the surface were usually proposed.[50]

Photon-induced activation: photocatalyst $+ h\nu \rightarrow e^- + h^+$ **(Eq1.1)**

Oxygen adsorption: $(O_2)_{ads} + e^- \rightarrow O_2^{\cdot-}$ **(Eq1.2)**

Water ionization: $H_2O \rightarrow OH^- + H^+$ **(Eq1.3)**

Superoxide protonation: $O_2^{\cdot-} + H^+ \rightarrow HOO^{\cdot}$ **(Eq1.4)**
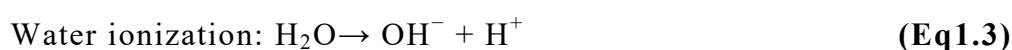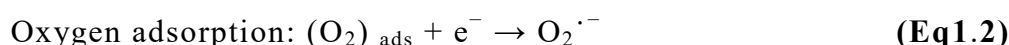
HOO radical in Equation4 exhibit comparable scavenging characteristics as oxygen, extending the lifespan of photoholes equation **(1.5)** and **(1.6).**

$$HOO^{\cdot} + e^- \rightarrow HO_2^-$$ **(Eq1.5)**

$$HOO^- + H^+ \rightarrow H_2O_2$$ **(Eq1.6)**

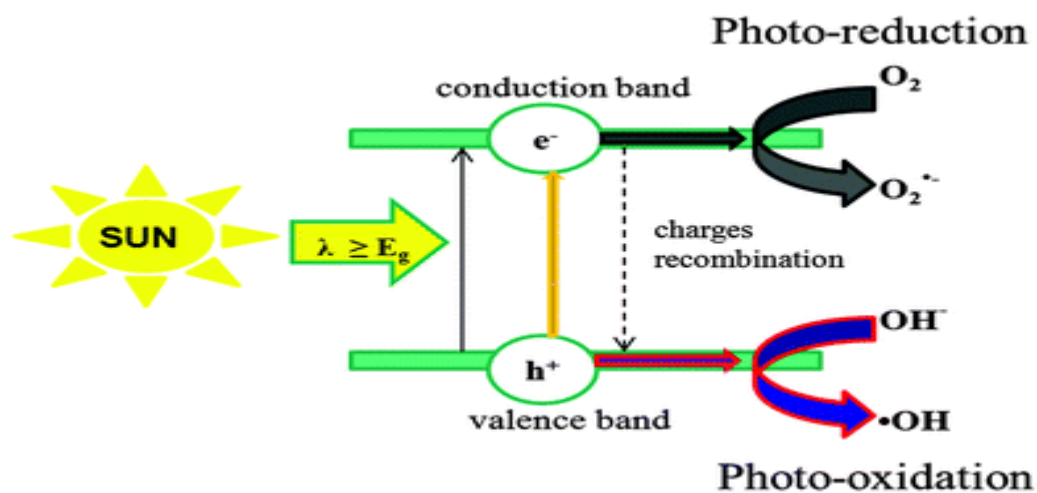Figure 1.3: primary reaction taking place on surface of semiconductor [48]

A photocatalysis reaction can be broken down into a series of separate steps.:

(1) Organic pollutants are mass transferred from a aqueous phase to be adsorb onto the surface of photocatalyst.

(2) Photocatalysis undergo on the surface of photocatalyst and pollutant.

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 (3) Transitional desorption from the photocatalyst surface and mass transfer from the interface region to the liquid phase.

1.6.2. Importance of photocatalysts

Titanium-based nanoparticles are widely recognized as efficient photocatalysts for degrading less biodegradable chemicals. Numerous studies on the photocatalytic degradation of dyes in aqueous matrices have been conducted using single-component catalysts (such as TiO_2, ZnO, and CdS). [51]

Titanium dioxide (TiO_2) has been extensively employed photocatalyst due to its thermal and chemical stability, low toxicity, economic viability, and high oxidizing power when stimulated by UV or near-UV–vis irradiation. Surface-excited electrons and holes generated by high-energy photons above 3.2 eV. Photogenerated electrons and holes are responsible for the successive oxidation and reduction of organic contaminants by the generation of free radicals such as hydroxyl (HO•) and superoxide.[52]

There are many factors that affect TiO_2's ability to be a photocatalyst. These include its crystal structure, surface area, particle size and the distribution of hydroxyl groups.[53] Sol-gel and hydrothermal processes can be used to produce photoactive TiO_2 powders, and the ability to integrate TiO_2 with other materials is a further benefit.[54]

Due to its piezoelectric and ferroelectric capabilities, compounds such as $Bi_{12}TiO_{12}$, $BaTiO_3$, $ZnTiO_3$, $CaTiO_3$, and $SrTiO_3$ are employed in fuel cells, sensors, memory devices, and spintronic applications as catalyst electrodes. These compounds are great replacements for TiO_2 in solar cells because they are non-toxic, chemically stable, and very good at photocatalysis in the visible range.[43,55]

1.7. Proposed system

Bismuth is rarely used as a dopant in titanium based catalyst, due to high reactivity and structural composition, bismuth oxides has been commonly used as visible light driven photocatalyst. Bismuth titanate is a type of semiconductor with wide band gap and several crystal phases, including dielectric pyrochlore phase $Bi_{12}T_{12}O_7$,ferroelectric perovskite phase $Bi_{14}Ti_{13}O_{12}$ and refractive sillenite phase $Bi_{12}TiO_{20}$. High dielectric constant, ferroelectric and photoelectric properties these semiconductors are widely studied.[56] In actual, $Bi_{12}TiO_{20}$, $Bi_2Ti_2O_7$, and $Bi_4Ti_3O_{12}$

have been attracting great attention as photocatalyst a number of works have been reported.[57,58] It was reported in previous literature that $Bi_{12}TiO_{20}$ have the desirable band gap and potential to degrade organic pollutants This research projects focuses on the synthesis of $Bi_{12}TiO_{20}$ at different calcination temperature.
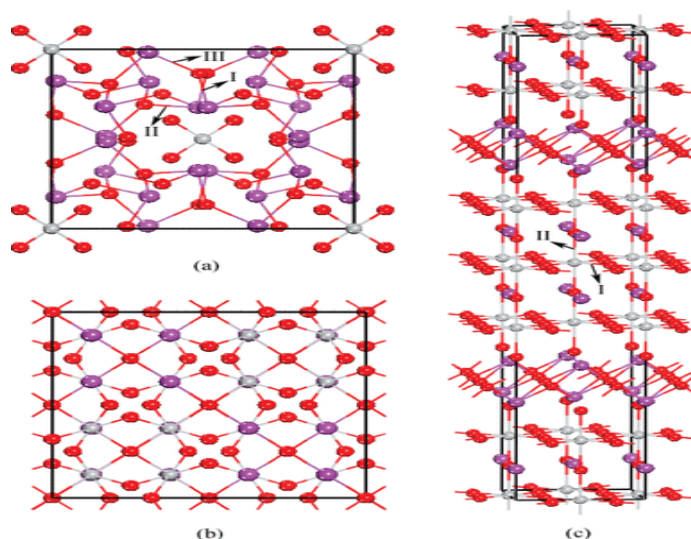
Figure 1.4: Bulk structures of (a) $Bi_{12}TiO_{20}$, (b) $Bi_2Ti_2O_7$, and (c) $Bi_4Ti_3O_{12}$. The purple spheres represent Bi atoms, the grey spheres represent T atoms, and the red spheres represent O atoms.

1.8. Problem statement

The presence of developing organic compounds from various pharmaceutical industries in treatment plant effluents has been documented. Even at low concentrations, these chemicals had some physiological effects on both humans and animals. They are able to persist in the ecosystem long enough to transmit contamination to the aquatic environment. Pharmaceutical pollutants, at both low and high quantities, pose a threat to the environment. Despite this, traditional wastewater handling is expensive and requires a vast space for degradation. To this end, a low-tech approach to effluent degradation can be used. Photocatalysis employing nanomaterials may be a viable option for resolving some of these issues. Photocatalytic activity has been demonstrated in numerous well-known materials to date. In addition, new materials with higher photocatalytic reactivity are in high demand, which is helping to propel technological advancements.

1.9. Aims and Objectives

This work aims to degrade CAF under solar spectrum using a class of photocatalysts synthesized by a simple alcohol-assisted hydrothermal process.

To accomplish, the following objectives are stated,

1. Synthesis of refractive sillenite phase $B_{12}TiO_{20}$, via simple alcohol assisted hydrothermal process
2. Study the effect of different calcination temperature on structure of $B_{12}TiO_{20}$
3. Estimate and compare efficiency of formed catalyst for the degradation of CAF using solar irradiation.
4. Study the effects of pollutant concentration and catalyst dose on degradation of caffeine
5. Proposed degradation mechanism of CAF by $Bi_{12}TiO_{20}$

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Materials and Experimental methods

It provides thorough information on the substances, synthesis procedure, and experiments that were used to synthesis nanostructures of bismuth titanate and barium titanate, respectively. This chapter also provides a quick overview of the testing and evaluation characterization approach

2.1. Materials and reagents

Bismuth titanate is synthesized through the alcohol-assisted hydrothermal method through these techniques different morphologies are easily prepared by simple varying calcination temperature. The chemicals used are bismuth nitrate, titanium oxyphoshate, isopropanol, NaOH, HNO_3. And reagent plus grade CAF powder. Deionized water was utilized for the synthesis of catalysts. Unless otherwise specified, all compounds are of analytical grades and utilized without purification. The chemicals were purchased from Sigma-Aldrich, respectively.

2.2. Glassware and instrumentation

Glassware used were beakers, spatula, magnetic stirrer, centrifuge tubes, falcon tubes, graduated cylinder, pastel, and mortar, pipettes, and PPEs (nitrile gloves, face mask, lab coat, goggles). Similarly, instruments that are used during synthesis were a muffle furnace, weighing balance, drying oven, autoclaves, and centrifugation machine.

2.3. Hydrothermal method

The synthesis of compounds via chemical reactions in a sealed and heated solution above ambient temperature and pressure is referred to as hydrothermal synthesis. This technique is used in preparation of catalyst via stainless steel autoclaves and drying oven. It is also called chemical bath deposition technique. NaOH act as a pH buffer and maintains a pH of 9 to 12. The conditions of the reaction are critical during the hydrothermal reaction process. The synthesis of the products is influenced by the solvent type, temperature, and duration.[59]
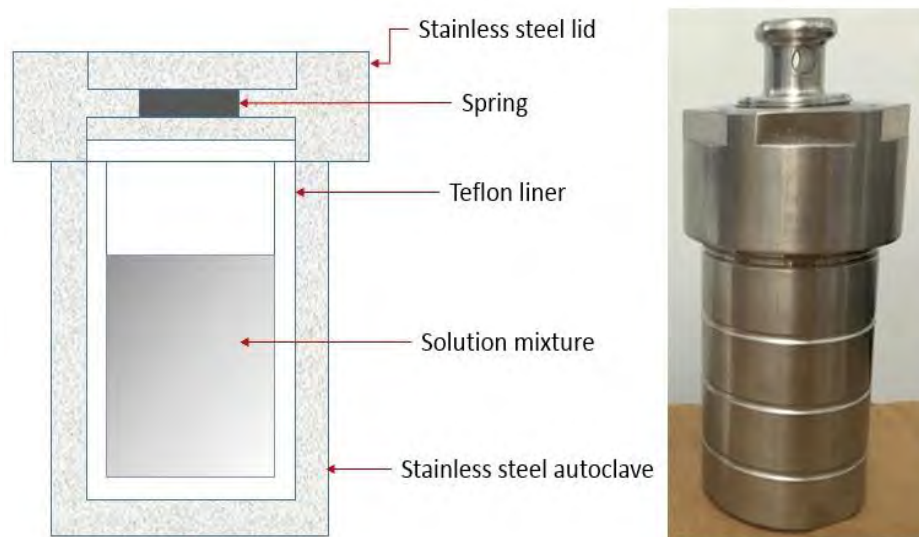
Figure 2.1: Teflon lined autoclave for hydrothermal process[60]

2.4. Synthesis of Bismuth Titanate

Bismuth titanate nanocrystals are synthesize using $Bi(NO_3)_3 .5H_2O$ and $TiOSO_4.H_2O$ as reactants. Stoichiometric amount of 3.34g of bismuth nitrate and 0.295g of titanium oxysulphate are taken. These reactants were dissolved in HNO_3 aqueous solution to make 12:1 as shown in figure 2.2.[61] The solution was placed on a hot plate with continuous stirring for 30 minutes. During stirring isopropanol was added. Initial and final pH was measured using pH meter. The acidic pH of the solution is adjusted by using 1M NaOH. The solution was then transferred to stainless steel autoclaves and placed in drying oven at $120^{\circ}C$, for 24hrs. After cooling at room temperature solution were filled in 15ml falcon tubes for washing afterwards solution was centrifuged three times at 4000 rpm for 10 minutes and rinsed with ethanol. Then solution was air dried, crushed. The final products were calcinated in muffle furnace at $500^{\circ}C, 700^{\circ}C$, and $900^{\circ}C$, to get three different nanocrystals.[62 ,61]

Figure 2.2: Hydrothermal synthesis of $Bi_{12}TiO_{20}$
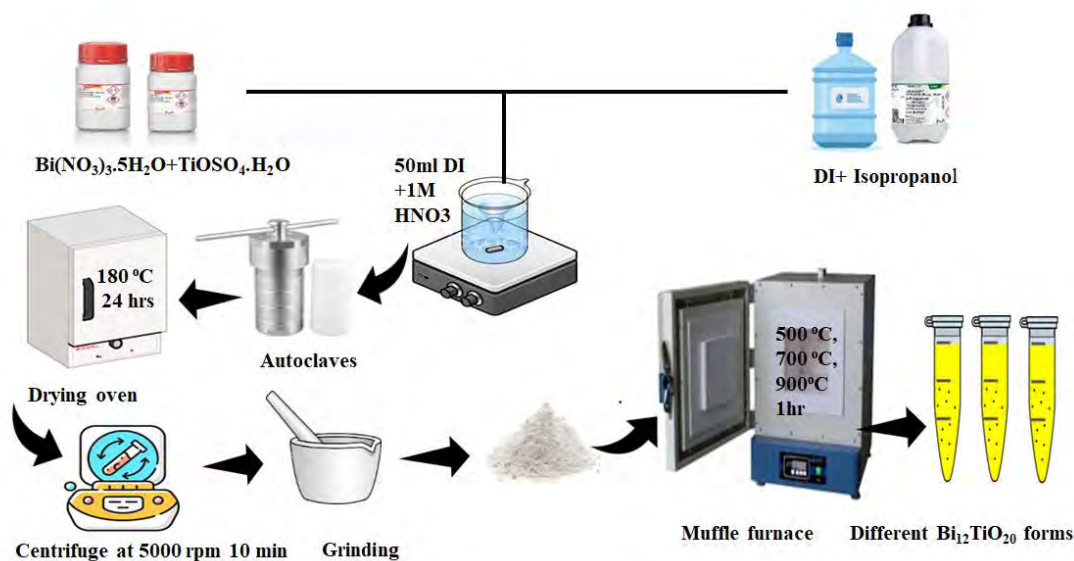
2.5. Photocatalytic Tests

Incident light intensity, initial pollutant concentration, and photocatalyst concentrations are all critical components in any photocatalytic degradation study. [63]Caffeine pure powder was used for to check the catalyst degradation efficiency .To figure out the optimized conditions for degradation, experiments were conducted at different pollutant concentration ranging from 20 to 100 ppm, also the effect of photocatalyst dose (0.1 to 0.5 g L−1) was studied in order to find the optimal concentration necessary for CAF degradation. The effect of pH was also conducted at different acidic and basic conditions. All other reaction parameters were held constant. The samples were taken after equal interval of time. All solution was made in distilled water. After 30 minutes of dark reaction, the adsorption of CAF on the catalyst surface reached equilibrium regardless of the initial concentration of CAF or the photocatalyst used. Then the solution was placed under sunlight and samples were taken with regular interval of 30 minutes. All the samples were centrifuged at 5000 rpm for 10 minutes. UV visible spectrum was used to measure caffeine absorption.

Photocatalytic degradation of caffeine using bismuth titanate under visible light

Characterization Techniques

This chapter gives brief insight about the analytical and characterization techniques for material. Here instrument type, working principle, and information obtained is briefly stated.

Detail of characterization techniques are given below:

- XRD
- SEM
- TEM
- UV Visible spectroscopy
- PL spectroscopy
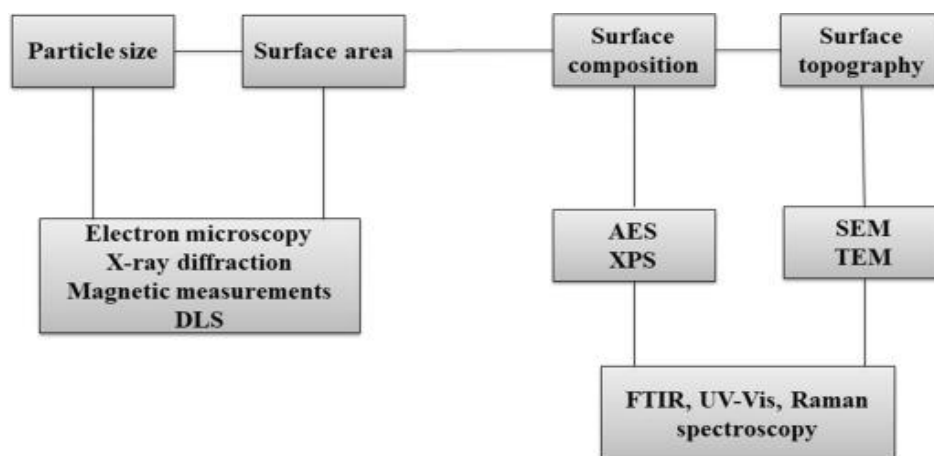
Figure 3.1: Common characterization techniques

3.1. X-ray diffraction spectroscopy

Xray powder diffraction is rapid assessment technique that relies on the dual (wave and particle) nature of xray used to distinguish variants of nanomaterial, as well as its phase and crystalline attributes. crystalline material possesses long range ordering, observed as sharp peaks in XRD based on diffraction patterns.[64]

Photocatalytic degradation of caffeine using bismuth titanate under visible light
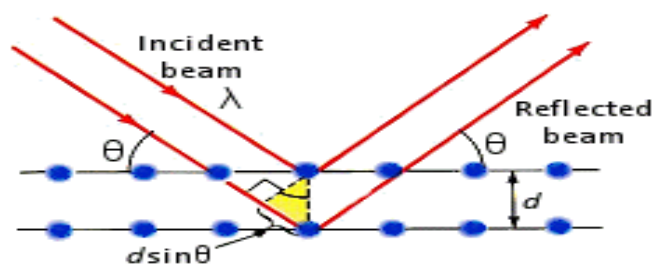
Figure 3.2: Schematic diagram of Braggs law [65]

There are XRD peaks caused by a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample. The X-rays make constructive interference with each other when conditions satisfy Bragg's Law that is

$$n\lambda = 2d \sin\theta \qquad \qquad \textbf{(Eq 3.1)}$$

Here

n= any integer displaying order of diffraction

λ= wavelength of incident x-ray beam

d= the spacing between crystal lattice planes

θ= Bragg's angle of diffraction from different planes

This law establishes a relationship between the wavelength of electromagnetic radiation and the diffraction angle and lattice spacing in a crystal. Peak intensities are determined by the lattice plane positions of the atoms. As a result, the XRD pattern is the fingerprint of a material's periodic atomic arrangements.

Typical X-ray diffractometers consist of three basic elements:

- X-ray tube,
- A sample holder
- X-ray detector

3.2. Scanning electron microscopy

In the field of surface examination, the scanning electron microscope (SEM) is a powerful and versatile tool that uses a powerful electron beam to generate a variety of signals on the surface of solid specimens with great accuracy and spatial resolution.

The signals created by electron-sample interactions include information about the sample's external morphology (texture), topography, chemical composition, and crystalline structure and orientation.[66]

Because the x-rays created by electron interactions do not cause volume loss in the sample, SEM examinations are said to as "non-destructive". This enables the analysis of the same materials many times.

The Scanning electron microscope uses kinetic energy to generate signals based on the electrons' interaction. This type of electron is used to look at crystals and photons since it is secondary, backscattered, and diffracted backscattered. An image is created using secondary and backscattered electrons. Backscattered electrons show differences in the composition of the elements in the specimen, which is the major role of secondary electrons emitted from the specimen. Because electrons have a shorter wavelength than light, SEMs have better resolution than light microscopes

Scanning Electron Microscope

Electron source

Anode

Condenser lense

Scan coils

Secondary electron detector

Objective lens
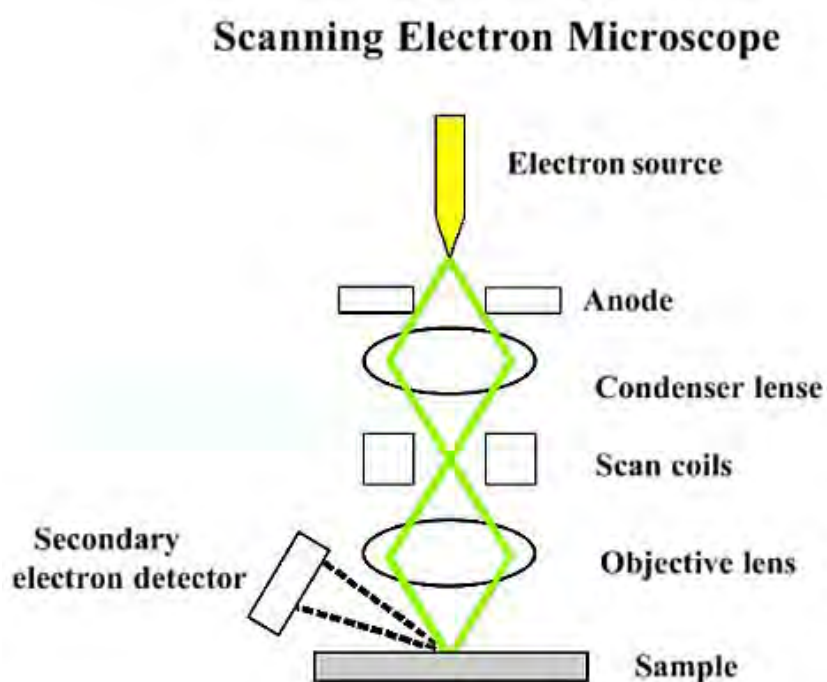
Sample

Figure3.3: Schematic diagram of principle of scanning electron microscopy [67]

3.3. Transmission electron microscopy

Material scientists rely heavily on the transmission electron microscope for their work. It is one of the most powerful techniques for deciphering the atomic structure of

Photocatalytic degradation of caffeine using bismuth titanate under visible light

a material. In addition to morphological and crystalline information, tem microscopy also gathered data on the materials' chemical composition.
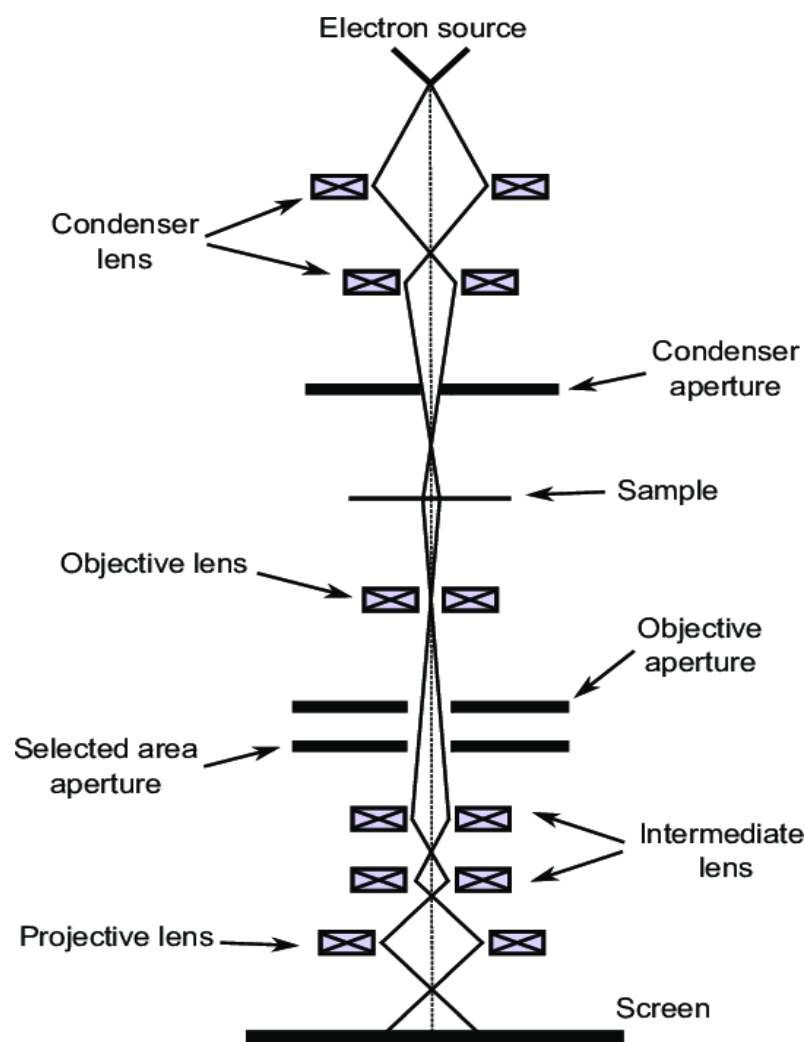
Figure 3.4: Schematic diagram of principle of transmission electron microscopy [67]

The TEM uses electrons instead of light to perform the same functions as the light microscope. In comparison to a light microscope, a TEM's image resolution is hundreds of orders of magnitude greater due to the electron's shorter wavelength. For example, in some instances, an electron microscope (TEM) may see down to the individual atoms within an object's interior structure. Because TEM requires specimens that are semi-transparent to electrons, thin specimens are required.

3.4. Ultraviolet-Visible spectroscopy

UV-visible spectroscopy is one of the oldest methods of molecular spectroscopy. It is possible to detect the amount of UV or visible light absorbed by or transmitted through samples using UV-Vis spectroscopy, which is an analytical technique. If the

sample composition is known, it could provide information about what is in the sample and how much of it is present. The band gap energy of synthetic photocatalysts can also be measured using the UV-visible spectrum. The Bouguer-Lambert-Beer law is the underlying premise of this approach. The intensity of the reducing radiations and the thickness of the absorbing solution are proportional to the concentration of the solute and the path lamp of the sample when a monochromatic beam of light is introduced into a solution containing an absorbent solute, according to the bouguer-Lambert-Beer law. [69]

Mathematical representation of Bouguer-Lambert-Beer law is given below:

$$A = \varepsilon \, l \, c \hspace{6cm} \textbf{(Eq 3.2)}$$

where

A= absorbance of the catalyst.

ε= molar absorptivity constant that is different for every chemical at every wavelength. (L /mole /cm)

l= optical path length. (cm)

c= molar concentration. (mole/L)
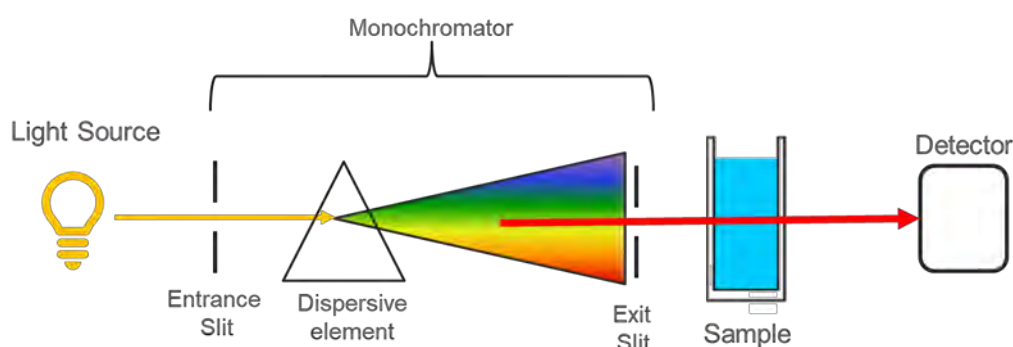
Figure 3.5: Schematic diagram of UV-vis spectroscopy [70]

Spectrophotometry uses a grating monochromator to divide the incoming light into its constituent wavelengths. These instruments, also known as dispersive spectrometers, allow continuous change of incident wavelength over the entire spectrum range using a deuterium lamp and a tungsten lamp as light sources in the (ultraviolet) and (visible)

Photocatalytic degradation of caffeine using bismuth titanate under visible light

regions, respectively. The majority of equipment cover a range of 190 to 900 nm in wavelength.

The energy differences in the ultraviolet and visible absorption spectroscopy region resemble the electronic configurations of atoms and molecules relaying "electronic spectroscopy," despite the fact that this region of electromagnetic radiation's total frequency or wavenumber range being small."

3.5. Photoluminescence spectroscopy

It is a very useful approach for optical investigations, material characterization, and other dynamical processes. Spectroscopic methods are used to study semiconductors' photoluminescence. Photons emitted following optical stimulation are measured using these techniques. The material's properties, such as the transfer of photogenerated charged species and defect concentrations, are subsequently studied in order to administrate them. Photon absorption is the polar opposite of this action. An electron in a higher energy state is shifted to a lower-energy state by itself during the emission process. Radiative transitions and phonon transitions are two forms of changes (non-radiative transitions). There may be emission between a small band of occupied states (containing thermalized electrons) and a limited band of vacant states (holes) near the top of the valence band, depending on the circumstances.[71]
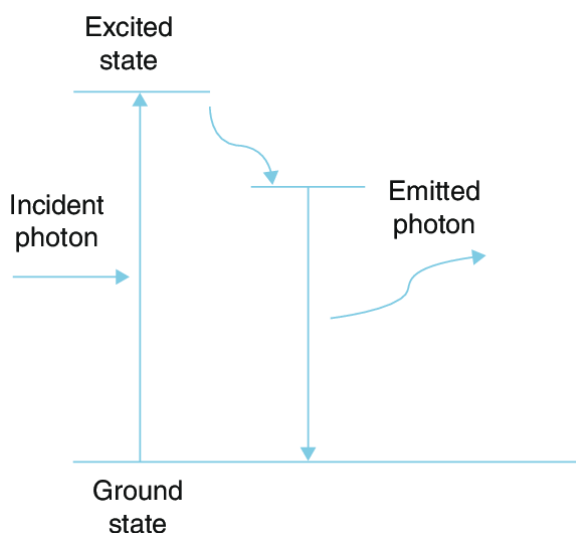

Figure 3.6: Basic principle of photoluminescence [72]

Photocatalytic degradation of caffeine using bismuth titanate under visible light

Result and Discussion

All the results obtained from different experimental and characterization techniques are included in this chapter. As prepared bismuth titanate were characterized by studying their optical properties using Photoluminescence (PL), UV-Vis techniques. The detailed morphological characterization of materials was examined by TEM and structural analysis by XRD. Photocatalytic activity of all catalysts was tested in Solar light and caffeine was used as a model pollutant. UV-Vis spectroscopy was done to evaluate degradation of pollutant.

4.1. Physicochemical properties

4.1.1. Xray diffraction (XRD)

Phase identification and structural morphology showed the successful synthesis of bismuth titanate. **Figure 4.1** shows the XRD patterns of BIT prepared at different calcination temperature i.e. 500°C, 700°C, 900°C under 12:1 molar ratio respectively. By indexing the JCPDS cards (PDF cards 34-0097.) diffraction peaks at $2\theta = 24.7\circ$, $27.7\circ$, $30.3\circ$, $32.9\circ$, $37.5\circ$, $39.6\circ$, $41.5\circ$, $43.5\circ$, $45.4\circ$, $49.1\circ$, $52.4\circ$, $54.0\circ$ and $55.5\circ$, can be indexed to (220), (310), (222), (321), (330), (420), (332), (422), (510), (521), (530), (600) and (611), can be indexed to cubic as reported in literature. [57,73].Though, the intensities of the peaks from three curves are slightly different which shows that there are some alterations among the samples prepared at different temperatures. However, the similar peaks positions indicate that different temperature has almost the same effect on the phase of BIT sample.[74] The strong and sharp diffraction peaks show a good crystallinity and purity of the bismuth titanate. According to XRD patterns, the increase in temperature made the diffraction peaks sharper with enhanced intensity, indicating an increase in single phase related to BIT with increased grain size.[73]
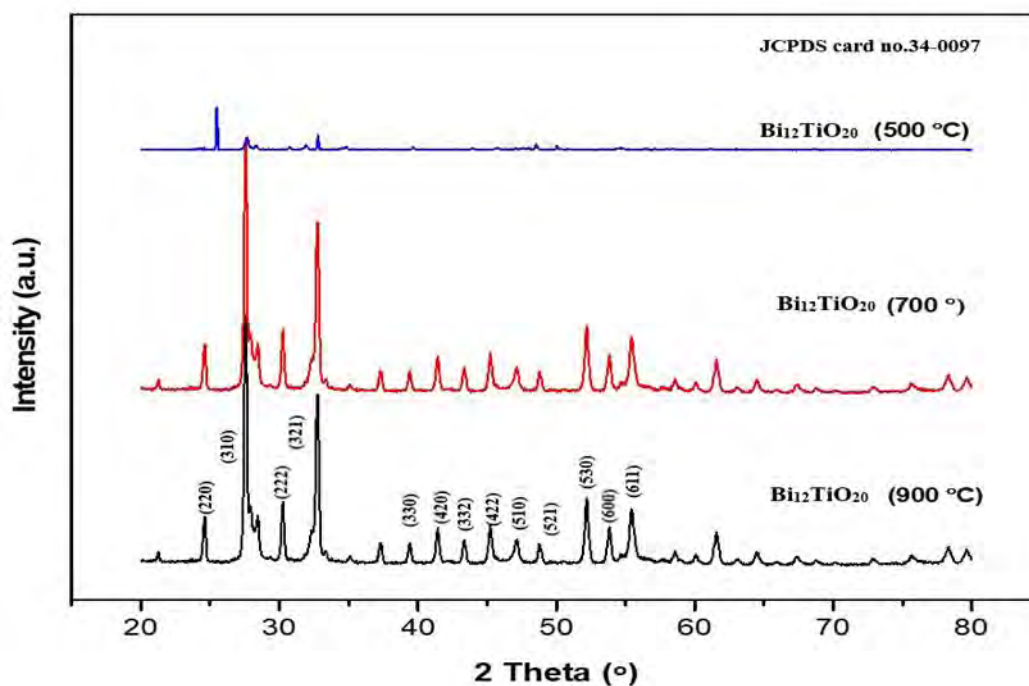
Photocatalytic degradation of caffeine using bismuth titanate under visible light

Figure 4.1: XRD pattern of BIT prepared at different calcination temperatures

4.1.2. Transmission electron microscopy (TEM)

In order to study the effects of calcination temperature on the surface area, TEM was used to observe the morphologies and structure details of these bismuth titanate products. The TEM images of the BIT figure show, along with well-defined cubic particles of different sizes which were prepared by simple alcohol assisted hydrothermal process at different temperatures. **Figure 4.2 (a)** shows the structure formed at 500°C, which are highly spherical in shape and have a size of 5nm which is comparatively smaller than the b, and c. On the other hand, it can be clearly seen in **Figure 4.2 (b)** and **(c)** densely shaped spherical sized particles with size of almost 10nm.[73] These images shows no significant differences among particles at 700 $^\circ$C and 900°C .It was also observed in these images with the increases in temperature the smaller particles begin to agglomerate resulting into clusters of bigger particles with consequently decreases the surface areas hence reduces its efficiency.[75,76]
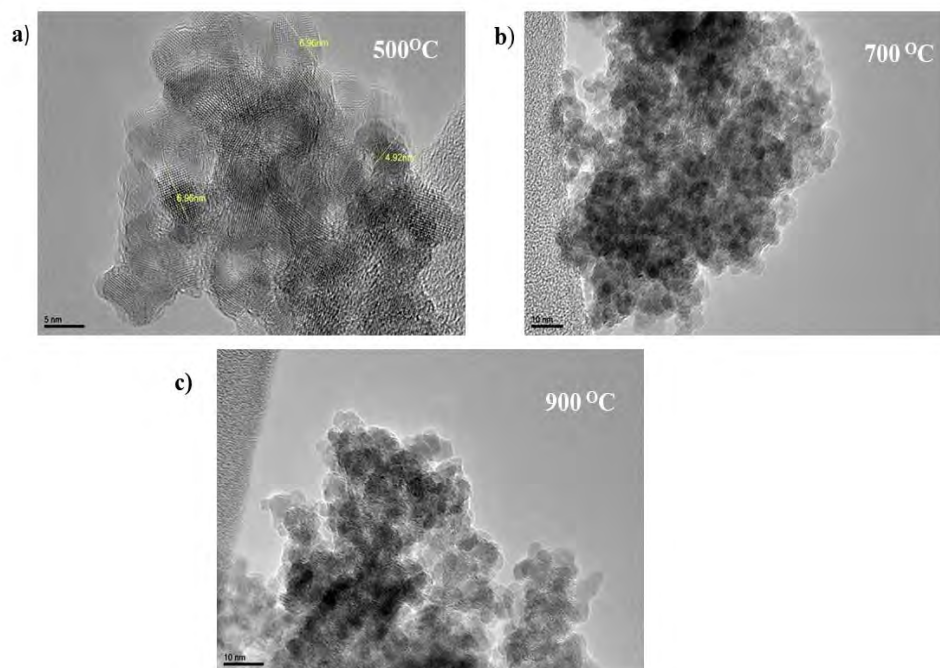
Figure 4.2: TEM images of BIT synthesized at different calcination temperatures (**a**) 500 $^\circ$C (**b**) 700 $^\circ$C (**c**) 900 $^\circ$C.

4.2. Optical properties

4.2.1. Photoluminescence (PL)

Photoluminescence spectra were used to investigate the rate of recombination of photoexcited electrons and holes. By the recombination of electrons and holes pl signal is generated. High intensity of signal indicates high recombination of electron and hole pairs. The pl spectra of bismuth titanate is shown in the figure 4.3. A distinct decrease in the peak can be seen with temperature difference. This reveals that recombination rate is high in the samples treated at low temperature. As the temperature is increased, variation in the luminescence response can specify different types of structural defects and densities.[61]   Following is the sequence of recombination rate BIT-900 $^\circ$C<BIT- 700 $^\circ$C< BIT-500 $^\circ$C .
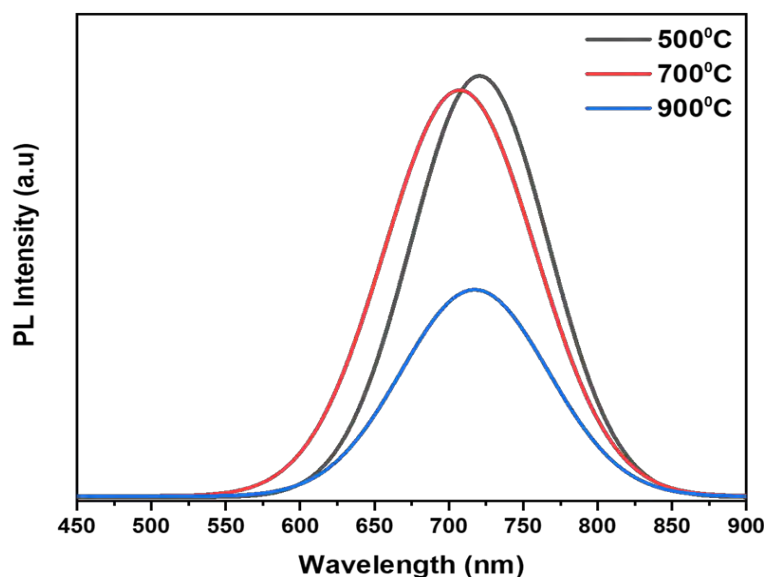
Figure 4.3: Photoluminescence spectra of as synthesized samples of BIT at different calcination temperatures.

4.2.2. UV-Vis Spectroscopy

UV-Vis spectrum was used to analyse the optical properties and charge behaviour of as prepared samples via NIR spectrophotometer UV vis 3600 plus instrument. Figure 4.4 shows the BIT spectra all samples. The spectrum exhibits that as prepared sample are visible light active as the peaks appears to be in visible region.

Figure 4.4: UV-Vis spectroscopy of synthesized samples at different temperatures

Photocatalytic degradation of caffeine using bismuth titanate under visible light

The band gap is calculated by Kubelka Munk function by the following equation

$$FR \times h\upsilon = B\ (h\upsilon - Eg)$$ **(Eq 4.1)**

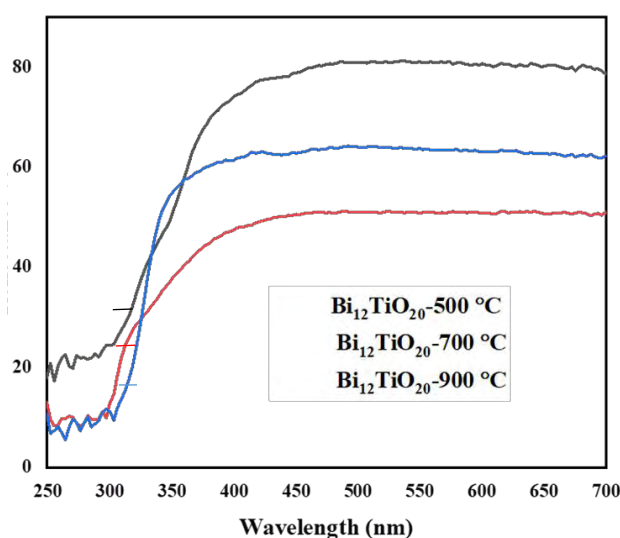Where FR is kubulka Munk function, $h\upsilon$ is Energy of photon and its value can be calculated by $1240/\lambda$. Eg is band gap of samples that can be calculated from aboveequation[77].Peaks are obtained by plotting $(FR \times h\upsilon)^2$ on Y axis, and $h\upsilon$ on axis as shown in the figure 4.4. Band gap of BIT-500°C is 2.75eV as well as reported in literature.[78]This indicates that above sample have a desirable bandgap to degrade organic pollutants under visible light. In comparison to 2.87 eV and 2.95 eV at high temperatures.

Figure 4.5: Band gap of as synthesized samples $Bi_{12}TiO_{20}$ at different temperatures.

4.3. Photocatalytic activity test

The photocatalytic behavior of the material was evaluated in the photocatalytic degradation of caffeine as a test molecule. Incident light intensity, initial concentration of pollutant, and catalyst dose play a significant role in any photocatalytic reaction.[63] In solar light of 120,000 lux all synthesized samples were tested. Caffeine in pure form was used. For testing 50 ml of 20ppm of caffeine solution were taken in three separate beakers each for the three different prepared samples of $Bi_{12}TiO_{20}$.The photocatalyst dose of 0.3g/L of each were added in the specific beakers. To achieve the absorbance equilibrium beakers were kept in the dark for 30 minutes with continuous stirring. After that beakers were kept in direct sunlight

Photocatalytic degradation of caffeine using bismuth titanate under visible light

for 3 hours. During testing samples were taken out after every 30 minutes. After the completion of testing, all samples were centrifuged and UV-Vis spectrum was analysed to check the absorbance spectra changes. Figure 4.6 shows the absorbance spectra changes of caffeine with irradiation times. UV absorption spectra of caffeine show a pair of main absorption bands at 205 nm and 273 nm which is in accordance with literature. [79]
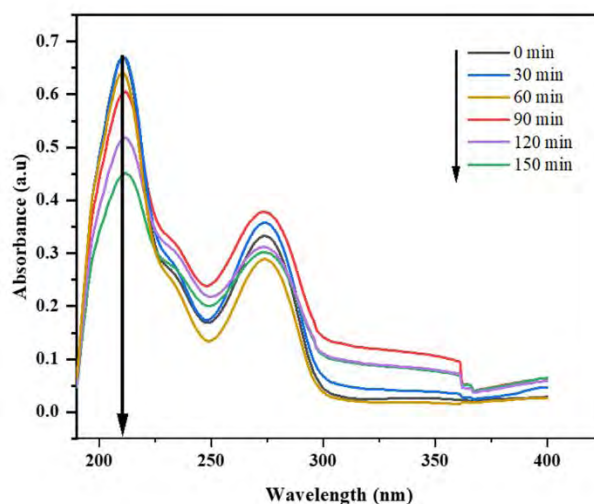
Figure 4.6: UV-Vis absorbance changes of 20ppm caffeine under solar light using 0.3g/L of BIT-500°C.

It is necessary to keep photocatalyst in dark before testing them. If dark reactions are not performed the efficiency of photocatalyst will not be justified. Saturation in the dark differentiates the contribution of adsorption and photocatalytic degradation. It is quite obvious, that decrease in the concentration is due to adsorption and photocatalysis, not due to any phenomena working alone. Figure 4.7 shows a curve between C/C_o and irradiation times. It can be seen that caffeine concentration changes insignificantly in dark. After 90 minutes of reaction equilibrium is attained with no further change.

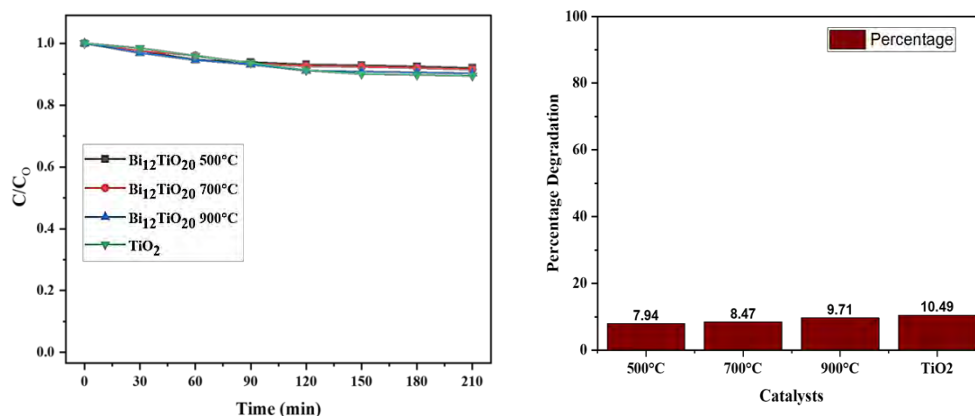**Figure 4.7: (a)** Time concentration plot of caffeine with all samples **(b)** Percentage degradation using all photocatalysts.

For comparison, testing was carried out without photocatalysts in the presence of sunlight under same conditions as shown in figure 4.8. The caffeine concentration is nearly same as conducted in dark showing that CAF cannot be degraded merely in presence of sunlight without photocatalyst. It has been reported in literature that caffeine does not degrade under photolysis, hence photocatalysis is solely responsible for CAF degradation. [80]
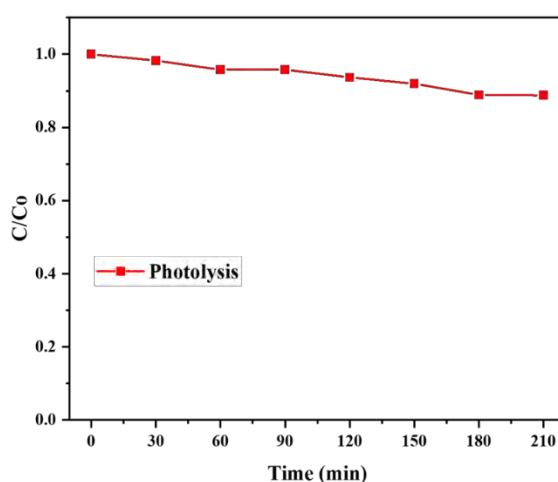

Figure 4.8: Kinetic absorbance spectra changes of CAF solution (20PPM) after different irradiation times without catalyst under visible radiation.

4.4. Optimization study

To study the effect of various independent parameters on the photocatalytic activity of $Bi_{20}TiO_{20}$ following parametric tests were performed

1. Effect of photocatalyst dose
2. Effect of initial pollutant concentration
3. Effect of pH

4.4.1. Effect of photocatalyst dose on CAF degradation:

To establish the effect of photocatalyst dose on caffeine degradation experiments were carried out at different doses ranging from 0.1g/L to 0.5g/L at constant caffeine concentration for each photocatalyst. Figure 4.9 shows with increasing catalyst dose from 0.g/L to 0.3g/L, the degradation of CAF was increased.
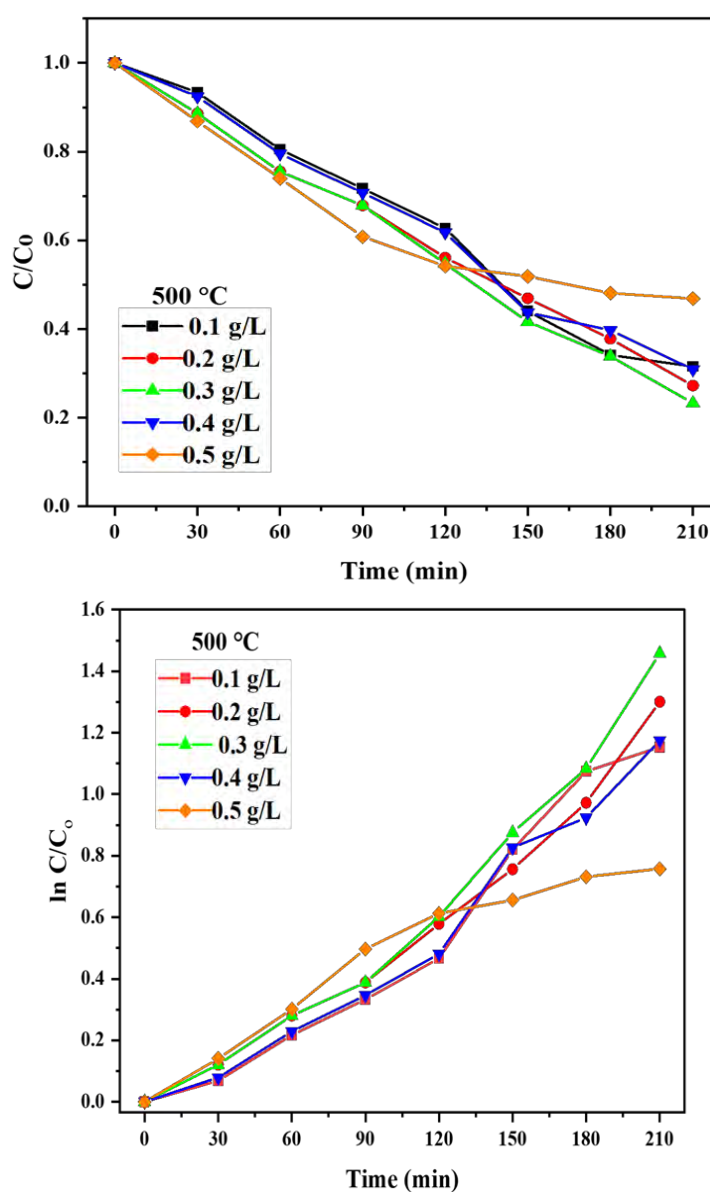

Figure 4.9: (a) Effect of BIT-500 °C dose on the degradation of caffeine **(b)** $\ln C/C_o$ verses time plot.

Photocatalytic degradation of caffeine using bismuth titanate under visible light

Further increased in dose to 0.5 g/L resulted in no significant change in rate of CAF degradation. Hence for the degradation of CAF the optimum dose is 0.3g/L. This phenomenon can be described by the tendency of the photocatalysts particles to agglomerate, causing loss of their active sights and scattering of the incident light which is in good agreement with TEM micrograhs.[81] It is obvious that at low photocatalyst dose, all active sites are vacant for adsorption thus rate of degradation is highest.

As the amount of catalyst resulting in loss of their active sites for adsorption and scattering if incident light intensity. This result is due to the catalyst agglomeration caused by increased particle size at higher temperatures. [82]

Degradation of caffeine by all the photocatalysts are shown in **Figure 4.9** and **figure 4.11** It has been reported in literature that caffeine does not degrade under photolysis, hence photocatalysis is solely responsible for CAF degradation.[80] The degradation of molecule is determined by its ability to absorbs the radiation resulting in the excitation , if not then ,molecules can be indirectly degraded by hydroxyl radicals from water.[83] The linear fitting curve of ln C/Co is plotted against time indicates that CAF degradation over all catalysts follow pseudo-first-order kinetics.[84] It can be seen that with the increase in calcination temperature, the crystal size of $Bi_{12}TiO_{20}$ also increases, which is damaging to photocatalytic activity of $Bi_{12}TiO_{20}$.
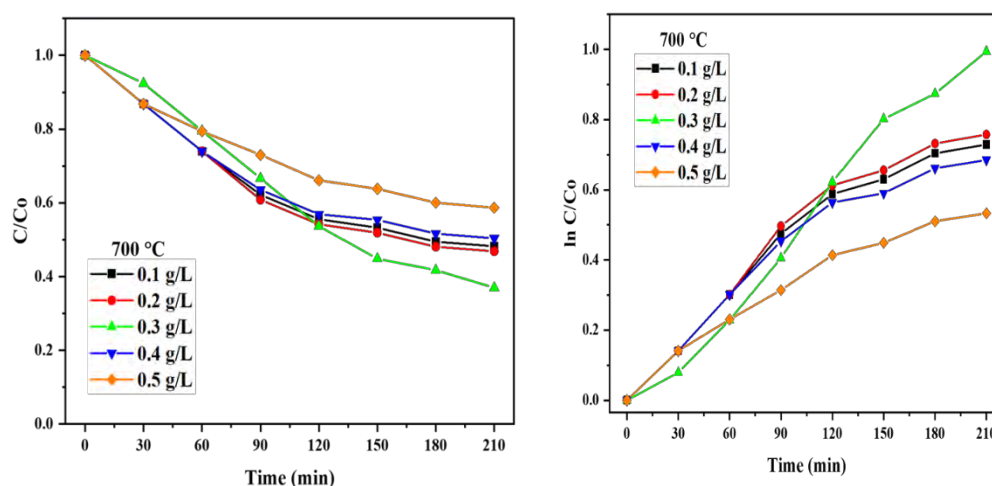

Figure 4.10: (a) Effect of BIT-700 ºC dose on the degradation of caffeine **(b)** lnC/C_o verses time plot.

Photocatalytic degradation of caffeine using bismuth titanate under visible light
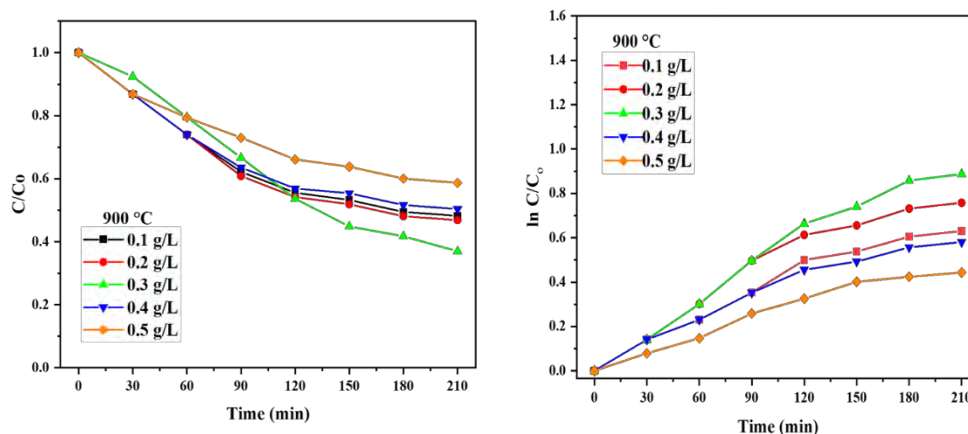
Figure 4.11: (a) Effect of BIT-900 ⁰C dose on the degradation of caffeine **(b)** $\ln C/C_o$ verses time plot.

To get a high photocatalytic reaction, before the rate of recombination of electrons and holes should be migrated to surface and effectively take part in redox reaction. Thus, utilization efficiency depends on the migrated distance of photogenerated electrons and holes.[61] Smaller crystal size just in case of $Bi_{12}TiO_{20}$ prepared at 500⁰C shows maximum degradation of CAF because of the smaller distance electrons and holes migrates.

4.4.2. Effect of initial concentration of pollutant:

To evaluate the effect of initial concentration of caffeine efficiency of BIT-500C, experiments were conducted at five different initial concentrations i.e. 20 ppm ,40ppm, 60ppm, 80ppm and 100 ppm at constant photocatalyst dose of 0.3g/L. It is evident in the figure 4.6 that with increasing pollutant concentration, degradation is decreasing. At 20ppm, 76% degradation was achieved. By increasing the initial concentration above 20ppm, the rate of degradation is decreased. It is due to the fact, saturation of all available active sites with increased initial concentration reduce the efficiency. Figure 4.6 (b) shows that pseudo first order kinetics is followed by all the reactions.
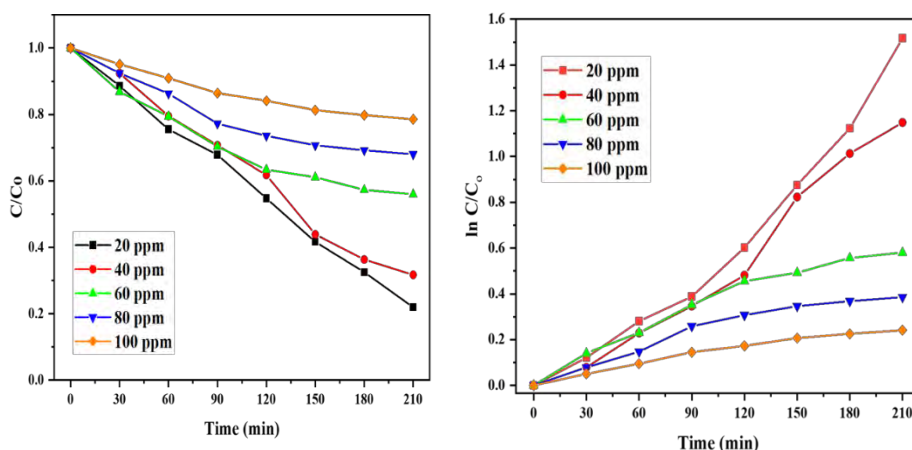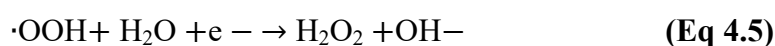
Figure 4.12: Effect of initial pollutant concentration of the solution on the degradation (%) of the caffeine by BIT.

4.4.3. Effect of pH on CAF degradation:

The effect of pH on the photocatalytic activity of BIT-500°C was evaluated at various pH values of (2 ,5 ,7 ,9 , and 12). 1M HNO$_3$ and NaOH solutions were added to initial solution to adjust the pH. Figure 4.7 shows the results; highest degradation occurs at pH 2 (86%). The result proves that, the photocatalytic degradation of CAF was increased under acidic condition. The possible reason might be referring to the surface protonation of photocatalyst particles, which boost the transfer of photogenerated electrons to the surface of the particles. This also reduced the rate of recombination of electron hole pair and increasing the degradation.[62] Moreover, OH- could be produced from the photocatalytic process as follows

$$O_2 + e- \rightarrow \cdot O_2 - \qquad\qquad \textbf{(Eq 4.2)}$$

$$H_2O + \cdot O_2 \rightarrow \cdot OOH + OH- \qquad\qquad \textbf{(Eq 4.3)}$$

$$2 \cdot OOH \rightarrow O_2 + H_2O_2 \qquad\qquad \textbf{(Eq 4.4)}$$

$$\cdot OOH + H_2O + e - \rightarrow H_2O_2 + OH- \qquad\qquad \textbf{(Eq 4.5)}$$

$$H_2O_2 + e- \rightarrow \cdot OH + OH- \qquad\qquad \textbf{(Eq 4.6)}$$

The formation of OH radicals is increased in acidic conditions because H^{+} and OH^{-} to form water.

Photocatalytic degradation of caffeine using bismuth titanate under visible light
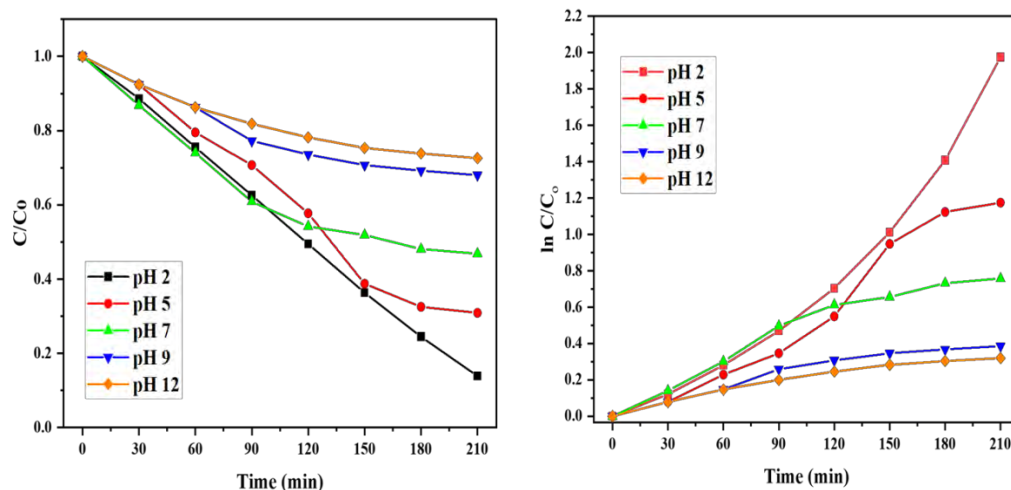
Figure 4.13: Effect of pH of the solution on the degradation (%) of the caffeine by BIT (Caffeine concentration: 20 PPM; photocatalyst dosage: 0.3 g/L).

4.5. Kinetics of optimization reactions:

Kinetic parameters including, Adjacent R^2, rate constant values, and percentage degradation are given in the table 4.3

Table 4.3: Overall reaction kinetics

Experiment	Conditions	K min^{-1}	R^2	Percentage Degradation (%)
Effect of catalyst dose g/L	0.1	0.00597	0.95424	68
	0.2	0.00594	0.97012	72
	0.3	**0.00675**	**0.96171**	**76**
	0.4	0.0057	0.96713	69
	0.5	0.00374	0.92984	53
Effect of CAF concentration (ppm)	**20**	**0.00699**	**0.95426**	**78**
	40	0.0058	0.95426	68
	60	0.00279	0.94899	44
	80	0.0019	0.92669	31
	100	0.00116	0.96094	21
Effect of pH	**2**	**0.009**	**0.92937**	**86**
	5	0.00627	0.95541	66
	7	0.00374	0.92984	53
	9	0.0019	0.92669	31
	12	0.00151	0.93819	27

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4.6.Proposed degradation mechanism

The degree of mineralization of caffeine has been reported in many studied, showed that complete mineralization of CAF is not po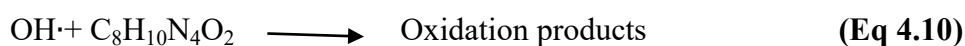ssible photocatalytically, even though it is completely degraded in to oxidation byproducts.[80] Some of the possible oxidation products of caffeine. There are several studies in literature where proposed degradation mechanism of CAF has been already investigated using Fe(VI), hypochlorite ions and ozone.[85,86] Following oxidation products are identified in previous literature including N,N'-dimethyloxamide, N-methylurea and N,N'-dimethylurea were detected as the oxidation products of CAF when oxidized by Fe(VI). Loses of fragments as C_2H_5NO, NH_3 and C_2H_5N from CAF results in the formation of the above mentioned three OPs. [86] Likewise, above three mentioned products were identified when CAF is oxidized by hypochlorite.

The possible mechanism of CAF degradation by $Bi_{12}TiO_{20}$ is given in **Figure 4.9.** Incident solar radiations on the surface of semiconductors, results in the excitation in CB and Vb thus electron –hole pair is generated. The hybridization between Bi 6s and O 2p states, increase the motion of the photogenerated carriers and eliminate the recombination center, was expected to be responsible for the high photocatalytic activity of $Bi_{12}TiO_{20}$. Holes are powerful oxidative ions, are directly responsible in the degradation of CAF and also reacts with H_2O to form OH·. In general degradation mechanism of CAF is as follow

$$Bi_{12}TiO_{20} + h\nu \longrightarrow Bi_{12}TiO_{20} (e^- + h\nu^+) \qquad \textbf{(Eq 4.7)}$$
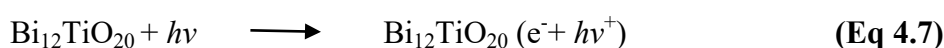
Electrons reacts with O_2 to form O_2^- on Cb while h^+ reacts to form OH with water

$$h^+ + H_2O \longrightarrow OH· \qquad \textbf{(Eq 4.8)}$$

$$e^- + O_2 \longrightarrow O_2·^- \qquad \textbf{(Eq 4.9)}$$

$$OH· + C_8H_{10}N_4O_2 \longrightarrow \text{Oxidation products} \qquad \textbf{(Eq 4.10)}$$

$$h^+ + C_8H_{10}N_4O_2 \longrightarrow \text{Oxidation products} \qquad \textbf{(Eq 4.11)}$$

OH^- and h^+ are the crucial species and they exert a critical influence on the photodegradation of CAF.

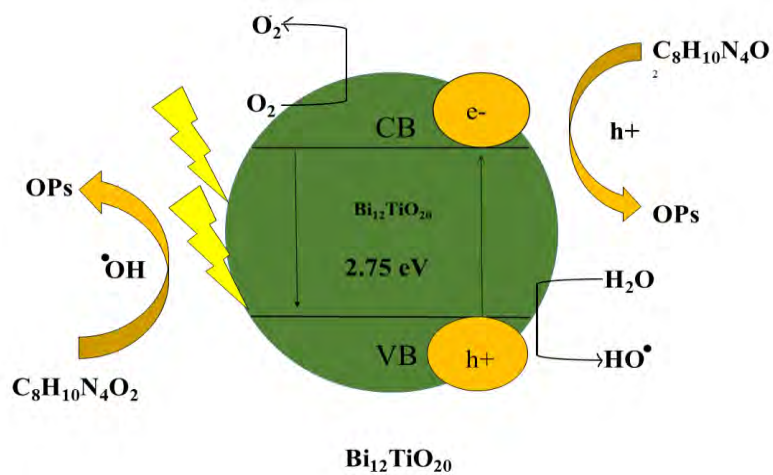**Figure 4.14:** Mechanism of CAF degradation by $Bi_{12}TiO_{20}$.

CONCLUSION

The conclusive finding of this study is that, a simple alcohol assisted hydrothermal method has been employed to synthesize single phase of $Bi_{12}TiO_{20}$ at different calcination temperatures for 1 hour. TEM and XRD confirmed that material have all the desired constituent elements. Optical analysis showed that material exhibit tremendous photocatalytic activity towards CAF under visible light irradiation A parametric study shows that 86% degradation is achieved at 0.3g/L of photocatalyst dose and pH = 2 of mixture. This study also confirmed that the caffeine photodegradation reaction in the presence of all photocatalysts follows the pseudo first-order kinetics. The finding of this study can be used to construct more efficient photocatalysts for application in wastewater treatment plants.

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Authors
Laiba Gul; Dr.Abdullah Khan

Affiliations
Quaid-i-Azam University, Islamabad

1 Graphical Abstract
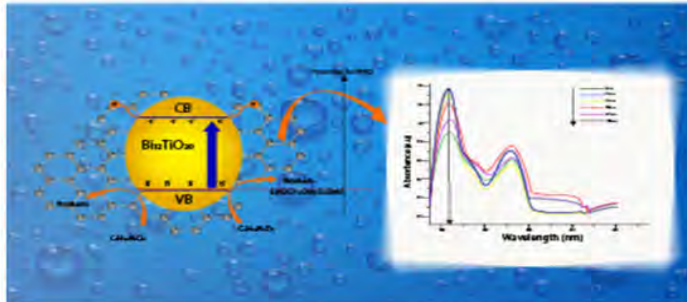
2 Introduction

Caffeine ($C_8H_{10}N_4O_2$, CAF), the most extensively used alkaloid in the world is present in natural species, wide variety of beverages and food products and core pillar in the pharmaceutical industry. PCs are now considered as emerging organic pollutants due to their ubiquitous nature in environmental matrices. It is detrimental to humans and ecosystems since a large number of them are unregulated. Several process were reported to remove these ECs from WWTPs. In the past few years photocatalytic degradation has become an interesting field due to its potential to degrade the contaminants.

3 Aims and Objectives

- Synthesis of refractive sillenite phase $B_{12}TiO_{20}$, via simple alcohol assisted hydrothermal process.
- Study the effect of different calcination temperature on structure of $B_{12}TiO_{20}$.
- Estimate and compare efficiency of formed catalyst for the degradation of CAF using solar irradiation.
- Study the effects of pollutant concentration and catalyst dose on degradation of caffeine.
- Proposed degradation mechanism of CAF by $Bi_{12}TiO_{20}$.

4 Methodology

Simple alcohol assisted hydrothermal synthesis

5 Result and Discussion
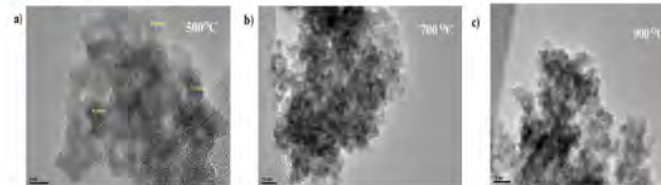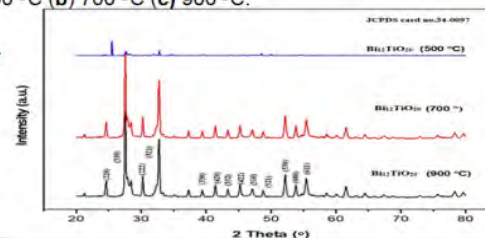
TEM and XRD

Fig. TEM images of $Bi_{12}TiO_{20}$ synthesized at different calcination temperatures (a) 500 °C (b) 700 °C (c) 900 °C.

Fig. XRD pattern of $Bi_{12}TiO_{20}$ prepared at different calcination temperatures

6 Result and Discussion
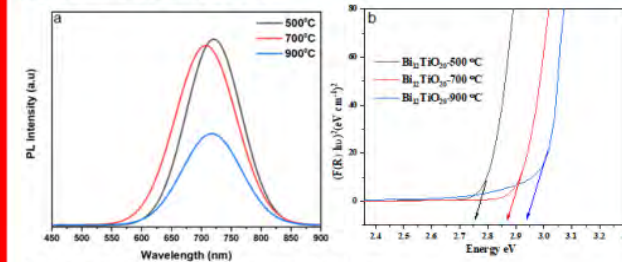
Photoluminance and UV-DRS

Fig. (a) Photoluminance spectra (b) UV-DRS

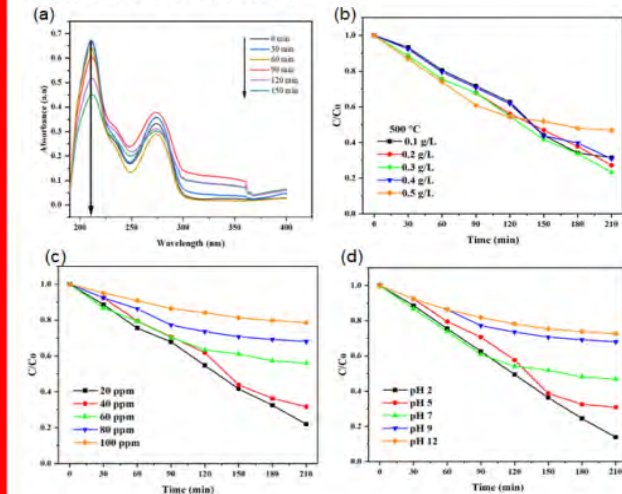**Photocatalytic Activity Testing**

Fig. (a) Absorbance spectra changes of caffiene at 20ppm, Photocatalytic degradation of caffeine (b) at different dose of bismuth titanate (c) pollutant concentration and (d) pH.

6 Result and Discussion

- Characterization confirmed that material have all the desired features desirable for photocatalysis.
- The $Bi_{12}TiO_{20}$ structure is efficient at 500°C calcination temperature. It is important to note that no change in phase and morphology at increased temperature yet a noticeable change in absorption behavior and in recombination rate ,that in turns to have effect on degradation.

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