PHOTOCATALYTIC DEGRADATION OF PRODUCED WATER USING TIO2-ACID ACTIVATED BENTONITE COMPOSITE.

BY

JAPARI LUCAS

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CERTIFICATION

This is to certify that this Research project work was carried out by JAPARI LUCAS with Matriculation number ENG2002052 of the Department of Chemical Engineering at the University of Benin, Benin City Edo State.

ENGR. PROF. F.A. AISIEN DATE

Project Supervisor

ENGR. PROF. S.E. UWADIAE DATE

Project Coordinator

PROF.MRS. EGHE OYEDOH DATE

Head of Department

EXTERNAL EXAMINER DATE

DEDICATION

This project is dedicated to Jehovah Almighty, for his unfailing love, guidance and protection.

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ABSTRACT

Produced water, a major byproduct of petroleum extraction, contains a complex mixture of organic and inorganic contaminants such as hydrocarbons, heavy metals, and suspended solids, which pose severe environmental risks if discharged untreated. Conventional treatment methods are often expensive and inefficient in achieving complete degradation of such pollutants. This study investigates the photodegradation of produced water using bentonite clay doped with titanium dioxide (TiO_2) as an efficient and eco-friendly treatment approach.

The bentonite–TiO_2 composite was synthesized and characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray Fluorescence (XRF) to determine its structural and morphological properties. Photocatalytic degradation experiments were performed with a photocatalytic reactor, utilizing natural sunlight as the irradiation source varying operational parameters such as pH, contact time, and catalyst dosage (2–10 g).

The treatment performance was evaluated using Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) analyses before and after photodegradation. Results showed a consistent decrease in both BOD and COD values with increasing catalyst dosage from 8.13 to 3.55 mg/L (BOD) and 5270 to 1420 mg/L (COD) representing approximately 56% and 73% reductions, respectively. This demonstrates the effectiveness of the TiO_2–bentonite composite in degrading organic pollutants in produced water.

Contents

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF STUDY

One of the most significant and prevalent elements in the environment is water. Water is essential to the life and flourishing of all living things on Earth. Currently, the only planet with almost 70% water is Earth. However, it is heavily contaminated with many dangerous pollutants as a result of the growing human population, industrialization, fertilizer usage in agriculture, and human activities. Because the human population contracts a variety of water borne illnesses as a result of drinking water contamination, it is essential that the quality of drinking water be monitored on a regular basis. Since the chemistry of water reveals a lot about the ecosystem's metabolism and explains the general hydro-biological relationship, it is challenging to fully comprehend the biological phenomenon (Basavaraja simpi et al 2011). Water is very necessary for life to exist, but it also greatly improves our quality of life. Numerous studies have shown the direct and indirect harmful effects of heavy metals on skin allergies, malignancies, and tumors. Water is also crucial for enhancing quality of life. In 2021, Parvatham et al. Many attempts are made to provide alternatives to the issues brought on by excessive water usage, and one of the most well-known solutions is wastewater treatment and reuse. Kitchenette wastewater, cleaning water, and washing and rinsing water are all combined to create the massive wastewater, which has a very high concentration of organic materials including protein, carbohydrates, and fats. Many techniques are used to treat wastewater, and in this study, an attempt was made to investigate the use of bentonite clay with titanium oxide for treating the wastewater by photocatalysis with activated clay and un activated clay. When pollutants and pathogens are present in excess of a certain threshold, water pollution results. The majority of pollution is brought on by human activity, including sewage emissions, wastewater, and garbage from homes and businesses, metals and particulate matter from mining and metallurgy, and fertilizer and pesticide runoff from agricultural operations. To keep water from turning into waste, it must be treated (Bhalwe et al., 2022). One way to treat contaminated water is by coagulation. It involves mixing chemicals or natural materials with water to change the physical characteristics of the suspended and dissolved solids, which facilitates flocculation or sedimentation. (Bhalwe and others, 2022). The coagulation-flocculation process is a frequently utilized and crucial phase in the treatment of water and wastewater because of its affordability and ease of usage. Coagulation-flocculation is often used as a pre- or post-treatment phase, regardless of the kind of treated sample (such as different kinds of water or wastewater) and the overall treatment plan that is being used. Enhancing the coagulation stage's efficiency seems to be a crucial component in raising the total treatment efficiency as the effectiveness of coagulation flocculation has a significant impact on the entire treatment performance. Coagulation flocculation therapy may be broken down into two separate steps that should be used one after the other. The first, known as coagulation, is the process by which a particular colloidal suspension or solution becomes unstable. Coagulation serves the purpose of overcoming the element that supports a system's stability. It is performed with the addition of suitable chemicals, mainly aluminium or iron salts, the so-called coagulant agents. The second sub process, dubbed flocculation, relates to the induction of destabilized particles in order to come together, to establish contact and so, to form big agglomerates, which may be separated 2 easily generally by gravity settling, (Tzoupanos & Zouboulis, 2014) The poor treatment and disposal of wastewater pose harm to the environment and human health, making wastewater management a critical challenge on a worldwide scale. Synthetic chemical coagulants are extensively employed in traditional wastewater treatment techniques to remove suspended particles and contaminants. The usage of these substances raises issues however, because of the probable damage they might inflict to ecosystems and human health. Because they may efficiently treat wastewater without posing any environmental risks, natural coagulants derived from plant materials have gained attention as an alternative.

Four categories may be used to classify wastewater:

- Domestic: wastewater released from homes, businesses, and other comparable establishments
- Industrial: wastewater with a high concentration of industrial waste Extraneous water that enters the sewage system directly or indirectly, for example, via porous walls, leaky joints, or fractures, is known as infiltration or influx. Storm water that enters the sewer system via manhole covers, foundation and basement drains, roof headers, or storm drain connections is known as inflow.
- Storm water: discharge from rainfall-induced floods. For a long time, the primary objective of treating municipal wastewater was to lower the amount of dangerous bacteria, dissolved inorganic compounds, suspended particles, and oxygen-demanding elements. However, in recent years, there has been an increased focus on developing better ways to dispose of the solid wastes from municipal treatment systems.

Primary treatment, which includes grit removal, screening, grinding, and sedimentation; secondary treatment, which uses biologically active sludge to oxidize dissolved organic matter before filtering it off; and tertiary treatment, which uses chemical and physical techniques like granular filtration and activated carbon absorption along with sophisticated biological methods of nitrogen removal. Both within and across sectors, the features of industrial wastewaters may vary significantly. The effects of industrial discharges are determined by the presence of particular inorganic and organic compounds as well as by their overall properties, such as the quantity of suspended particulates and the biochemical oxygen demand. There are three ways to manage industrial wastewater. Control may occur at the plant's site of production, wastewater can be fully treated at the plant and either reused or released straight into receiving waters, or wastewater can be pre-treated before being discharged to municipal treatment sources. Wastewater from manufacturing operations and industrial facilities is known as industrial wastewater. Industrial wastewaters might comprise, collectively, a major component of community wastewaters and must be addressed for effective wastewater treatment plant operation. In certain situations industrial wastewater discharge is collected with other community wastewaters and the combined wastes are treated jointly. In other cases, enterprises could partially or completely cleanse their effluent before releasing it into the municipal sewers. In yet other cases, separate collection and disposal are required due to the size and nature of the industrial waste. Depending on the particular industry or manufacturing facility in the town, industrial wastewaters might differ greatly in terms of composition, strength, velocity, and volume. Naturally, the use to which the water has been put will determine the precise composition and amount of the industrial waste. Paper and fiber mills, steel mills, petrochemical and refining facilities, chemical and fertilizer plants, meat and poultry packers, vegetable and fruit packing facilities, and many more are examples of typical businesses that generate large amounts of wastewater. Unwanted substances that may harm sewers and other infrastructure or very potent organic wastewaters with a high oxygen demand can be found in industrial discharges. They could include substances that are resistant to biological deterioration or harmful elements that prevent the wastewater treatment plant from operating effectively. Thermal discharge is a less evident source that must be 14 regarded as an industrial waste since it reduces dissolved oxygen levels. Large amounts of cooling water are used by many sectors, but the electric power sector uses the most. However, significant amounts of cooling fluids are also used by the major metal and chemical sectors. Wastewater degradation is the process by which pollutants and toxins in wastewater are broken down or changed into less dangerous forms by a variety of physical, chemical, and biological processes. For wastewater to be safe for reuse or release back into the environment, this deterioration is necessary. Usually, a number of steps and processes are involved in wastewater degradation.

Photocatalysis employs light energy, usually ultraviolet (UV) or visible light, to activate a semiconductor catalyst (such as **titanium dioxide, TiO_2**) that generates reactive radicals capable of degrading organic contaminants into harmless end-products like **CO_2 and H_2O**. The addition of naturally available materials such as **bentonite clay** enhances the photocatalytic process by improving surface area, adsorption capacity, and catalyst dispersion. Bentonite, a type of aluminosilicate clay with a high cation exchange capacity and porous structure, provides an excellent support for TiO_2 nanoparticles, preventing agglomeration and promoting efficient light utilization.

Hence, the integration of **TiO_2 with bentonite clay** offers a cost-effective and sustainable photocatalytic system for degrading organic and inorganic pollutants in produced water. This research aims to explore this hybrid system's potential for improving wastewater treatment efficiency while minimizing environmental impacts.

1.2 PROBLEM STATEMENT

Produced water generated from oil and gas operations contains toxic organic and inorganic pollutants such as hydrocarbons, phenols, heavy metals, and suspended solids. These substances are highly persistent, non-biodegradable, and pose serious environmental and health risks when discharged into natural water bodies. Conventional treatment methods often fail to completely degrade these contaminants and may involve high operational costs, energy consumption, and sludge generation.

There is therefore a need for an environmentally friendly, efficient, and economically viable method to treat produced water and ensure safe disposal or reuse. This study seeks to address this problem through photodegradation using bentonite clay doped with TiO_2, a process that combines adsorption and photocatalysis to achieve enhanced pollutant removal.

1.3 PURPOSE AND GOALS

This research aims to evaluate the potential of bentonite clay doped with titanium dioxide (TiO_2) as a composite photocatalyst for the treatment of produced water.

1.4 SPECIFIC OBJECTIVES

1. To synthesize and characterize TiO_2–bentonite composite using analytical techniques such as XRD, XRF, FTIR, SEM.
2. To investigate the photocatalytic degradation efficiency of the composite in treating produced water under varying operational parameters.
3. To analyze the influence of catalyst dosage, contact time, on photodegradation performance.

4. To study the kinetic behavior of the photodegradation process using models such as pseudo-first-order, pseudo-second-order, and Langmuir Hinshelwood kinetics.
5. To determine the optimum operating conditions that yield maximum removal of organic pollutants and improved water quality.

1.5 SCOPE OF STUDY

This study focuses on the photocatalytic degradation of produced water using bentonite clay supported with TiO_2 nanoparticles. The scope includes:

1. Characterization of the catalyst using XRD, XRF, FTIR, SEM, to determine its crystalline structure, chemical composition, surface morphology, and elemental makeup.
2. Photocatalytic experiments to investigate how process variables contact time, catalyst dosage, affect degradation efficiency.
3. Kinetic and isotherm studies to model the degradation process using pseudo-first-order, pseudo-second-order, and Langmuir–Hinshelwood equations.
4. Comparative analysis of bentonite clay before and after TiO_2 modification to assess performance enhancement.
5. Determination of the optimum operating conditions for maximum degradation efficiency and evaluation of the catalyst's reusability.

1.6 IMPORTANCE OF THE STUDY

The treatment and safe disposal of produced water remain a major environmental concern in the petroleum industry. This research contributes to sustainable water management by proposing an eco-friendly, low-cost, and effective treatment technique based on photocatalysis. The TiO_2–bentonite composite offers several advantages:

- Enhanced degradation efficiency due to combined adsorption and photocatalysis.

- Utilization of abundant natural clay, reducing cost and dependence on expensive synthetic catalysts.
- Potential application for large-scale produced water treatment with minimal secondary pollution.

The findings from this study will not only deepen understanding of photocatalytic mechanisms and kinetics but also support the development of sustainable technologies for wastewater treatment in oil-producing regions.

CHAPTER TWO

2.1 OVERVIEW OF WATER POLLUTION

Water pollution is increasingly recognized as a critical global challenge requiring immediate attention [(Liang et al., 2024). The discharge of industrial wastewater and domestic sewage introduces significant quantities of harmful substances, including carcinogenic chemicals, into aquatic systems. These pollutants not only cause severe ecological damage but also pose serious risks to human health (Schwarzenbach et al., 2010), highlighting the urgent need for effective wastewater treatment.

Our existence on our planet is dependent on three fundamental resources: water, air, and soil, which are three of nature's most precious gifts to humanity. Water is the most essential component, since it is the primary channel for the emergence of life. Between 1900 and 1995, water demand increased six fold, more than twice the pace of population expansion. The United Nations Conference on the Human Environment, held in Stockholm in June 1972, was the first major attempt to take notice of the environmental problem on a worldwide scale. Following that, environmental, sustainability, and Earth's carrying capacity have been the major themes of policymaking all over the world (Afroz et al., 2014).

When water is contaminated by anthropogenic pollutants, it is referred to as polluted water. It either cannot be used for human purposes, such as drinking water, or it suffers a significant reduction in its capacity to sustain biotic organisms, such as fish, as a result of these pollutants.

Volcanoes, algae blooms, hurricanes, and earthquakes are all natural occurrences that produce significant changes in water quality and biological condition (Wang & Yang, 2016).

Water contamination is a significant issue all around the world. It necessitates continuous review and modification of water resource policies at all levels (from the world to individual aquifers and wells). Water contamination is thought to be the biggest cause of mortality and illness in the globe. In 2015, 1.8 million people died as a result of water contamination (Staff, 2017). Water pollution, according to the Global Oceanic Environmental Survey (GOES), is one of the most serious environmental issues that may jeopardize life on Earth in the next decades. One of the major problems is water pollution, which kills cardiac phytoplankton, which produces 70% of oxygen and removes a significant portion of carbon dioxide from the atmosphere. The group suggests a variety of solutions to the problem, but they must be implemented within the next ten years to be successful. India and China are two nations with serious water pollution problems(Dwivedi & Shikha, 2016). Every day, about 580 persons in India die as a result of water pollution related illnesses (including waterborne infections). In China's cities, about 90% of the water is contaminated. In 2007, half of China's population lacked access to clean drinking water. Developed nations, in addition to the severe challenges of water contamination in poor countries, continue to face pollution issues

2.1.1 SIGNIFICANCE OF WATER

Water is essential to life since it occupies a significant amount of the Earth's surface and is vital to human health. It transfers organic materials and nutrients throughout the body and the earth, dissolves them, refills them, and removes waste. All body processes, including those involving fluids, tissues, cells, lymph, blood, and glandular secretions, are governed by water. As little as 2.7 liters of water loss may produce dehydration, which can lead to symptoms including headaches, weakness, irritability, exhaustion, anxiety, and even illness. In his book "Your Body's Many Cries for Water," Dr. F. Batmanghelidj talks on the importance of water and how it helps "water-starved" cultures. He asserts that as water is essential for cell function, a reduction in daily water consumption might reduce the efficiency of cell activity, leading to chronic dehydration and disease-like symptoms. Water also has a big effect on the world economy since 70% of the freshwater used by humans is used for agriculture (Baroni et al., 2007). Fishing in fresh and saltwater bodies is a major source of sustenance for many parts of the globe. Boats travel great distances transporting manufactured products and commodities like natural gas and oil over rivers, lakes, canals, and the ocean. A lot of water, ice, and steam are utilized to heat and cool buildings. Industrial operations utilize water. cooking, and cleaning, since it works well as a solvent for a variety of materials, including both organic and mineral ones. In addition, water, ice, and snow are necessary for many sports and recreational pursuits, such as surfing, boat racing, swimming, and recreational boating. sport skiing, ice skating, diving, and fishing. Industrial wastewater is categorized based on the purpose of the industry's product processing. Chemical fertilizer wastewater, tannery wastewater, textile printing and dyeing wastewater, coking coal gas wastewater, papermaking wastewater, metal pickling wastewater, and metallurgical wastewater are among them. (Sokolovic-Secerov and others, 1992) It is categorized based on the characteristics of the main contaminants found in industrial wastewater. Inorganic wastewater is mostly composed of inorganic contaminants. Organic wastewater is mostly composed of organic contaminants. For instance, effluent from food or petroleum processing is classified as organic wastewater, whereas wastewater from electroplating and mineral processing is classified as inorganic wastewater. This categorization scheme is rather easy to understand. It is good to think about the therapy approach. One common biological treatment technique is the biodegradation of organic wastes. Additionally, physical, chemical, and physical-chemical procedures are often used to treat inorganic wastewater. Nonetheless, effluent from industrial manufacturing processes often includes both organic and inorganic materials. (Sokolovic-Secerov and others, 1992) The most effective technique for removing contaminants from effluents is adsorption. Chukwujike and colleagues (2015) The adsorptive qualities of an adsorbent's surface determine how effective it is. One crucial step in the treatment of wastewater is the sorption of these contaminants from aqueous solutions. It has also been shown that employing adsorbents like clay may avoid producing the massive volumes of sludge that are often produced by other wastewater treatment methods. There are many applications for clays, and it's crucial to have a unique variety with specific qualities for each one. Clays have recently gained importance in a number of environmental research and remedial fields (Chukwujike et al, 2015). As a result, clays are regarded as alternative adsorbents that are easily accessible in large quantities and may compare well in terms of both cost and efficiency. However, the adsorption capability of clays for the removal of pollutants from effluents is significantly increased when the clay minerals are modified using various techniques, such as acid, alkali, and heat treatment. In general, natural clays feature electrically charged and hydrophilic surface properties owing to isomorphous substitutions in their crystal structure and so they are particularly effective adsorbents of heavy metals and polar compounds. The utilization of clay for the elimination of non-ionic organic contaminants, on the contrary is restricted. One of the most used chemical techniques for treating clay is acid activation. Increases in specific surface area, porosity, and surface acidity are the outcomes of this process (Chukwujike et al., 2015). The kind and kind of clay, the acid concentration, the temperature, and the activation time are all crucial factors in the acidification process, which affects the final products' characteristics. Furthermore, by expanding the number of Bronsted and possible Lewis sites, this acid activation is thought to increase the clay's catalytic activity.

2.1.2 MONITORING WATER QUALITY

Gathering information on the physical, chemical, and biological properties of a body of water is the aim of non-laboratory water monitoring. The traditional method, which entails routine sample collection, may be costly and provides only a limited view of the water quality. Monitoring the environment, searching for drinking water violations, analyzing temporary water trends, and tracking the release of industrial wastewater are just a few of the objectives that can be pursued by a water monitoring program. Early detection is vital to mitigate the damage and identify the source of pollution. Human health, aquatic life, and ecosystems can all suffer from declining water quality. Short-term pollution events, such as the inappropriate disposal of hazardous material, are difficult to identify with samples; but, early discovery may help prevent more damage. The amount of characteristics that need to be tracked varies; some call for simple indicators, while others call for more intricate ones. Pollutants are very harmful and poisonous, Acid and alkali-contaminated wastewater is caustic, unpleasant, and contains organic oxygen-containing compounds such ethers, aldehydes, and ketones. These chemicals are reductive and may consume dissolved oxygen in water, causing hypoxia. Additionally, it causes aquatic creatures to perish. In addition to being rich in nitrogen, phosphorus, potassium, and other nutrients, industrial wastewater may encourage the development of algae by consuming a large amount of dissolved oxygen in the water, which causes eutrophication and water pollution. The amount of suspended particles in industrial wastewater may reach 3000 mg/L, which is ten times more than that of home wastewater. (Sokolovic-Secerov and others, 1992).

2.1.3 WATER QUALITY STANDARDS AND PARAMETERS

The pH, alkalinity, turbidity, and nutrients (total nitrogen and total phosphorus) are the most important water quality metrics that are evaluated in the lower lakes. A short explanation of these characteristics and their usual historical values may be found below.

1) The acidity or basicity of a solution may be determined using the pH scale. On the logarithmic scale, a pH shift of one unit is equivalent to a 10-fold change. Neutral water has a pH of 7, whereas acidic solutions vary in pH from 0 to 6 and basic solutions range in pH from 8 to 14. Before the present drought, the pH range in the region was normally between 7 and 9.

ii. The power of water to regulate pH and neutralize acids is known as alkalinity. It is determined by the total amount of titratable bases in the water. It serves as a buffer for the pH of the water. The alkalinity of the region, which has traditionally varied between 80 and 250 mg/L of CaCO3, may be raised by adding limestone to counteract any acid generated from sediments.

III. The degree of cloudiness or haziness in water caused by suspended particles such as silt or algae is measured by turbidity. In Nephelometric Turbidity Units (NTU), the quantity of light reflected by a sample is calculated. The turbidity of the water in the Lower Lakes varies greatly and is greatly affected by wind. The average turbidity of Lake Alexandrina (at Milang), the tributaries (at Goolwa), and Lake Albert (at Meningie) was around NTU for Lake Alexandrina, NTU for the rivers, and NTU for Lake Albert prior to the onset of the drought.

IV. A body of water's nutritional content may be determined by measuring its total nitrogen and total phosphorus levels. These nutrients, which can take many different forms, can lead to aquatic plants overgrowing if they are present in large quantities. Filamentous algae, macrophytes, phytoplankton, and cyanobacteria are examples of this.

2.1.4 THE FOUR BASIC ELEMENTS OF WATER QUALITY STANDARDS

i. A body of water's intended purposes, such as serving as a recreational area, sustaining aquatic life, or providing clean drinking water.

ii. Water quality requirements specific to the intended uses of a water body are set in order to protect those authorized uses. By regulating the quantity of certain chemicals and contaminants in the water, these standards which may be stated as textual criteria or numerical concentrations are created.

iii. A plan to safeguard present usage, high-quality waterways, and the decrease of water quality.

iv. Regulations that, with regard to enforcement and compliance, address pertinent practical concerns such as low water levels, exceptions, and places where water quality may be temporarily lower. Drinking water standards involve more information than simply a list of numbers; they also include data like the site, manner, and frequency of sampling, as well as the analytical techniques and lab that were applied. In order to account for factors like seasonal fluctuations and the counting of relevant metrics, several standards additionally require computations and statistical processing of the data. The World Health Organization's Drinking-water Quality Guidelines contain recommended limits on naturally occurring components that may directly harm human health.

2.2 PRODUCED WATER CHARACTERISTICS AND TREATMENT CHALLENGES

2.2.1 DEFINITION, SOURCES, AND VOLUME OF PRODUCED WATER

Produced water (PW) is the principal liquid waste stream generated in oil and gas operations, emerging alongside hydrocarbons during both primary and secondary recovery processes. It comprises a complex mixture of native formation water, any injected fluids (e.g., seawater, polymer-enhanced water, steam), and residual oilfield chemical additives. Because its origin and history vary widely from field to field, PW composition is highly site-specific and can change over the life of a well (Nwosi-Anele & Iledare, 2016).

Produced water refers to the water that is brought to the surface during crude-oil and natural-gas production operations. It originates from subsurface formations that contain a mixture of oil, gas, and formation water. When hydrocarbons are extracted, this formation water becomes the primary waste stream known as *produced water* (Abbas et al., 2021). Its generation also results from secondary recovery methods, such as water injection, which push hydrocarbons toward the surface but subsequently increase the volume of water produced from aging reservoirs. The water-to-oil ratio in most oil fields averages about 3:1 and can reach 98 % in mature fields (Abbas et al., 2021).

Global estimates indicate very large volumes of produced water. For instance, the United States generates approximately 21 billion barrels per year, while countries such as Oman, Australia, Iraq, Colorado, and China each produce hundreds of millions of barrels annually. The quantity depends on reservoir geology, age, and extraction technology (Abbas et al., 2021).

2.2.2 CHEMICAL COMPOSITION OF PRODUCED WATER

The composition of produced water is complex, containing both organic and inorganic pollutants. Its properties vary with geological formation, extraction technique, and reservoir chemistry. Major contaminants include oil and grease, total dissolved solids (TDS), chemical oxygen demand (COD), phenols, BTEX compounds (benzene, toluene, ethylbenzene, xylenes), organic acids, and production chemicals such as corrosion and scale inhibitors (Abbas et al 2021). Phenolic compounds are particularly concerning due to their solubility and toxicity; concentrations can reach up to 10 000 mg/L in certain samples. COD levels are also high typically 1220 – 2 600 mg/L but sometimes as high as 21 000 mg/L making conventional treatment difficult. Metals such as Fe, Mn, Ba, Sr, and Zn further contribute to the chemical load, while chloride and sulfate ions often appear in extremely high concentrations (Abbas et al., 2021).

2.2.3 ENVIRONMENTAL CONCERNS AND REGULATORY CONTEX

In Nigeria's Niger Delta, the uncontrolled discharge of produced water (PW) has emerged as a chronic environmental hazard. When untreated PW is released into freshwater swamps, creeks, and farmlands, the high salinity and dissolved hydrocarbons can lead to soil salinization, loss of vegetation cover, and contamination of surface and shallow groundwater used for drinking and irrigation. Toxic constituents such as polycyclic aromatic hydrocarbons (PAHs), phenols, and trace metals bioaccumulate in aquatic organisms, posing risks to both biodiversity and human health through the food chain. Moreover, the visible sheen and oil droplets that linger on water bodies disrupt photosynthesis in plankton and submerged plants, undermining the productivity of fishing grounds on which many Delta communities depend.

Regulatory oversight of PW in Nigeria is anchored primarily in the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN). First issued in 1985 by the

Department of Petroleum Resources (DPR) and updated in 2002, EGASPIN prescribes maximum allowable concentrations for key effluent parameters including oil and grease, total dissolved solids (TDS), heavy metals (e.g., lead, cadmium, chromium), biochemical oxygen demand (BOD), and pH before PW may be discharged onshore or offshore. Under these guidelines, operators must secure discharge permits and are held "cradle to grave" responsible for the management of PW and other wastes. The DPR's interim guidelines as far back as 1981 already mandated gravity-separator treatment at flow stations to remove bulk oil prior to any discharge.

Despite this regulatory framework, enforcement has historically been uneven. The DPR was reconstituted as the Nigerian Upstream Petroleum Regulatory Commission (NUPRC) in 2021, but gaps remain particularly in offshore settings where no separate federal statute governs oilfield waste beyond EGASPIN itself. Nigeria's principal environmental law, the National Environmental Standards and Regulations Enforcement Agency (NESREA) Act of 2007, explicitly exempts upstream oil and gas activities, further diluting accountability for PW management. Field audits and independent studies have repeatedly documented basic non-compliance: some Niger Delta platforms reportedly discharged PW by simple dilution in open water, bypassing even gravity separation and skirting permit requirements (Nwosi-Anele & Iledare, 2016).

The scale of the challenge in the Delta is immense. Ukpohor (2001) estimated that approximately 82% of Niger Delta reservoirs are water-drive systems, meaning that as oil is produced, large volumes of formation water are concomitantly ejected to the surface. Without widespread reinjection or reuse schemes and in the face of lax enforcement this generates tens of millions of barrels of PW daily, perpetuating soil and aquatic degradation. In many onshore communities, stagnant discharge ponds have become breeding grounds for mosquitoes and other vectors, compounding public health concerns.

Moving forward, experts emphasize the need for:

1. Strengthened Monitoring and Penalties – Regular third-party audits, real-time effluent tracking, and substantial fines or production shutdowns for non-compliance.
2. Capacity Building – Training and equipping NUPRC inspectors and community watchdog groups to detect and report infractions.
3. Infrastructure Investment – Incentivizing operators through tax breaks or co-funding schemes to install advanced PW treatment units (e.g., ultrafiltration, advanced oxidation) and to implement beneficial reuse programs (e.g., agricultural irrigation, aquaculture) under strict controls.

By closing legislative loopholes, bolstering enforcement, and promoting sustainable PW management technologies, Nigeria can mitigate the longstanding ecological and social harms wrought by produced water in the Niger Delta.

If discharged untreated, produced water can degrade soil, surface, and groundwater quality. Its elevated salinity and hydrocarbon content can cause plant dehydration, soil sodicity, and oxygen depletion in aquatic ecosystems. Moreover, the presence of heavy metals and chemical additives (e.g., H_2S scavengers, corrosion inhibitors) poses risks to human health and aquatic life (Abbas et al., 2021).

These concerns have driven strict environmental regulations worldwide, requiring oil and gas operators to meet effluent-quality standards before discharge or reinjection. Many countries promote reuse after adequate treatment for example, in drilling operations, irrigation, or industrial applications to minimize freshwater consumption (Abbas et al., 2021).

2.2.4 LIMITATIONS OF CONVENTIONAL PRODUCED-WATER TREATMENT METHODS

Produced-water treatment generally involves three stages: pre-treatment, main treatment, and final polishing. Conventional approaches such as skimming tanks, gravity separators, flotation units, coagulation, and filtration can effectively remove dispersed oil and solids but often fail to achieve full mineralization or eliminate dissolved organics (Abbas et al., 2021).

Biological methods like activated-sludge and aerated-filter systems are low-cost but require long residence times, large infrastructures, and oxygen supply, generating excess sludge (Abbas et al., 2021).

Chemical methods, including precipitation and oxidation, can remove metals and organics efficiently but incur high reagent and energy costs, and they generate secondary sludge requiring disposal. Physical methods, such as membrane filtration and adsorption, provide high removal efficiency for COD and hydrocarbons but are limited by membrane fouling, energy consumption, and costly adsorbent regeneration (Abbas et al., 2021).

Consequently, conventional technologies alone are insufficient for complete mineralization of complex organic pollutants such as phenols and BTEX. Researchers recommend integrated or hybrid systems for instance, combining adsorption, electrochemical, and membrane processes to enhance treatment performance and meet modern regulatory discharge limits (Abbas et al., 2021).

2.3 PRINCIPLES OF HETEROGENEOUS PHOTOCATALYSIS

2.3.1 ADVANCED OXIDATION PROCESSES

Advanced oxidation processes (AOP) are technologies that break down toxic organic compounds in a medium (like soil and wastewater) by producing hydroxyl radicals, which are extremely reactive and non-selective substances. Due to its high oxidation potential (E0=2.8 V), the hydroxyl radical can react with almost any class of organic compound, either converting them into less aggressive products or completely mineralizing them

that is, forming carbon dioxide, water, and inorganic salts (Andreozzi et al., 1999; Bolton et al, 2001; Pignatello, 1992). Since traditional water treatment techniques like flotation, filtration, and adsorption with active coal are non-destructive physical separation processes that is, they only remove the pollutants, transferring them to other phases and creating concentrated deposits one of the primary benefits of AOP is the destruction of pollutants and the resulting inhibition of the generation of toxic residues. Hydrogen abstraction occurs when the hydroxyl radical reacts with a saturated aliphatic compound, electron transfer occurs when the hydroxyl radical is reduced into a hydroxyl anion by an organic substrate, and the electrophilic addition of a hydroxyl radical to organic compounds (unsaturated or aromatic) that contain a z bond results in the formation of organic radicals (Bossmann et al., 1998; Tang, 2004). The existence of various chemical species in water (or those that originate during the mineralization process), such as carbonate and bicarbonate ions, may have an impact on the hydroxyl radical assault on organic substrates. Through their ability to react with hydroxyl radicals, these ions may compete with organic substrates. Many AOP may produce hydroxyl radicals, which makes it possible to use a more effective procedure for every unique therapeutic situation.

There are two types of advanced oxidation process (AOP):

- Homogeneous
- Heterogeneous
- The high cost of reagents like H2O2 and , as well as the electricity required when UV light is used, make the AOP procedures costly. They are thus taken into consideration for alternative wastewater treatment methods that are not biologically treatable (Bossmann et al., 1998; Tang, 2004).

2.3.2 CLASSICAL WATER TREATMENT METHODS

To help consulting engineers, regulatory bodies, and others involved in water treatment, treatment facilities have been categorized based on the quality of the raw water. The main definitions of the procedures used in a contemporary conventional water treatment plant are as follows (Komolafe et al., 2011).

1)Aeration

When used in the context of water treatment, aeration is the process of bringing a gaseous phase typically air and water into close proximity to one another in order to transfer volatile substances, such as oxygen, carbon dioxide, nitrogen, hydrogen sulfide, methane, and other unidentified organic compounds that give off aroma and taste (Komolafe et al., 2011).

2) Coagulation

Water treatment professionals and chemists define coagulation as the whole process that involves adding chemicals known as coagulants, or aluminum or iron salts, to the water, such as polymers, iron chloride, or aluminum sulphate. These substances are positively charged and are referred to as coagulants. The coagulants' positive charge balances the water's dissolved and suspended particles' negative charge (Komolafe et al., 2011).

3) Flocculation

Water treatment procedures that assemble, mix, or "coagulate" tiny particles (Floc particles) that separate from the water as sediment are referred to as flocculation. As flocculated particles separate from the water, settling or sedimentation takes place naturally (Komolafe et al., 2011).

4) Sedimentation

To lower the amount of settleable particles suspended in water, settling tanks also known as sedimentation basins, settling tanks, or clarifiers are used in water treatment. Perhaps second only to chlorination, sedimentation is one of the most used methods for treating water (Komolafe et al., 2011). The physical and chemical process of filtering water involves passing suspended and colloidal pollutants through a porous media, often a bed of sand or another granular substance. Impurities are left behind in the pores or on the medium itself when water fills the pores (Komolafe et al., 2011).

5)Chlorination and disinfection

Disinfecting water entails specific treatment to eliminate organisms that are toxic and otherwise undesirable. Historically, the goal of disinfection has been to eliminate or render inactive pathogenic (disease-causing) organisms, especially gut bacteria. In addition to bacteria, a number of viruses, intestinal protozoa, and a few macro organism are pathogenic organisms that should be considered in relation to water disinfection (Komolafe et al., 2011).

2.3.3 DEMAND FOR BIOCHEMICAL OXYGEN (BOD)

An empirically standardized laboratory test called the Biochemical Oxygen Demand (BOD) gauges the amount of oxygen needed for the aerobic oxidation of decomposable organic matter and specific inorganic materials in water, contaminated waters, and wastewater under carefully monitored temperature and incubation conditions. As a measure of the amount of oxygen needed for oxidation processes, it is one of the primary indicators of the amount of pollutants present. It is also a parameter used to determine how much oxygen will be consumed by microorganisms during the biological reaction of oxygen with organic material. The test is used to determine the level of pollution, the water body's capacity to absorb pollutants, the efficacy of waste treatment facilities, and fresh water sources (lakes, rivers), wastewater (domestic, industrial), and polluted receiving water bodies (coastal, estuaries) (Barker, 1999).

2.3.4 COD OR CHEMICAL OXYGEN DEMAND

With the use of a strong chemical oxidant, the Chemical Oxygen Demand (COD) test calculates the oxygen demand equivalent of organic matter that is oxidizable. When assessing the organic strength of streams and other contaminated water bodies, it is a crucial characteristic that can be assessed quickly. Given its limits, the test may be experimentally linked to BOD, organic carbon, or organic matter in samples from a particular source. The test is helpful for monitoring somewhat contaminated water bodies and researching wastewater treatment facility performance assessment. Compared to BOD determination, COD determination has an advantage. In contrast to the three to five days needed for a BOD test, COD findings may be acquired in three to 3 four hours.

Additionally, unlike the BOD test, the test is reasonably simple, accurate, and immune to influence. The test's inherent drawback is its incapacity to determine the 20system rate constant of aerobic biological stabilization and to distinguish between material that is physiologically oxidizable and material that is biologically inert (Barker, 1999).

2.3.5 FACTORS AFFECTING PHOTOCATALYTIC EFFICIENCY

General factors affecting the photocatalytic activity, including pH, light wavelength and intensity, catalyst dosage, temperature, and concentration of salts and target contaminants

1 Dosage of Adsorbent

The dose of the adsorbent is a crucial factor as it establishes its capacity. As the dose of the adsorbent is increased, more metal ions are removed. By changing the number of adsorbents while maintaining the same values for the other parameters, the impact of adsorbent dose on adsorption was investigated (Sime, 2018). The size of the adsorbent particles affects the adsorption process because of their connection. For instance, the adsorption capacity and surface area of adsorbents both increase when the number of particles is small. The adsorption capacity is inversely related to the size of the adsorbent particle, although the adsorbate surface area is directly proportional to the adsorption capacity. In contrast, particle size rises when adsorption reduces, even if the surface area likewise decreases (Sime, 2018). Similarly, because of their physicochemical characteristics, adsorbents' surface area is crucial to the adsorption process (Sime, 2018).

2 Contact Time

The removal efficiency increased with an increase in contact time before equilibrium is reached. The amount adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating conditions Mohammad et al., 2011)

3 Initial Metal Concentration

The initial metal ion concentration is an important driving force overcomes all mass transfer resistances of metal ion between aqueous and solid phases (Sime, 2018) initial concentration of metal ions can alter the removal efficiency through a combination of factors such as the availability of specific surface functional groups and the ability of surface functional groups to bind metal ions(Sime, 2018).

4 Effects of Temperature

Adsorption involves specific relations between the properties of activated carbon and the solute. Therefore, the quantitative effects of temperature are not the same with all carbons and solutes(Sime, 2018) The extent of adsorption should increase with decreasing temperature because the adsorption reactions are exothermic. However, increased temperature also increases the rate of diffusion of the solute through the liquid to the adsorption sites, which eventually leads to an increased adsorption. An important difference in the adsorption of solutes versus gases is found in the role of temperature. An increase in temperature increases the tendency of a gas to escape from the interface and thus diminishes adsorption. However, in adsorption from the liquid, the influence of temperature on solvent affinities is more dominant (Sime, 2018)

2.4 PHOTOCATALYSIS

Photocatalysis is a light-driven catalytic process in which a semiconductor material absorbs photons to accelerate redox reactions that degrade or transform pollutants. The process involves using photons (light energy) to excite electrons from the valence band to the conduction band of the photocatalyst, creating electron-hole pairs that participate in oxidation and reduction reactions (Lin, 2020).

In simpler terms, photocatalysis uses light usually ultraviolet (UV) or visible to activate a catalyst that breaks down harmful organic compounds into harmless end products such as carbon dioxide (CO_2) and water (H_2O). The technique can completely mineralize complex pollutants, making it one of the cleanest and most sustainable water purification processes available today.

2.4.1 MECHANISM OF PHOTOCATALYSIS

The photocatalytic process proceeds through several key steps (Lin, 2020):

1. PhotonAbsorption:

   The semiconductor catalyst (commonly TiO_2, ZnO, or doped variants) absorbs photons of energy equal to or greater than its bandgap.

2. Excitation

   When light hits the catalyst surface, electrons (e^-) are promoted from the valence band (VB) to the conduction band (CB), leaving behind positive holes (h^+) in the VB.

3. Formation of Reactive Species:

Electrons in the CB react with dissolved oxygen (O_2) to produce superoxide radicals ($O_2^-•$).

Holes in the VB react with surface hydroxyl groups (–OH) or water molecules to generate hydroxyl radicals (•OH).

4. Pollutantdegradation:

   These reactive radicals are extremely oxidative and attack organic pollutants, converting them into intermediate compounds and eventually mineralizing them into CO_2 and H_2O.

5. RecombinationandStability:

   The efficiency of the process depends on minimizing electron-hole recombination, which otherwise dissipates energy as heat and reduces catalytic activity.

This mechanism makes photocatalysis particularly suitable for decomposing persistent organic pollutants (POPs) that resist conventional biological or chemical treatments.

2.4.2 APPLICATION OF PHOTOCATALYSIS TO PRODUCED WATER TREATMENT

Produced water is the largest byproduct of oil and gas production. Due to the complexity of produced water, especially dissolved petroleum hydrocarbons and high salinity, efficient water treatment technologies are required prior to beneficial use of such waste streams. Photocatalysis has been demonstrated to be effective at degrading recalcitrant organic contaminants, however, there is limited understanding about its application to treating produced water that has a complex and highly variable water composition. Therefore, the determination of the appropriate photocatalysis technique and the operating parameters are critical to achieve the maximum removal of recalcitrant compounds at the lowest cost. The objective of this review is to examine the feasibility of photocatalysis-involved treatment for the removal of contaminants in produced water. Recent studies revealed that photocatalysis was effective at decomposing recalcitrant organic compounds but not for mineralization. The factors affecting decontamination and strategies to improve photocatalysis efficiency are discussed. Further, recent developments and future research prospects on photocatalysis-derived systems for produced water treatment are addressed. Photocatalysis is proposed to be combined with other treatment processes, such as biological treatments, to partially reduce total organic carbon, break down macromolecular organic compounds, increase biodegradability, and reduce the toxicity of produced water.(Lin et al., 2020)

Produced water from oil and gas operations is one of the most challenging waste streams due to its complex chemical makeup and large volume. Photocatalysis has been applied successfully to treat produced water by oxidizing hydrocarbons, phenolic compounds, and other dissolved organics that contribute to toxicity and color (Lin, 2020).

Key studies have demonstrated that TiO_2-based photocatalysts are highly effective in degrading total organic carbon (TOC), oil and grease, and aromatic compounds in produced water. Under UV or solar irradiation, these catalysts achieve significant reductions in chemical oxygen demand (COD) and total petroleum hydrocarbons (TPH). Additionally, modified TiO_2 composites, such as doped or heterojunction variants (e.g., TiO_2/Fe_2O_3, TiO_2/ZnO, TiO_2/graphene), show improved performance by extending light absorption into the visible region and reducing recombination losses.

Hybrid systems that couple photocatalysis with membrane filtration or oxidant addition (e.g., H_2O_2, persulfate) have also been reported to improve efficiency and stability when treating high-salinity produced water. These combinations enable deeper degradation and better resistance to fouling and ionic interference (Lin, 2020).

2.4.3 TITANIUM DIOXIDE (TIO2) AS A PHOTOCATALYST

The term ‘photocatalysis’ has recently gained high popularity, and various products using photocatalytic functions have been commercialized. Of all the materials that may be used as photocatalysts, TiO_2 is virtually the only one that is now and most likely will remain appropriate for industrial application. Water and air purification systems, sterilization, hydrogen evolution, self-cleaning surfaces, and photoelectrochemical conversion are just a few of the products and applications in the environmental and energy domains that make extensive use of TiO_2 photocatalysis. This is due to the fact that TiO_2 has the lowest cost, most stability, and most effective photoactivity. Furthermore, history attests to its safety for both people and the environment because it has been used as a white pigment since antiquity.

Titanium dioxide is a whitish powdery chemical substance of semiconductor origin. It can be used as white pigment, in sun shielding, in cosmetics, etc. it is biologically and chemically inert chemical substance that is stable to light and economically suitable in many applications. Tio2 stands out as the most effective photocatalyst and has been extensively used in water and wastewater treatment studied because it is cost effective, thermally stable, non- toxic, chemically and biologically inert and is capable of promoting oxidation of organic compounds (Tang, 2004). The catalytic activity of Tio2 is dependent on surface and structural properties which include crystal composition, surface area, particle size distribution, porosity and band gap energy.

2.4.4 CRYSTAL STRUCTURE (ANATASE, RUTILE, BROOKITE)

Titanium dioxide (TiO_2) is one of the most widely studied semiconductor materials in photocatalysis, existing in three naturally occurring crystalline polymorphs: anatase, rutile, and brookite (Dharma et al., 2022; Hanaor & Sorrell, 2011). Each form exhibits distinct lattice structures, bandgap energies, and photocatalytic behaviors.

- Anatase (tetragonal) has a lattice composed of Ti^{4+} ions octahedrally coordinated by O^{2-} ions, forming corner-shared TiO_6 octahedra. Anatase typically shows superior photocatalytic performance due to its higher surface area, smaller crystal size, and slower electron-hole recombination rate compared with rutile (Hanaor & Sorrell, 2011).
- Rutile (tetragonal) is the thermodynamically most stable phase at high temperatures. It possesses a slightly lower bandgap energy (~3.0 eV) than anatase (~3.2 eV) and is more optically active in the near-UV region. Although rutile often displays lower photocatalytic activity, coupling anatase and rutile can enhance charge separation due to interfacial electron transfer (Dharma et al., 2022; Scanlon et al., 2013).
- Brookite (orthorhombic) is less common and metastable under ambient conditions but has drawn attention because of its strong surface energy and potential synergistic effects when combined with anatase (Diebold, 2003).

Phase composition influences photocatalytic efficiency. For instance, the P25 TiO_2 (from Evonik) a benchmark photocatalyst composed of ~80% anatase and ~20% rutile exhibits superior activity compared to pure anatase or rutile, demonstrating the benefit of heterojunction formation between the two phases (Chen & Mao, 2007).

2.4.5 OPTICAL AND ELECTRONIC PROPERTIES

TiO_2 functions as an n-type semiconductor with a wide bandgap (3.2 eV for anatase, 3.0 eV for rutile, and 3.1 eV for brookite), allowing photoexcitation mainly under ultraviolet (UV) light (<387 nm) (Chen & Mao, 2007; Kumar & Devi, 2011). When photons with energy equal to or greater than the bandgap are absorbed, electrons are promoted from the valence band (VB) to the conduction band (CB), leaving behind positively charged holes in the VB. These photo-generated charge carriers participate in redox reactions with adsorbed species on the TiO_2 surface, generating hydroxyl radicals (·OH) and superoxide anions ($O_2^{-}\cdot$), which are primarily responsible for the degradation of organic pollutants and other reactions in photocatalysis (Dharma et al., 2022; Liu et al., 2019).

However, a major limitation is the rapid recombination of electron-hole pairs, which reduces the quantum efficiency. Researchers have addressed this through doping, composite formation, and heterojunction design to extend activity into the visible-light region and suppress recombination (Kumar & Devi, 2011; Scanlon et al., 2013).

TiO_2 also shows strong UV absorption, high refractive index (~2.5–2.9), and chemical inertness properties that make it suitable for both environmental photocatalysis and optoelectronic applications (Diebold, 2003; Chen & Mao, 2007).

2.4.6 SURFACE CHEMISTRY AND MORPHOLOGY

The surface chemistry of TiO_2 plays a vital role in its photocatalytic performance, as reactions primarily occur at the solid–liquid or solid–gas interfaces. The TiO_2 surface is typically terminated with hydroxyl groups (-OH) and coordinatively unsaturated Ti^{4+} sites, both of which act as active centers for adsorption and subsequent photoreaction of pollutants (Diebold, 2003; Liu et al., 2019).

Surface hydroxylation enhances hydrophilicity and provides sites for radical generation through hole trapping, which is essential for oxidative degradation processes (Chen & Mao, 2007). Furthermore, surface defects such as oxygen vacancies and Ti^{3+} centers contribute to localized electronic states within the bandgap, enhancing visible-light absorption and acting as trapping sites for photogenerated electrons (Scanlon et al., 2013).

Morphologically, TiO_2 can be synthesized in various nanostructures — nanoparticles, nanotubes, nanorods, and thin films — each offering unique surface areas and charge transport characteristics. For example:

- Nanotubes and nanorods enhance electron transport due to one-dimensional charge paths, reducing recombination losses.
- Nanoparticles provide high surface area and short diffusion paths for charge carriers.
- Thin films and immobilized layers facilitate catalyst recovery and durability, essential for continuous water treatment systems (Dharma et al., 2022; Liu et al., 2019).

Control of crystallite size, surface area, and defect density through synthesis parameters (temperature, pH, dopant presence) remains key to optimizing TiO_2's photocatalytic activity.

2.5 ADSORPTION

A popular technique for treating industrial effluent that contains color, heavy metals, and other inorganic and organic contaminants is adsorption. The advantages of the adsorption process are its ease of use, low cost when compared to other separation techniques, and the absence of sludge formation (Mojiri et al., 2014). The attachment of chemicals from a liquid or gaseous phase to solids is known as adsorption. The solid is referred to as the adsorbent. The adsorbate is the material that is absorbed. For industries that use adsorption to remove metal from industrial wastewater, it is crucial. Dye removal from industrial wastewater, dye recovery from diluted solution, gas masks with adsorbents to purify the air from harmful gases and vapors, impurity removal from petroleum oils, inactivation of bacteria, hormones, or minerals or as an antidote in poisoning cases, enzyme purification, sugar liquid clarification, gas mixture separation, chromatographic analysis, softening of hard water, decolorization, and purification (Halnor, 2015). Various low-cost adsorbents, generated from agricultural waste, industrial by-product, natural material, or modified biopolymers, have been recently created and employed for the removal of heavy metals from metal-contaminated wastewater. Both physical and chemical factors may cause atoms or molecules of adsorbate to adhere to the surface of solids and liquids.

Adsorption may be classified into two categories based on the forces involved: chemical adsorption, also known as chemisorption, and physical adsorption, also known as physisorption (Halnor, 2015).

- Physical adsorption : is the process by which gas molecules are adsorbed onto a solid face using weak Van der Waal forces.
- Chemical adsorption: This occurs when chemical bonds serve as the adsorbent and adsorbate's forces of attraction.

2.5.1 ADSORPTION ISOTHERM MODELS

Langmuir isotherm model

This adsorption isotherm model was originally developed for the description of gas adsorption on solid phase adsorbate like activated carbon(Al-ghouti & Da, 2020). According to Langmuir theory, adsorption process onto a solid surface is based on a kinetic principle in which a continuous bombardment process of molecules onto the surface with corresponding molecules' desorption or evaporation from the surface with zero accumulation rate at the surface(Al-ghouti 29 140 & Da, 2020). In other words, rates of adsorption and desorption should be equal. Traditionally, the Langmuir isotherm model has been utilized for quantifying and contrasting adsorption capacity of various bio-sorbents (Al-ghouti & Da, 2020). Six different and simple adsorption mechanisms were identified and classified by Langmuir due to the surface chemistry diversity and structural geometry of solid materials (Al-ghouti & Da, 2020). These classifications are (Langmuir, 1918):

(i) single-site Langmuir adsorption, the simplest case of gas-solid adsorption, where the surface has identical elementary adsorption sites able to host single adsorbed molecule;

(ii) multisite Langmuir adsorption, where more than one type of elementary adsorption sites is available on the surface and each site might fit for single adsorbed molecule. In this case the binding sites are independent and the interactions between adsorbate and adsorbent are neglected;

(iii) generalized Langmuir adsorption, where an amorphous material that is treated as a continuum might consist of an intractable number of various adsorption sites with various adsorbate affinities. Since adsorbate-adsorbent interactions are negligible, adsorption isotherm follows the binding energy distribution of the adsorption sites;

(iv) cooperative adsorption, in this case binding site on the surface is identical but can host multiple molecules. The energetics of further adsorption is affected by the presence of various adsorbates on the same adsorption site;

(v) dissociative adsorption, in this case adsorption is assumed to be 2-fold process: chemical bonding will cause residence at the surface adsorption site and molecular dissociation, then it will undergo desorption where neighbouring atoms on the surface have to reassociate into a diatomic molecule and leave the surface;

(vi) multilayer adsorption, in this case it is assumed that each adsorption site is independent and identical, and molecules are permitted to adsorb above each other as there is no limit for the number of adsorbed molecules. Langmuir isotherm is an empirical model that assumes that the thickness of the adsorbed layer is one molecule (monolayer adsorption) in which adsorption process occurs at identical and equivalent definite localized sites. There should be no steric hindrance and lateral interaction, even on adjacent sites, between the adsorbed molecules (Al 24 ghouti & Da, 2020). The Langmuir isotherm model assumes that adsorption is homogenous in which sorption activation energy and constant enthalpies are possessed by each molecule. All sites should have equal affinity towards the adsorbate, as well as no adsorbate transmigration in the surface plane (Al-ghouti & Da, 2020). Based on Langmuir theory, there is a relation between the rise of distance and the rapid decrease of the intermolecular attractive forces (Al ghouti & Da, 2020). Furthermore, Weber and Chakravorti (1974), defined the separation factor (RL) as a dimensionless constant which is represented as: RL = 1/1 + KLCO Where, $Co_{\circ}$ refers to the initial concentration of the adsorbate in (mg/L) and KL is Langmuir constant which is related to the adsorption capacity in (mg/g). A variation of the suitable area and the adsorbent's porosity can be correlated with KL constant, implying the fact that higher adsorption capacity can be resulted from large surface area and pore volume. The adsorption nature is indicated by the separation factor to either be linear ($RL = 1$), irreversible ($RL = 0$), unfavourable ($RL > 1$), or favourable ($0 < RL < 1$). The Langmuir isotherm equation can be modified for aqueous-phase adsorption as follows (Parker and Garth, 1995): $q = qm.\ KLC/1 + KLC$ At low concentration and low pressure, the isotherm equation reduces to Henry's law isotherm. A linear increase of the adsorbed amount occurs with pressure, and the saturation capacity of the amount adsorbed is reached when the pressure is sufficiently high leading to the monolayer coverage. Larger affinity constant (b), leads to more surface coverage with the adsorbate molecule due to the strong affinity between them. Since the adsorption process is exothermic process and have positive heat of adsorption, increasing the temperature (T) causes the decrease in the affinity constant. In the adsorption process to occur free energy (ΔG) should decrease and the decrease in the degree of freedom leads to negatively change the entropy (ΔS), thus, $\Delta H\ \Delta G\ T\Delta S =+ < 0$ The negativity of the enthalpy (ΔH) indicates that the adsorption process released heat. Similarly, increasing the adsorption heat causes an increase in the adsorbed number of molecules, which could be attributed to the fact that the adsorbed molecules should overcome a higher energy barrier so they can evaporate back to the gaseous phase. At a given pressure, the adsorbed amount will decrease with increasing the temperature because of the greater energy needed by the adsorbed molecules for evaporation (Jin et al., 2017; Do, 1998). There are certain flaws in the Langmuir isotherm model in the description of contaminant adsorption onto the sediments due to the fact that sediments are heterogeneous adsorbent with different adsorption energy of each site, and the Langmuir model assumes a homogeneous adsorbent surface having similar adsorption energy for each site (Al-ghouti & Da, 2020). However, this isotherm model and its coefficients are mostly used by adsorption researchers to determine the contaminants distribution between water and sediments due to the ease of application (Al 1 ghouti & Da, 2020). The development and application of adsorption technology are limited by the adsorption behaviour complexity as well as the completeness and accuracy limitations of the adsorption experimental data. It was concluded by Harter and Baker (1977), that Langmuir equation parameters have the ability to only compare between different adsorbents but fail with the explanation of the reaction mechanism. For the explanation of the sorption surface heterogeneity, site energy distribution (SED) was developed. Its analysis was used to explain the isotherm parameters change and to demonstrate that natural sorbents have a heterogeneous adsorption distribution site (Al-ghouti & Da, 2020).

2.5.2 MODEL OF FREUNDLICH ISOTHERM

The non-ideal and reversible adsorption process is described by the Freundlich adsorption isotherm model. The Freundlich model may be used to multilayer adsorption since it is not limited to monolayer creation as the Langmuir isotherm model is. Adsorption heat and affinities do not have to be evenly distributed throughout the heterogeneous surface in this isotherm model (Al-ghouti & Da, 2020). The heterogeneity of the surface and the exponential distribution of the active sites and their energy are defined by the Freundlich isotherm model formulation. The Freundlich isotherm adsorption model was first created for the adsorption of animal charcoal. It showed that the ratio of the adsorbate onto a certain adsorbent mass to the solute was not constant at varying solution concentrations. In this case, the adsorbed quantity is the total of the adsorption on each site. When the adsorption process is finished, the adsorption energy will decrease exponentially once the stronger binding sites have been occupied (Al ghouti & Da, 2020). These days, the Freundlich isotherm model is widely used in heterogeneous systems, such as the adsorption of organic molecules or species that interact strongly with molecular sieves or activated carbon. Systems with heterogeneous gas-phase surfaces may use this adsorption isotherm model. Because this isotherm behaves improperly toward Henry's law at low pressure, it only offers a limited range of pressure. It does not have a finite limit when the pressure is high enough. As a result, a limited range of adsorption data may be used with this adsorption isotherm model. Plotting log qe vs. log Ce yields a straight line with 1/n as the slope and log (KF) as the intercept, indicating the parameters of this isotherm model. Its equation has both linearized and non-linearized variants. Logqe is equal to logKf +1/n logce in the linearized form. However, qe = Kfce is the non-linearized form. 1/n The value of n indicates the kind of isotherm, where temperature affects both the KF and n parameters. The intensity of adsorption or surface heterogeneity, which represents the energy relative distribution and the heterogeneity of the adsorbate sites, is 1/n. Adsorption occurs favorably when 1/n is bigger than zero ($0 < 1/n < 1$), unfavorably when 1/n is greater than 1, and irreversibly when $1/n = 1$. Prior to the desorption of adsorbate molecules from the surface, pressure or concentration must drastically drop to a low value, which is why the isotherm is irreversible (Al-ghouti & 51 Da, 2020). An empirical equation is the Freundlich isotherm model equation. It was first derived by supposing that the surface was heterogeneous, with patch-wise topography and dispersed adsorption energy. Patch-wise refers to a single patch that contains every site with a same adsorption energy. According to this viewpoint, the energy generated as a result of the interaction between the adsorbent and the adsorbate is known as adsorption energy. Each patch is independent of the others and does not communicate with them. Vans' Hoff equation may be used to calculate the isosteric adsorption heat since KF and n are temperature dependent, as was previously indicated.

2.5.3 MODEL OF TEMKIN ISOTHERMS

Initially, hydrogen adsorption onto platinum electrodes in an acidic solution which is regarded as a chemisorption system was described using the Temkin empirical isotherm model. This isotherm model excludes the very high and low concentration values while accounting for the interaction between the adsorbent and the adsorbate. According to this model, the increase in surface coverage causes the adsorption heat (ΔHads) of all molecules in the layer to decrease linearly as a function of temperature instead than logarithmically (Al-ghouti & Da, 2020). Only an intermediate concentration range may be used with this adsorption isotherm model (Shahbeig et al., 2013). Like the aforementioned isotherm models, the Temkin model's equation contains both non-linear and linear variants, which are as follows: Non-linear form: qe = RT/BT InATCe However, qe = RT/BTInAT + RT/BTInCe is the linear form. Both the AT and bT constants may be found by charting qe vs. ln(Ce) (Al-ghouti & Da, 2020). In the event that the gas phase does not need to be arranged in a densely packed structure with the same orientation, this model is very good in forecasting its equilibrium. Its equation implies that binding energies are equally distributed. However, complicated adsorption systems, such as aqueous phase adsorption isotherms, cannot be represented by this isotherm model.

2.5.4 MODELS OF ADSORPTION KINETICS

Adsorption capacity alone does not define an efficient adsorbent; adsorption rate is also a critical factor in determining adsorbent performance. Determining the effectiveness of an adsorbent requires a thorough understanding of adsorption kinetics. This is because the absorption rate, which determines the duration of adsorbate ion residence at the solid-liquid interface, is revealed by it. Comparing the performance of various adsorbents is made easier by the adsorption rate constant, a crucial kinetics metric (Overah, 2021). A number of kinetic models have been used to explain the mechanism of batch adsorption processes, including the pseudo first-order kinetics model (2.13.1).

The pseudo first-order kinetics model is one of the most used rate equations for explaining the adsorption of adsorbate from the liquid phase. The pseudo-first-order rate is often expressed linearly as log(qe-qt) = logqe - KLt/2.303. The following is true: where KL is the pseudo first-order kinetics rate constant (min-1) and qe and qt are the adsorption capacities at equilibrium and time t, respectively (mg/g).

1 Plotting log (qe-qt) against t should provide a linear connection, from which the slope and intercept of the plot may be used to get KL and qe, respectively.

Model of pseudo-second-order kinetics

The linear version of the pseudo-second-order kinetics model is tqt=1k2qe + tqe …. The following is true: where the pseudo-second-order rate constant is denoted by k2 (g 170 mg-1 min-1). Plotting t/qt versus t yields the intercept and slope of the graph, which are used to calculate k2 and qe, respectively.

Diffusion inside particles

In some situations, the process of solute diffusion through an adsorbent solid may not be entirely explained by either the pseudo-first-order kinetics model or the pseudo-second order kinetics model. In these circumstances, the kinetics data may be analyzed using Weber and Morris's (1963) intra-particle diffusion model (Overah, 2021). The equation for this is qt = kid(t)0.5 + C. The answer is yes. 2.7 63 where child (mg g-1 min-1/2) is the intra-particle diffusion rate constant, C (mg g-1) is the adsorption constant, and qt is as previously stated. Qt varies linearly with t when the rate-limiting stage of the adsorption process involves intra-particle diffusion.

2.6 CLAY

The very small mineral particles that make up clay, a naturally occurring substance, are mostly hydrous aluminum silicates. It is created when feldspar-rich rocks weather, and because of its resilience, malleability, and absorption capacity, it is essential to many different industries. While clay has historically been used for building, pottery, and artistic purposes, it is now extensively employed in ceramics, water filtration, medicines, cosmetics, and agriculture.

2.6.1 OCCURRENCE AND FORMATION

Igneous and metamorphic rocks, especially those containing feldspar, weather chemically and physically to produce clay. This process, called kaolinization, takes place over long periods of time when minerals are broken down by water and acidic substances, leaving behind tiny clay particles. There are two types of clay deposits: sedimentary (carried by wind or water and deposited elsewhere) and residual (made in situ). China, the United States, Brazil, Nigeria, and the United Kingdom all have notable clay deposits.

2.6.2 CLAY'S PROPERTIES

Several physical and chemical characteristics set clay apart and dictate its suitability for use in various industries: It has a velvety feel because to its very tiny particle size, which is often less than 2 microns.

Plasticity: Holds its form after drying and becomes moldable when combined with water.

Water Absorption: Capable of holding onto moisture, this material finds utility in cosmetics, filtration, and sealing. Certain forms of bentonite, for example, expand when wet and compress when dry. The ability to absorb and exchange metals and nutrients is known as cation exchange capacity, or CEC, and it is useful in wastewater treatment and soil conditioning.

pH Variability: Clay may have an acidic or alkaline pH depending on the minerals that make it up.

Thermal Resistance: Certain types, such fire clay and kaolin, can withstand high temperatures, which makes them perfect for industrial uses, refractories, and ceramics.

2.6.3 CLAY CLASSIFICATION

Clay may be divided into groups according to its formation, industrial uses, and mineral makeup.

By Composition of Minerals

1. Kaolinite clay, also known as China clay, is a non-expanding material with minimal flexibility that is often used in paper, pottery, and cosmetics.

2. Bentonite, also known as montmorillonite clay, is beneficial for drilling fluids, waterproofing, and detoxifying because it expands when exposed to water.

3. Illite Clay: Found in sedimentary layers and shale, this clay is rather malleable

4. Chlorite Clay: Less often used in industrial settings, this clay contains iron and magnesium.

Through the Process of Formation

1. Primary (Residual) Clays: These are often purer and stay where they formed.

2. Secondary (Sedimentary) Clays: These are carried by wind or water and often include extra minerals or contaminants.

For Use in Industry

1. Ball clay: Perfect for ceramics and pottery, it is very moldable.

2. Fire Clay: Used in refractory materials and firebricks, this substance is resistant to high heat.

3. Bentonite: Used in drilling, sealing, and purifying procedures, this material is well known for its swelling qualities. Fuller's Earth: Because of its great absorption capacity, it is used in oil filtering and purification.

2.6.4 CLAY'S ECONOMIC AND INDUSTRIAL SIGNIFICANCE

1. Ceramics & ceramics: Used in the production of ornamental ceramics, tiles, bricks, and porcelain.

2. Paper Industry: Kaolin clay enhances texture, opacity, and print quality by acting as a coating and filler.

3. Pharmaceuticals: Used in topical skin treatments and medications for detoxification and digestion.

4. Cosmetics: Because of its ability to absorb oil and cleanse, it is used in face masks, foundations, and powders.

5. Agriculture & Soil Enhancement: Increases nutrient retention and soil fertility.

6. Construction & Engineering: Crucial to the manufacturing of concrete, waterproofing barriers, and cement.

7. Environmental Uses: Used to eliminate pollutants and enhance sustainability in waste treatment, air filtration, and water purification

2.7 BENTONITE CLAY AS A CATALYST SUPPORT MATERIAL

2.7.1 STRUCTURE AND PROPERTIES OF BENTONITE (MONTMORILLONITE)

Bentonite is a natural clay rock whose dominant reactive mineral is **montmorillonite**, a member of the smectite group of layered aluminosilicates. Montmorillonite's basic structural unit is a 2:1 phyllosilicate sheet composed of an octahedral alumina (AlO_6) sheet sandwiched between two tetrahedral silica (SiO_4) sheets; isomorphic substitutions (e.g., Al^{3+} for Si^{4+} in the tetrahedral layer, or Mg^{2+}/Fe^{2+} for Al^{3+} in the octahedral layer) generate a net negative layer charge balanced by exchangeable interlayer cations (Na^+, Ca^{2+}, etc.). This layered, charged architecture produces a high cation-exchange capacity (CEC), strong swelling behavior, and interlayer nano-pores that make montmorillonite especially suitable for adsorption and as a support for dispersed catalytic phases (Park et al., 2016; Segad et al., 2010).

Key physicochemical properties relevant to catalysis and support function include:

- **High specific surface area and layered nano-mesoporosity**, which provide abundant surface sites for dispersion of active phases (Park et al., 2016; Krupskaya et al., 2017).
- **Cation exchange capacity (CEC)** and interlayer accessibility that permit ion exchange, intercalation and immobilization of metal cations or organometallic species used as active catalysts (Fatimah et al., 2022).
- **Acid–base surface properties.** Native montmorillonite exhibits surface acidity (Brønsted/Lewis sites) which can be tuned by modification to enhance catalytic activity for acid-catalysed reactions (Ochirkhuyag et al., 2024).
- **Mechanical and thermal stability** adequate for many heterogeneous processes, and an advantage in cost and availability compared with synthetic supports (Fatimah et al., 2022; Ochirkhuyag et al., 2024).

(These structural and property summaries are widely reported in authoritative reviews and experimental studies of montmorillonite and bentonite deposits.) (Park et al., 2016; Segad et al., 2010; Krupskaya et al., 2017).

2.7.2 ACTIVATION OF BENTONITE TO ENHANCE SURFACE AREA AND POROSITY

Acid activation is a common chemical modification method used to increase the surface area, develop micro/mesoporosity, and enhance surface acidity of bentonite/montmorillonite for catalytic applications. The treatment typically involves contacting natural bentonite with mineral acids (e.g., HCl, H_2SO_4) under controlled concentration, temperature and time conditions, followed by washing and drying. Acid treatment selectively leaches octahedral cations (Mg^{2+}, Fe^{2+}/Fe^{3+}, etc.), partially dissolves impurity phases, and can increase pore volume and accessible surface area while retaining the layered framework when properly controlled (Komadel, 2013; Önal, 2007).

Mechanism and structural changes.

Mineral-acid attack removes structural/exchangeable cations and dissolves less stable phases (carbonates, iron oxides), generating additional micropores/mesopores and exposing new acidic sites (Lewis and Brønsted). If acid strength, temperature, or reaction time are too aggressive, however, the layered structure can be excessively damaged decreasing swelling capacity and collapsing interlayer spacing so activation conditions are chosen to balance porosity development with structural integrity (Krupskaya et al., 2017; Komadel, 2013).

Effect on surface area/porosity experimental evidence.

Multiple experimental studies report that acid activation increases BET surface area and total pore volume of bentonite/montmorillonite by factors commonly between ~1.5 and 3× depending on clay source and activation parameters. For example, acid activation produced a near-doubling to tripling of BET area and significant increases in mesopore volume in several studies (Maged et al., 2020; Budash et al., 2023; Önal, 2007). These changes correlate with improved adsorption capacities and with greater dispersion/anchoring of supported metal nanoparticles or metal oxides.

Common variants and combined treatments.

Beyond simple acid activation, practitioners use pillaring (introduction of metal polyoxocations to create pillared interlayer structures), ion exchange (to load target cations), thermal pretreatment, or combined acid/base sequences to further tune porosity and surface chemistry. Recent work also investigates hybrid activation sequences (e.g., acid followed by pillaring or microwave/ultrasound-assisted methods) to achieve tailored pore architectures appropriate for specific catalysts and reactions (Alraddadi et al., 2025; Fatimah et al., 2022).

2.7.3 ADVANTAGES OF USING CLAY SUPPORTS

Bentonite (montmorillonite) and modified clays offer several clear advantages as catalyst supports compared with many conventional supports (e.g., supported oxides, carbon materials, zeolites) particularly where cost, environmental friendliness and adsorptive interactions are important.

1. High adsorption capacity and affinity for organics and gases. The layered structure and high surface area allow bentonite to adsorb organic molecules, pollutants and gases — an advantage in reactions where adsorption concentrates reactants at active sites (e.g., in advanced oxidation processes, CO_2 conversion, organic pollutant degradation). Clay supports can thus enhance local concentration of substrate near catalytic centers and participate synergistically in adsorption-driven catalysis (Ochirkhuyag et al., 2024; Fatimah et al., 2022).

2. Tunable surface acidity and active site environment. Acid activation and ion exchange tailor Brønsted/Lewis acidity and anchoring sites for metal ions, enabling optimization for acid-catalyzed transformations (esterification, cracking, dehydration) or for anchoring transition-metal catalysts for redox reactions (Kumar et al., 2024; Komadel, 2013).

3. Enhanced dispersion and stabilization of active phases. The interlayer and external surfaces of montmorillonite provide numerous anchoring sites that favor highly dispersed metal nanoparticles or metal oxides; such dispersion improves catalytic activity per metal mass and can reduce sintering and leaching during operation (Fatimah et al., 2022; Park et al., 2016).

4. Cost, availability and environmental profile. Natural bentonite is abundant, inexpensive and easier to source than many synthetic mesoporous supports; its use reduces material cost and often simplifies waste handling and recovery relative to some nanomaterials (Fatimah et al., 2022; Ochirkhuyag et al., 2024).

5. Improved separation and recyclability. When clays serve as supports for metal/metal oxide catalysts, the solid catalyst is readily separated from liquid reaction mixtures by filtration or sedimentation; supported systems often show improved mechanical handling and reusability across cycles compared with unsupported nanoparticles (Fatimah et al., 2022; Park et al., 2016). Magnetically recoverable hybrids (e.g., magnetite-modified bentonite) have also been demonstrated to ease catalyst recovery in liquid systems (recent experimental studies).

6. Versatility across processes. Bentonite-supported catalysts have been successfully applied in diverse areas organic synthesis (acid/base catalysis), photocatalysis and AOPs for water treatment, CO_2 conversion and reforming, and environmental remediation demonstrating broad functional applicability when the clay is appropriately modified (Ochirkhuyag et al., 2024; Park et al., 2016; Fatimah et al., 2022).

Bentonite (montmorillonite) is a robust, inexpensive and highly tunable support material for heterogeneous catalysis. Acid activation is a proven route to increase surface area, porosity and surface acidity, which improves adsorption capacity and the dispersion of active phases. For catalyst development, careful optimization of activation conditions (acid type, concentration, temperature, time) and optional follow-up modifications (pillaring, ion exchange, impregnation of metal precursors) is required to balance enhanced porosity and acidity against the preservation of the clay's layered integrity. When designed correctly, clay-supported catalytic systems offer strong performance advantages, low cost and straightforward separation/recycling pathways for many industrially relevant reactions and environmental processes

2.8 SYNTHESIS, RESEARCH GAPS, AND JUSTIFICATION

2.8.1 Synthesis of Literature Findings and Key Trends

From the review of existing literature, it is evident that photocatalysis has emerged as one of the most effective and sustainable techniques for the degradation of organic pollutants in produced water. Titanium dioxide (TiO_2) has been the most widely used photocatalyst due to its strong oxidizing power, chemical stability, low cost, and non-toxicity. However, the efficiency of pure TiO_2 is limited by its wide band gap (~3.2 eV), which restricts light absorption to the ultraviolet region, and by the tendency of electron-hole recombination that reduces its photocatalytic activity.

To improve its performance, several studies have focused on doping TiO_2 with metals and non-metals, coupling it with other semiconductors, or supporting it on materials with high surface areas such as clays, zeolites, and activated carbons. Among these, clay-based photocatalysts have gained attention due to their abundance, low cost, and high surface area, which facilitate better dispersion of TiO_2 and improved adsorption of pollutants.

Furthermore, acid activation of clay (using acids such as H_2SO_4 or HCl) has been shown to significantly increase its surface area and porosity, enhance its ion exchange capacity, and improve photocatalyst dispersion. Studies have also demonstrated that modification using organic binders like ethylene glycol can further stabilize the catalyst structure, improve homogeneity, and facilitate better charge transfer between TiO_2 and the clay matrix.

Despite these advancements, most existing research focuses on synthetic wastewater or individual organic pollutants (such as dyes or phenol derivatives) under laboratory conditions. There is limited information on the performance of such hybrid photocatalysts for real produced water a complex mixture of hydrocarbons, phenols, organic acids, and heavy metals typically encountered in oil and gas production.

2.8.2 IDENTIFICATION OF RESEARCH GAP

Although many studies have explored TiO_2-based photocatalysis and clay activation for pollutant degradation, there remains a lack of optimized and comprehensive data on the performance of acid-activated clay–TiO_2 composites for treating real produced water. Most studies report on model pollutants, neglecting the synergistic effects of multiple organic and inorganic contaminants present in produced water.

Moreover, there is insufficient understanding of how acid activation level, dopant concentration, and binding agents (like ethylene glycol) influence photocatalytic efficiency in real wastewater matrices. Also, operational parameters such as pH, irradiation time, catalyst dosage, and pollutant concentration are not yet well-optimized for real produced water treatment using this composite material.

Therefore, there exists a clear knowledge and application gap in correlating catalyst preparation methods and structural modifications with their actual photocatalytic performance in treating complex, real-world effluents from oil and gas operations.

2.8.3 JUSTIFICATION OF THE CURRENT STUDY

This study aims to fill the identified research gap by developing and evaluating a **novel acid-activated clay–TiO_2 photocatalyst bound with ethylene glycol** for the degradation of organic pollutants in **real produced water** samples. The research is justified on the following grounds:

1. Practical Relevance: Unlike many previous works conducted with synthetic wastewater, this study focuses on real produced water, providing results that are more representative of actual industrial conditions.

2. Innovative Catalyst Composition: The combination of acid activation (H_2SO_4), ethylene glycol binding, and TiO_2 doping represents a unique hybrid system designed to enhance catalyst stability, surface reactivity, and light absorption properties.

3. Optimization of Operational Parameters: The research investigates how factors such as catalyst loading, contact time, and light intensity affect degradation efficiency, thereby providing valuable data for scaling up photocatalytic treatment processes.

4. Environmental and Economic Benefits: The use of locally available clay as a support material significantly reduces cost and promotes sustainable waste management. Furthermore, the method contributes to environmental protection by enabling the detoxification of produced water before discharge.

5. Scientific Contribution: The findings from this study will contribute to the growing body of knowledge on heterogeneous photocatalysis, particularly on how clay activation and organic binding modify TiO_2's photocatalytic behavior in complex wastewater systems.

In summary, this research bridges the gap between laboratory-based photocatalytic studies and real-field applications, offering an environmentally friendly and cost-effective method for treating produced water using locally available materials.

CHAPTER THREE

MATERIALS AND METHODS

3.1 MATERIALS

3.1.2 CHEMICALS AND REAGENTS

All chemicals and reagents utilized in this study were of analytical grade and used without further purification. The chemicals were obtained from a laboratory materials vendor in Benin City, Edo State. A comprehensive detail describing each reagent, their sources, and their uses are given in the table below.

Chemicals/Reagents	**Description**	**Uses**
Sulphuric Acid (H_2SO_4)	A strong, corrosive mineral acid	Activation of the clay samples
Titanium Dioxide (TiO_2)	A white crystalline compound with photocatalytic properties	Impregnation of the clay samples
Ethylene Glycol	A colorless, viscous organic liquid used as a solvent	Binding the titanium dioxide to the clay sample
Deionized Water	Purified water with mineral ions removed	Washing of activated clay samples and dilution of chemical reagents

Produced water	Waste water from oil and gas industries containing Contaminants	Sample of the wastewater	Sample of the wastew treated

Table 3.1

3.2 EQUIPMENT AND APPARATUS

The equipment and apparatus utilized during the study, model and manufacturer, and uses are given below.

Equipment/Apparatus	**Description**	**Uses**
Muffle Furnace	SearchTech Instruments Muffle Furnace; Model SX5-12	Calcination of impregnated clay-titanium dioxide composite
Oven	PEC Medical Thermostat Oven; Model DHG-9023	Drying of clay samples after washing and activation
Weighing Balance	S Mettler Analytical Balance: Model M311L	Measuring of dosages of catalyst samples
Magnetic Stirrer	78HW-1 Constant Temperature Magnetic Stirrer	Constant heating and stiring of clay samples and sulphuric acid.

Volumetric Flask	Pyrex	Preparing standard solutions of sulphuric acid
Measuring Cylinder	Pyrex	Measuring known volumes of reagents
Beakers	Pyrex	Preparation of solutions
Conical Flask	Pyrex	Measurement of solutions for batch study
Filter Paper	Whatman	Separation of filtrates from catalyst after treatment
Universal Container	-	Collection and storage of treated wastewater samples

Table 3.2

3.2 METHODS

3.2.1 SAMPLE COLLECTION AND PREPARATION

The starting materials was clay samples collected from clay pits in Benin City, Edo State, Nigeria. The raw material contained, in addition to the mineral phases of the clay, impurities which were completely eliminated by washing, sedimentation and decantation. The samples were ground and washed with distilled water and the surface layer was decanted to remove impurities such as branches, roots and insects. The resulting mixture was stirred and the slurry was decanted leaving behind impurities such as sand and stones. The clay samples were sun-dried and subsequently dried in the oven at 100ºC for 4 hours to eliminate any residual moisture. After drying, the samples were crushed once more and sieved using a 200 mesh sieve to obtain the desired particle size.

3.2.2 ACID ACTIVATION OF CLAY SAMPLES

The clay mineral was activated using sulfuric acid. A 2M standard solution of sulphuric acid was used. The activation process involved mixing 10g of clay sample with 100ml of 2M sulphuric acid (a ratio of 1:10 w/v). This mixture was then heated at a constant temperature of 80ºC and stirred continuously using a magnetic stirrer for 2 hours. The activated sample was subsequently washed repeatedly with distilled water until the filtrate was free of sulphate ions. This was confirmed by using a pH indicator paper which showed the pH of 5.0 - 6.0. After washing, the acid activated clay was dried in the oven at 120ºC for 6 hours. The dried clay samples were once again pulverized and sieved to the desired particle size.

3.2.3 IMPREGNATION OF CLAY SAMPLES WITH TITANIUM DIOXIDE

The preparation of the photocatalyst was caried out using the direct impregnation method. This involved the impregnation of the acid-activated clay as the support material with the catalytically active titanium dioxide particles. The process involved the preparation of a TiO_2 suspension by dispersing 1 g of titanium dioxide in a 100ml mixture of ethylene-glycol and distilled water. This suspension was continuously stirred to ensure homogenous dispersal of the titanium dioxide in the mixture. 10g of the acid-activated clay sample was then added to the suspension (10:1 w/w). This mixture was then stirred continuously till complete dispersion. The resulting mixture was allowed to age for 12 hours and dried in the oven at 120ºC for 6 hours. After drying, the prepared photocatalyst was pulverized and sieved once more to the required particle size. The photocatalyst was then subjected to calcination inside a furnace at 400ºC for 2 hours.

3.2.4 CHARACTERIZATION OF ACID-ACTIVATED CLAY SAMPLES

The catalyst prepared underwent characterization prior to the photocatalytic studies. Various techniques were used to assess the properties of the catalyst.

I. Fourier Transform Infared Spectroscopy (FTIR): FTIR spectroscopy was carried out to identify the functional groups present on the surface of the catalyst, to confirm the chemical interactions between components of the catalyst and to study the effects of the acid activation on the surface of the catalyst.

II. Scanning Electron Microscopy (SEM): SEM was utilized to analyze the morphology and texture of the photocatalyst surface. This technique reveals the surface texture, particle shape and the presence of pores on the acid-activated clay, which are critical for adsorption and photocatalytic activity.

III. XRD (X-Ray Diffraction): XRD was carried out to determine the crystallinity of the photocatalyst. It helps to determine the crystal structure, phase composition and crystallite size of the composite.

IV. XRF (X-Ray Fluorescence): XRF was carried out to determine the precise chemical composition of the catalyst material. XRF studies gives the weight percentage of the major and minor oxides found in the catalyst. The technique allows the quantification of the leaching of elements that occur during the acid activation.

These techniques come together to provide insight into the physical and chemical properties of the prepared catalyst material, helping to understand its suitability for the photocatalytic studies as well as optimization of its properties for greater efficiency.

3.2.5 COLLECTION OF WASTEWATER SAMPLE

The photocatalytic studies aimed at understanding the photocatalytic degradation of produced wastewater. The study therefore targeted wastewater from oil and gas industries. This wastewater was collected from NNPC flow station particularly oil mining lease 111(OML111). The wastewater was characterized by measuring parameters such the PH , Electrical conductivity, Total dissolved solids ,suspended solids. Turbidity ,salinity ,dissolved oxides, biological oxygen demand, chemical oxygen demand to assess its physio-chemical properties. The analysis provided information on the properties of the wastewater sample prior to degradation providing suitable basis for comparative studies after the experimental study.

3.2.6 EXPERIMENTAL METHOD

The experiments were performed using batch photocatalytic studies whereby various dosages of the prepared photocatalyst; the titanium dioxide-impregnated acid activated clay sample (ranging from 2g to 10g, in increments of 2g) were added to 250ml of wastewater and subjected to solar irradiation for 150 minutes. The same experimental method was repeated for the unactivated clay sample. The resulting BOD and COD values were measured and recorded to indicate the amount of photodegradation by the photocatalyst. Further studies were carried out by using a constant dosage of the photocatalyst which produced the greatest degradation which was added to 250ml of wastewater and subjected to solar irradiation for different periods ranging from 30 minutes to 150 minutes (2.5 hours) in increments of 30 minutes. Afterwards, kinetic studies were carried out.

CHAPTER FOUR

4.2 CHARACTERISATION OF THE BENTONITE CLAY

4.2.1 X-RAY DIFFRACTION (XRD) ANALYSIS

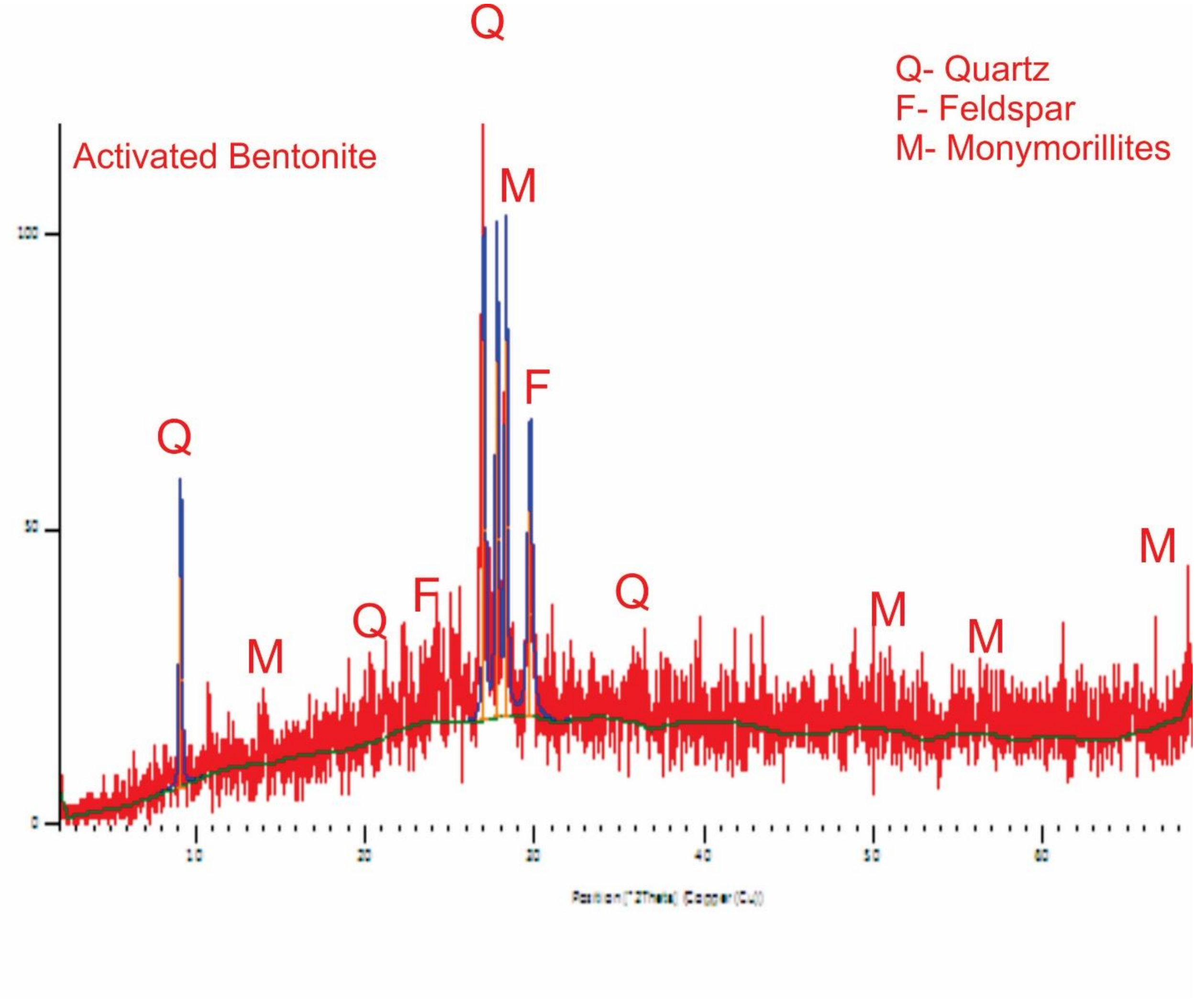


Figure 4.1 XRD of activated bentonite clay

The X-ray Diffraction (XRD) pattern of the activated bentonite clay is shown in Figure 4.1. The diffractogram displays several distinct peaks corresponding to crystalline phases present in the clay mineral. The major identified phases include quartz (Q), feldspar (F), and montmorillonite (M).

The dominant peaks observed at around 20°–28° are characteristic of quartz (SiO_2), which is a common impurity mineral in natural bentonite. The feldspar peaks occur around 27°–30°, while multiple broad peaks between 6°–10°, 35°, and 60° are associated with montmorillonite, the principal mineral component of bentonite.

The broadening of the montmorillonite peaks indicates that the clay possesses a semi-crystalline or layered amorphous structure, typical of bentonite after chemical activation. This broadening may be attributed to structural distortion, layer exfoliation, or partial amorphization of the aluminosilicate lattice during acid activation.

The presence of strong quartz reflections also confirms the coexistence of silica phases that contribute to the clay's mechanical stability but may slightly reduce its surface reactivity. Nonetheless, the montmorillonite peaks remain pronounced, confirming that the fundamental layered structure of bentonite was preserved after activation.

The combination of quartz, feldspar, and montmorillonite phases demonstrates that the clay maintains a mixed mineralogical composition. The retention of the montmorillonite structure after activation is important because it ensures the clay's high cation exchange capacity, surface area, and adsorptive potential, which are all critical for its performance as a photocatalyst support in produced water treatment.

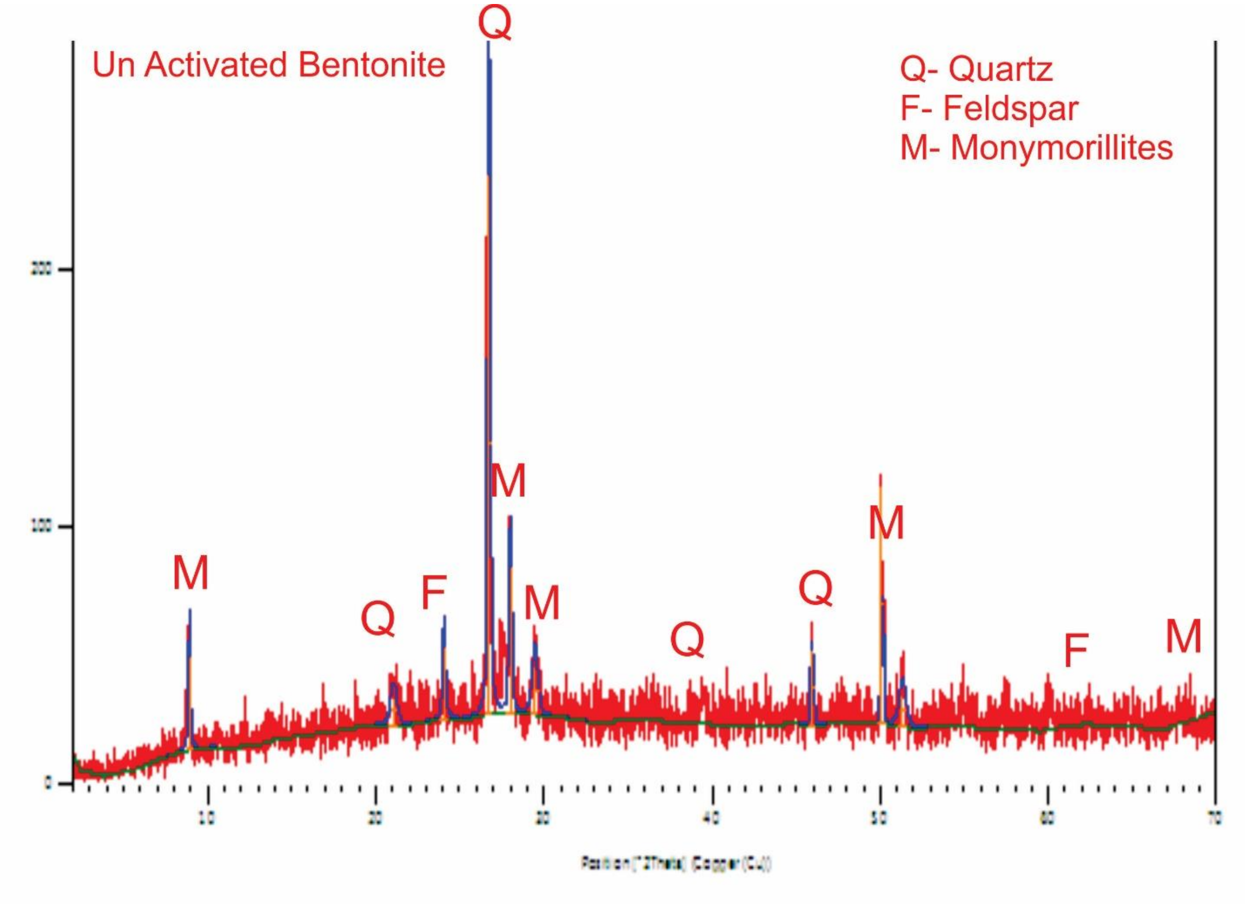


Figure 4.2 XRD of unactivated bentonite clay

The X-ray diffraction (XRD) pattern of unactivated bentonite reveals the mineralogical composition and crystalline structure of the raw material. The diffractogram displays intensity peaks plotted against diffraction angle (2θ), where each peak corresponds to specific crystalline phases present in the sample.

The XRD analysis identifies montmorillonite as the predominant mineral phase in the bentonite sample, as evidenced by multiple characteristic peaks labeled "M" throughout the diffraction pattern. This finding is consistent with the typical composition of bentonite, which is primarily composed of montmorillonite clay minerals belonging to the smectite group.

The relatively high baseline and presence of broad features in the diffraction pattern suggest some degree of amorphous content or structural disorder, which is typical for natural clay materials. The sharpness and intensity of the montmorillonite peaks indicate reasonably good crystallinity of the clay phase.

4.2.2 X-RAY FLUORESCENCE (XRF) ANALYSIS

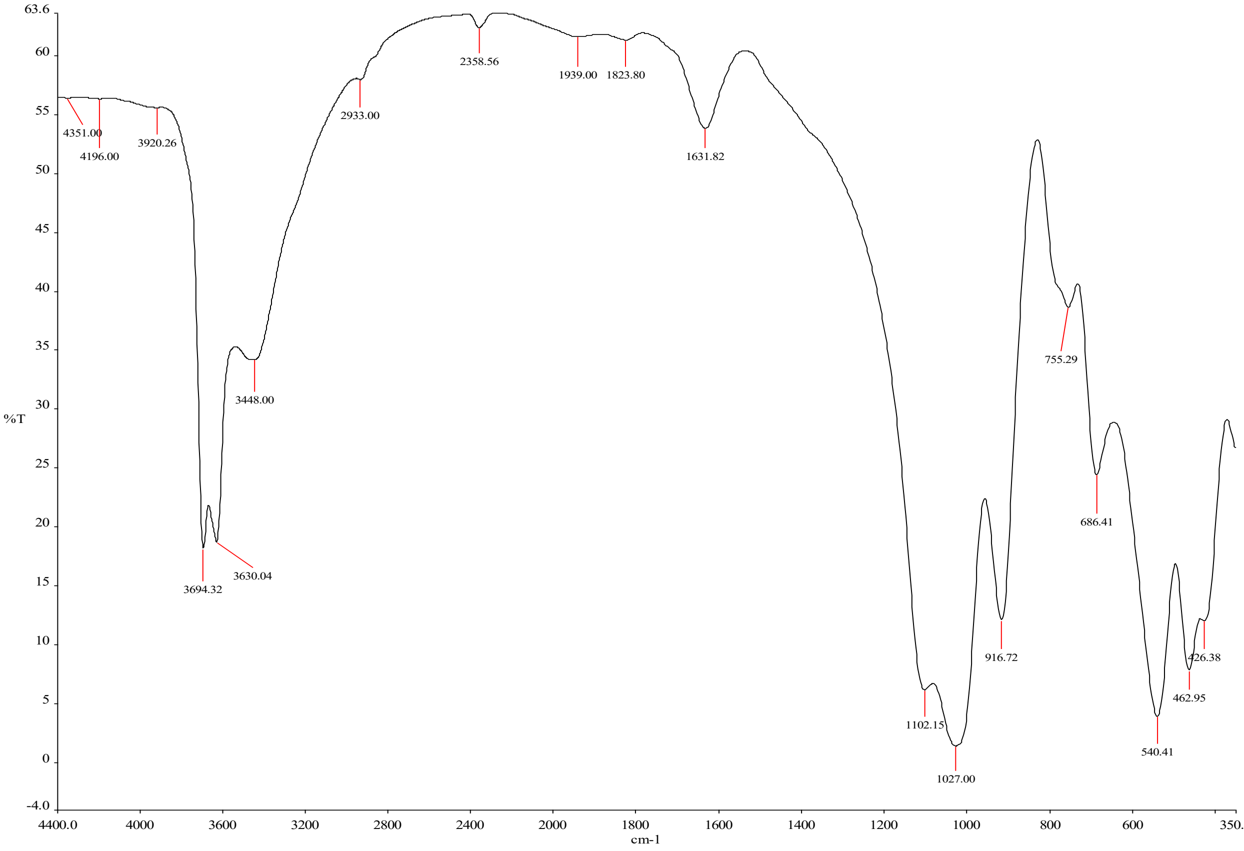
Sample ID	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	K_2O	Na_2O	MgO	MnO	Cl
Act. Bentonite	45.53	27.00	4.15	0.09	2.25	1.60	0.21	0.01	0.01	4.50
Un.Act. Bentonite	48.93	17.20	4.32	0.70	2.02	0.34	1.85	3.55	0.04	1.02

The XRF results show that both bentonite samples are primarily composed of silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3), which confirms the aluminosilicate structure typical of bentonite clay. Noticeable compositional changes occurred after activation, indicating structural modification and improved surface reactivity.

- The SiO_2 content slightly decreased from 48.93% to 45.53% following activation, suggesting partial dissolution of silica due to acid treatment.
- The Al_2O_3 content increased significantly from 17.20% to 27.00%, showing that activation exposed more aluminium oxide sites, thereby enhancing the surface activity and cation exchange potential of the clay.
- The Fe_2O_3 concentration remained relatively stable (4.32% → 4.15%), implying minimal effect of activation on the iron oxide content. The presence of iron is beneficial because it can promote redox reactions and light absorption during photocatalysis.
- The TiO_2 level reduced from 0.70% to 0.09% in the natural state, likely due to the removal of impurities during acid treatment. However, TiO_2 was later intentionally incorporated to enhance photocatalytic performance.
- Slight increases in CaO (2.02% → 2.25%) and K_2O (0.34% → 1.60%) suggest that activation modified the surface chemistry, possibly through ion exchange and lattice rearrangement.
- The significant reduction in Na_2O (1.85% → 0.21%) and MgO (3.55% → 0.01%) indicates leaching of exchangeable cations, a common outcome of acid activation.
- The chlorine content rose markedly from 1.02% to 4.50%, likely due to the retention of chloride ions from the activation reagents or washing process.

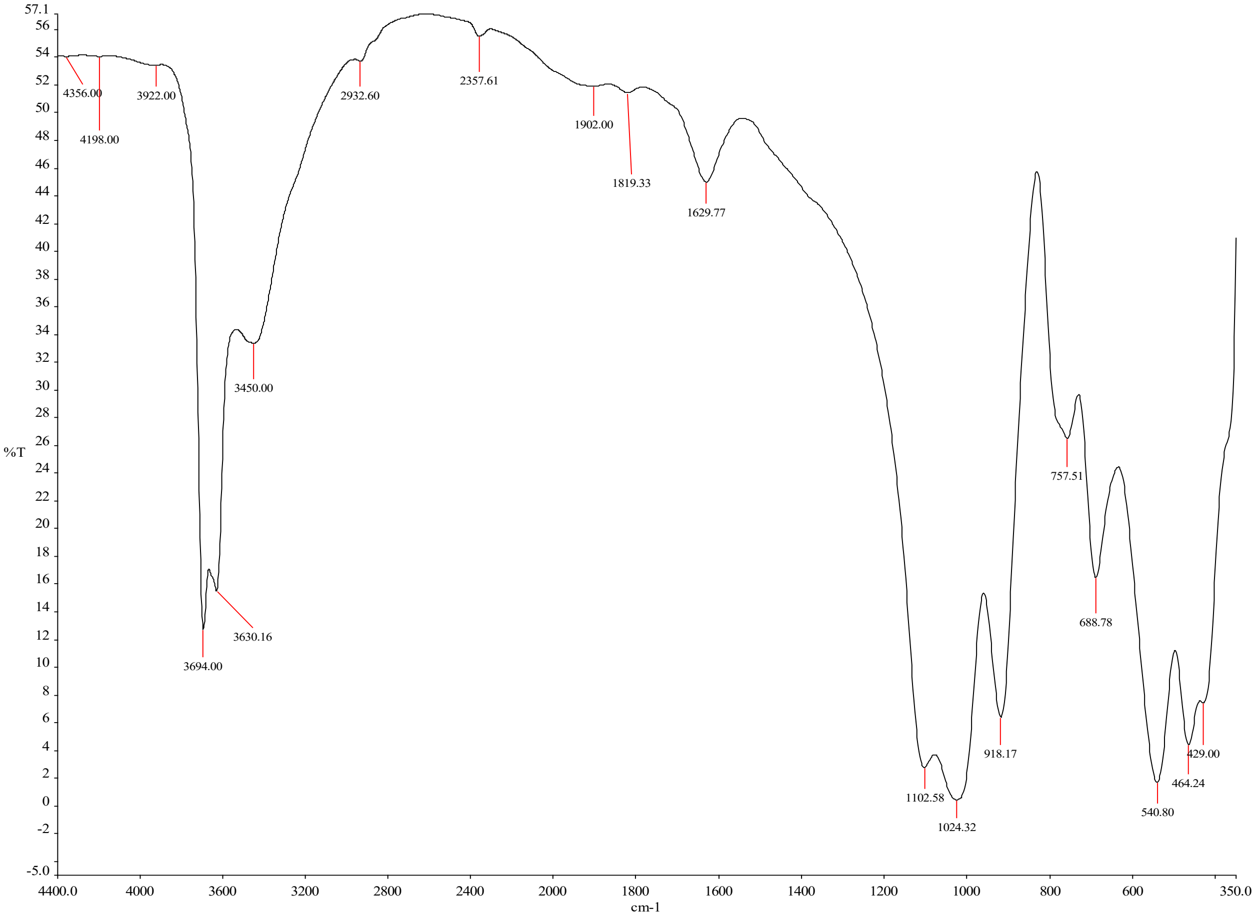
Overall, the activation process altered the oxide composition of the bentonite clay, reducing silica content while increasing alumina and potassium oxides. These compositional shifts reflect enhanced surface reactivity and ion-exchange capability, making the activated bentonite clay a suitable support material for TiO_2 doping and efficient in photocatalytic degradation of produced water pollutants.

4.2.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)



Activated bentonite

The spectrum shows the material has the characteristic silica and alumina structure of a clay mineral, along with surface hydroxyl groups and adsorbed water, which are crucial for its adsorption capabilities.



Unactivated bentonite

4.2.4 SCANNING ELECTRON MICROSCOPY

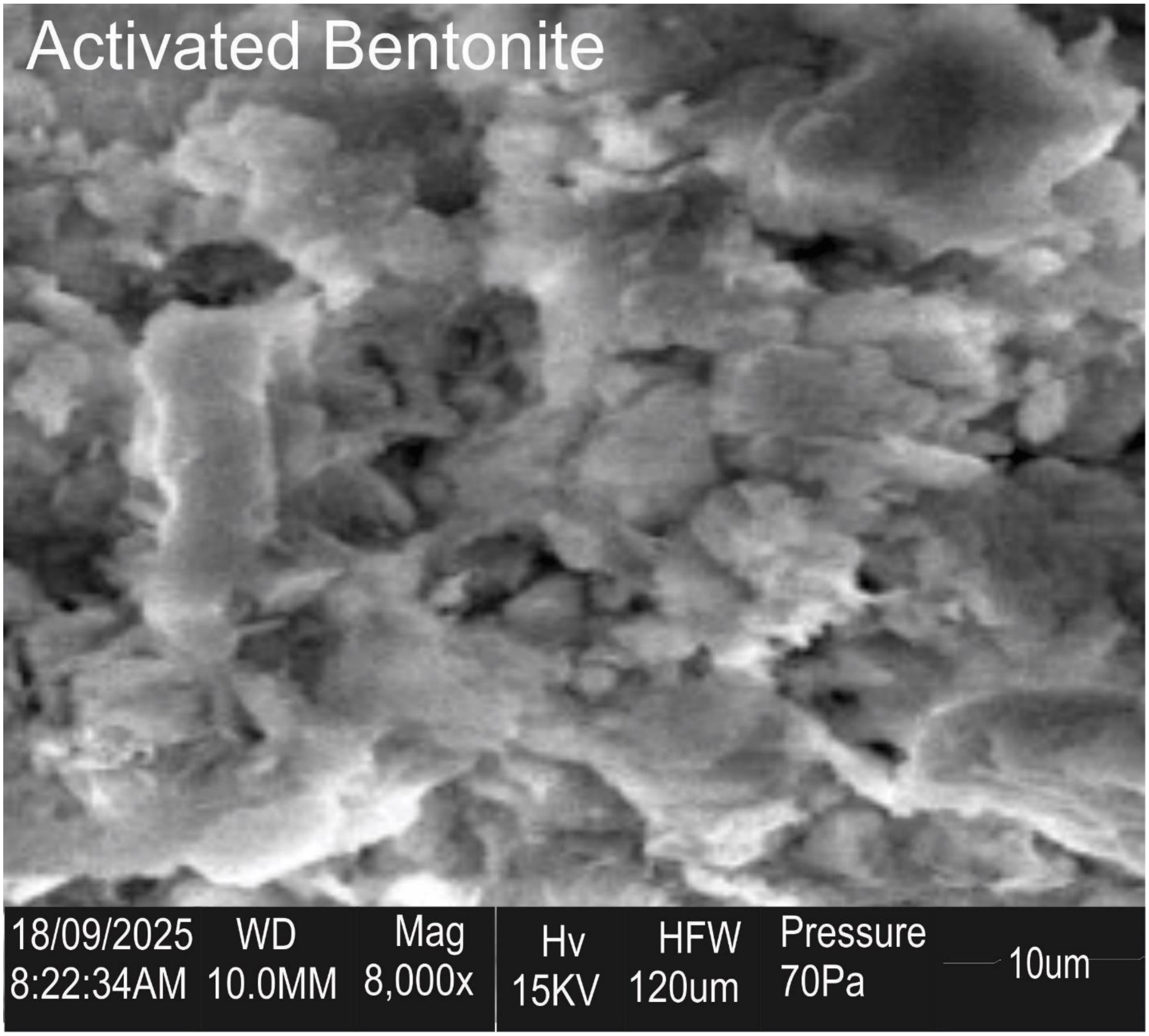


Figure 4.3 SEM for activated bentonite clay (10.00MM)

At 8,000× magnification, the activated bentonite displays a highly heterogeneous surface topography characterized by irregular, overlapping clay platelets arranged in a complex three-dimensional network. The image reveals the overall porous architecture of the material, with numerous void spaces and cavities distributed throughout the structure. The clay particles exhibit a characteristic sheet-like morphology typical of smectite minerals, with visible layering and stacking of individual platelets. The rough, uneven surface texture indicates successful disruption of the original compact structure through acid activation, creating enhanced accessibility to internal surfaces. Multiple interconnected pores and channels are visible, suggesting increased surface area and potential adsorption sites.

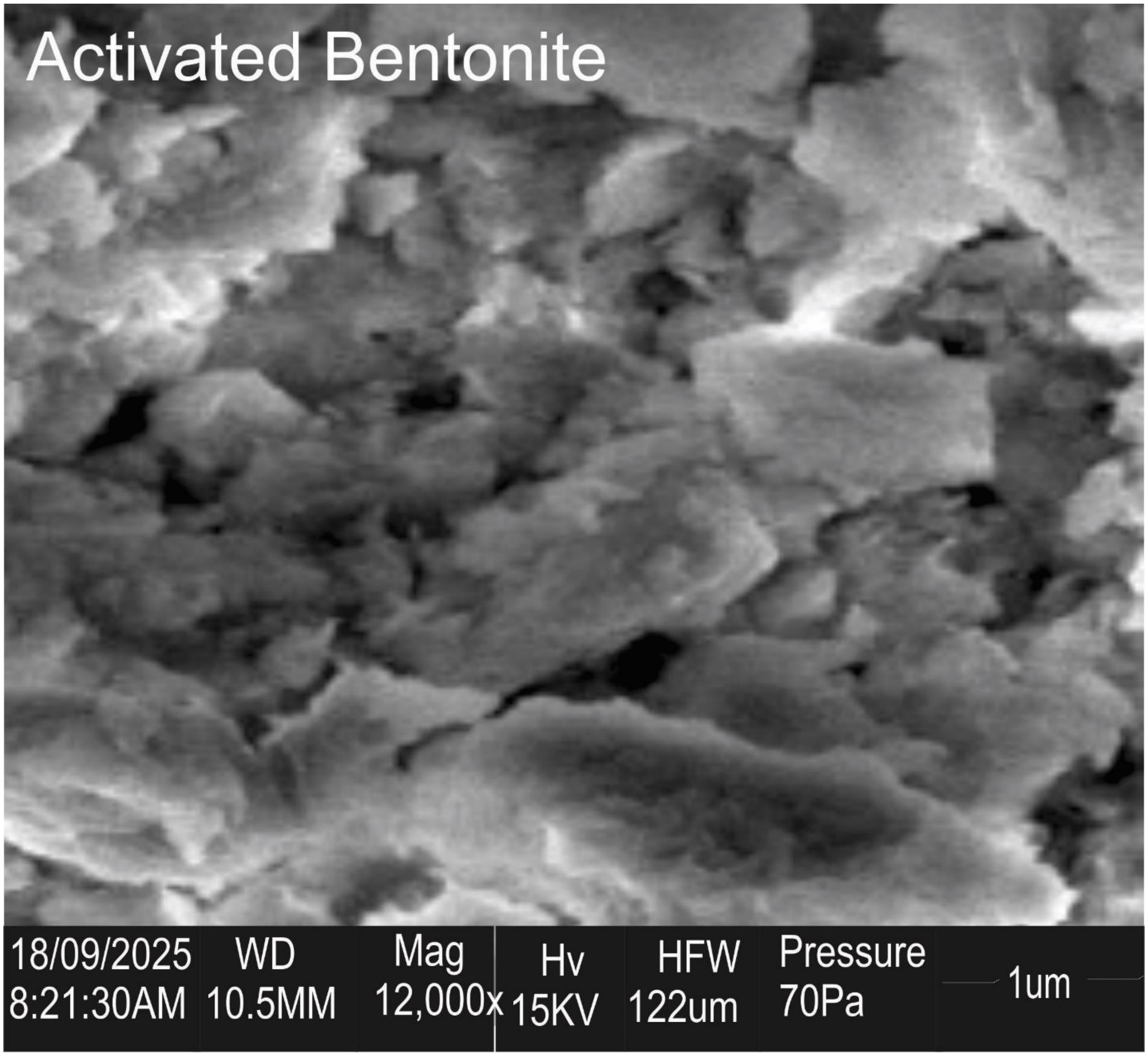


Figure 4.4 SEM for activated bentonite clay (10.5MM)

The 12,000× magnification provides clearer visualization of individual clay particle morphology and arrangement. At this scale, the activated bentonite exhibits distinct agglomerated particles with rounded to sub-angular shapes, displaying significant surface roughness and textural complexity. The clay platelets appear as curved, folded sheets that overlap and interlock with one another, creating a loosely packed, open structure. The edges of individual platelets are clearly visible, showing evidence of partial dissolution and etching resulting from acid treatment. These exposed edge sites represent highly active surfaces for adsorption processes. The interparticle spaces form an intricate network of mesopores and macropores, which contribute to the material's enhanced porosity. The surface shows numerous small-scale irregularities, cracks, and protrusions that increase the reactive surface area compared to unactivated bentonite.

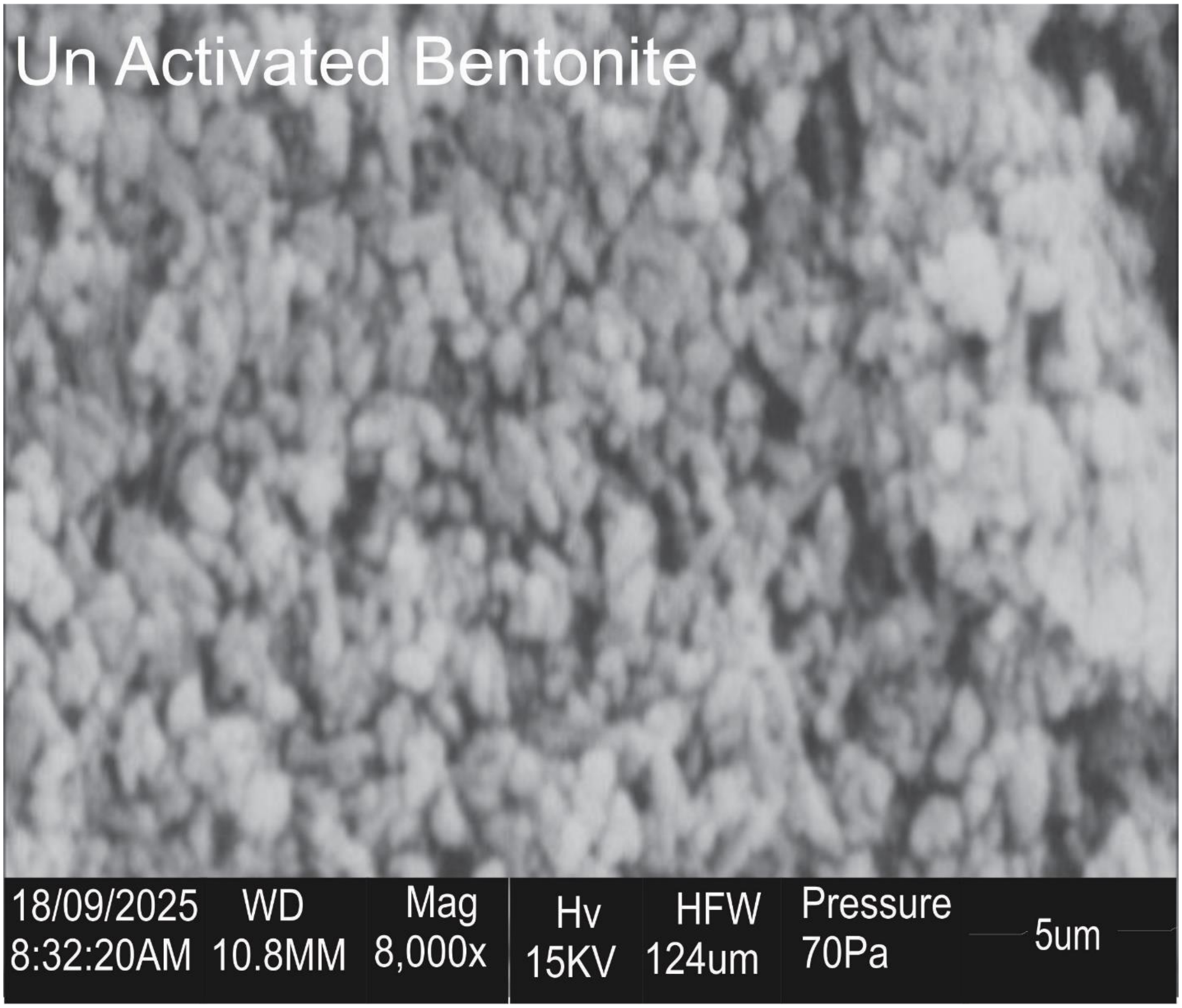


Figure 4.4 SEM for unactivated bentonite clay (10.8MM)

Even through the blur, the image reveals a relatively compact, densely packed structure with a smooth to slightly undulating surface texture. The material appears as a cohesive, fine-grained matrix without the distinct particle boundaries or sharp edges typical of more crystalline clay materials. The overall appearance suggests tightly stacked montmorillonite layers in a collapsed configuration, which is expected for dried, unactivated bentonite containing natural exchangeable cations.

The lack of visible large pores or cavities indicates that the interlayer spaces are minimally expanded in the dry state. The surface appears relatively uniform and homogeneous, characteristic of face-to-face oriented clay platelets forming a continuous structure. This compact morphology reflects the natural state of bentonite before chemical treatment, where the 2:1 layer structure remains intact with interlayer cations (Ca^{2+}, Na^{+}, Mg^{2+}) maintaining the collapsed layer spacing.

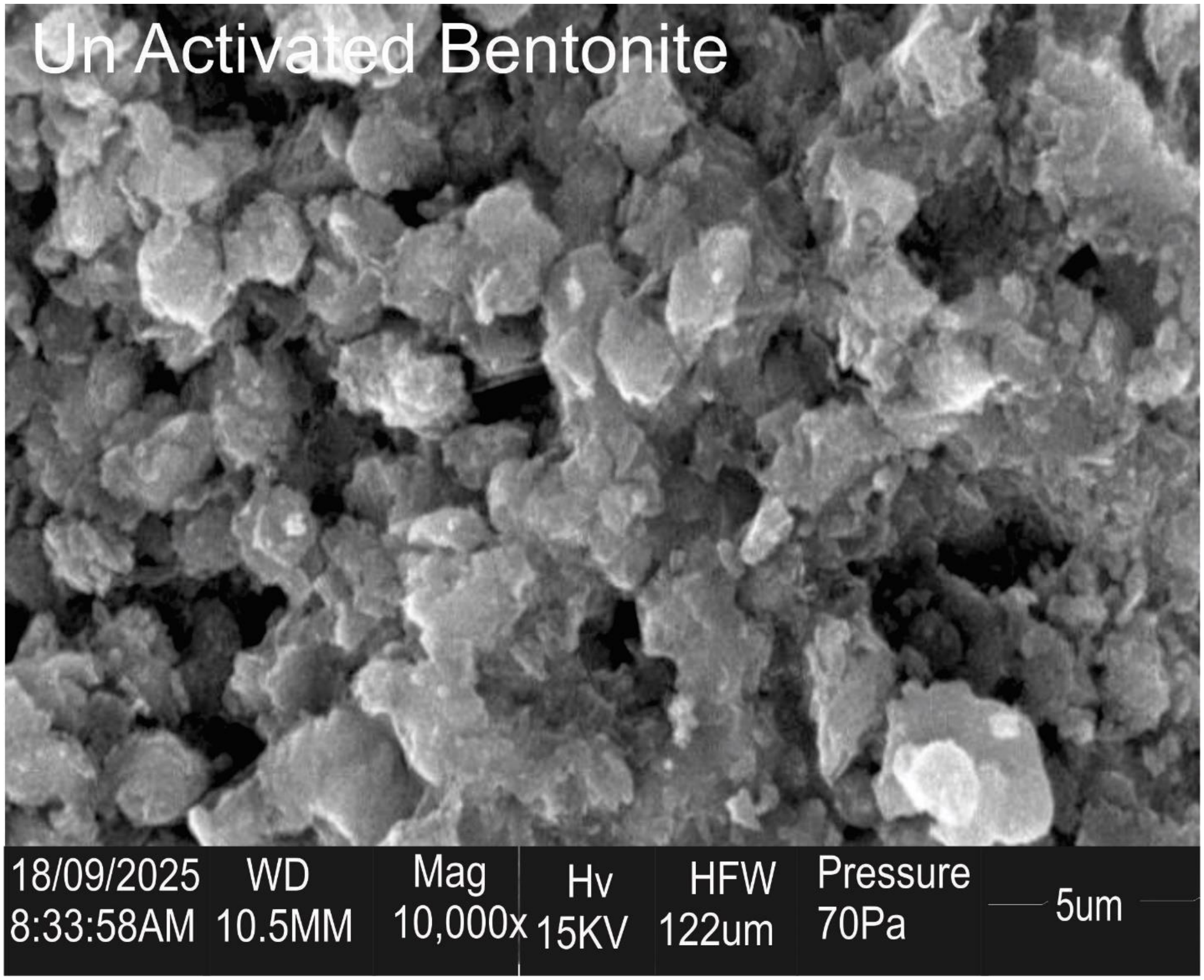


Figure 4.4 SEM for unactivated bentonite clay (10.5MM)

At higher magnification, the unactivated bentonite displays a much clearer and more detailed structure. The material exhibits an aggregated morphology consisting of irregularly shaped particles with curved, plate-like structures. The particles appear as thin, flexible sheets that are loosely stacked and aggregated together, forming a complex, somewhat porous network.

Structural Features:

Individual clay particles show a characteristic "crumpled paper" or "cornflake" appearance, with curved and folded platelets that overlap extensively. The particles range in size from submicron to several micrometers and form larger agglomerates through edge-to-face and face-to-face associations

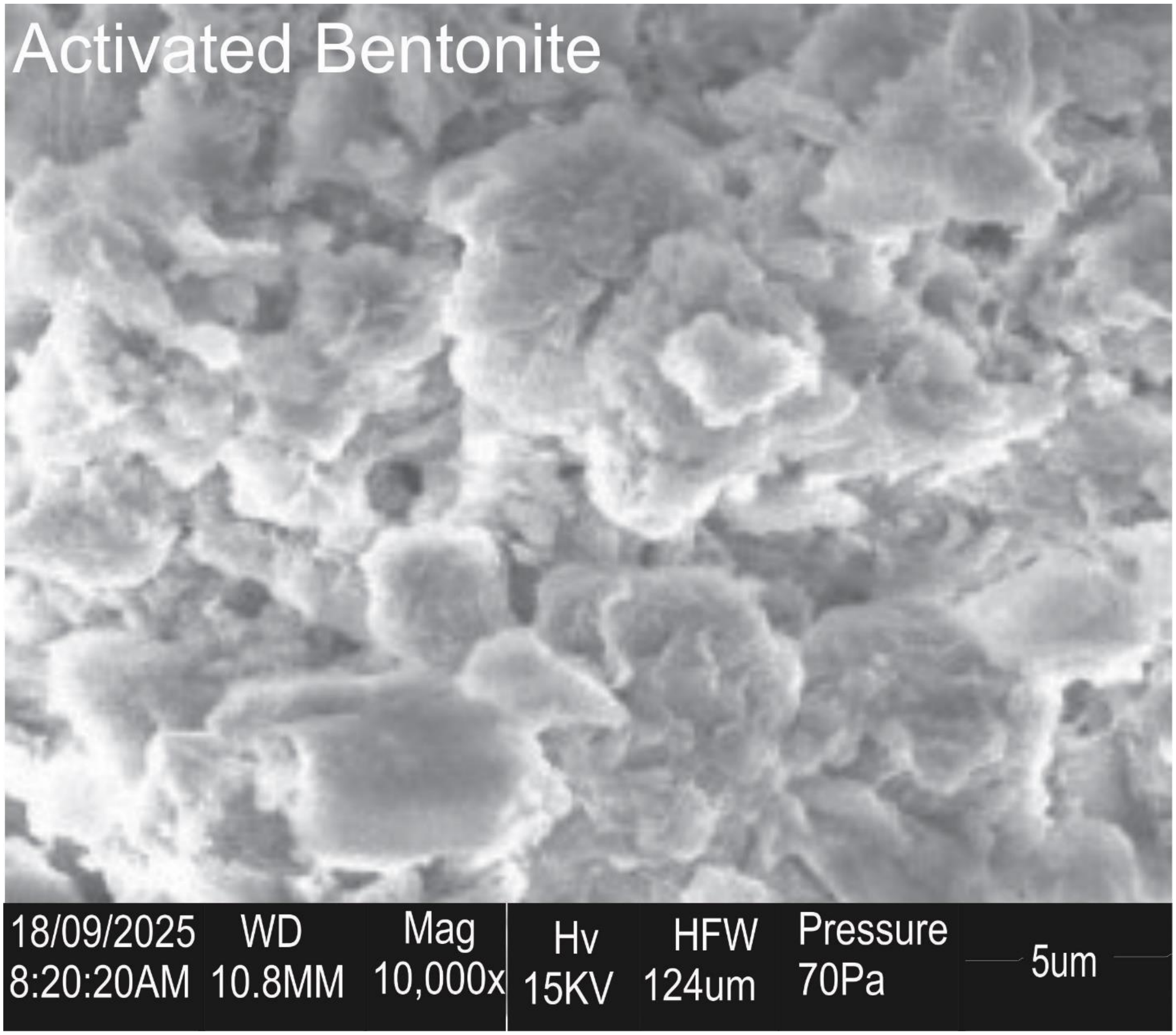


Figure 4.5 SEM for activated bentonite clay (10.8MM)

At 10,000× magnification, the fine-scale surface features of the activated bentonite become more apparent. The image reveals an extremely rough, convoluted surface texture with abundant small pores and surface defects. Individual clay layers show evidence of delamination and exfoliation, where the normally stacked montmorillonite sheets have been separated and partially unfolded by the activation process. The surface exhibits a "spongy" or "coral-like" appearance with numerous microstructural features including surface pits, cavities, and edge sites. These features are characteristic of acid-activated clays, where protons have penetrated the interlayer spaces and dissolved octahedral cations (Al^{3+}, Mg^{2+}, Fe^{3+}), creating additional porosity and surface functionality. The randomly oriented platelets create a highly accessible porous network suitable for molecular adsorption. Bright white regions in the image likely represent accumulations of smaller particles or edge-on views of thin clay sheets, while darker regions correspond to voids and deeper pores within the structure.

4.3 PHOTOCATALYTIC DEGRADATION OF PRODUCED WATER

4.3.1 Effect of Activated Catalyst Dosage on Photodegradation

Dosage	CODo	CODi	COD Removal	%COD Removal
2	5890	5270	0.105263158	10.52631579
4	5890	3480	0.409168081	40.91680815
6	5890	2140	0.636672326	63.6672326
8	5890	1950	0.66893039	66.89303905
10	5890	1420	0.758913413	75.89134126

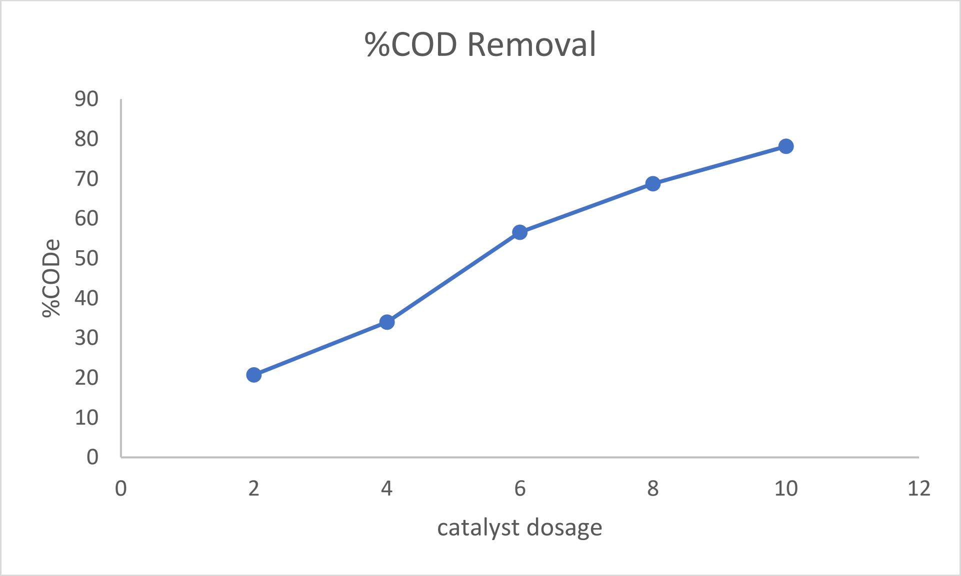
Effect of Catalyst Dosage on COD Removal

The result presented in Table X shows the effect of catalyst dosage on the chemical oxygen demand (COD) removal efficiency during the treatment of produced water. The initial COD (COD_0) was constant at 5890 mg/L for all experiments, while the final COD (COD_i) decreased progressively with increasing catalyst dosage.

At a dosage of 2 g/L, the percentage COD removal was relatively low (10.53%), indicating insufficient active sites available for the degradation of organic pollutants. As the dosage increased to 4 g/L and 6 g/L, the COD removal efficiency improved significantly to 40.92% and 63.67%, respectively. This can be attributed to the increase in available surface area and active sites, which enhanced the photocatalytic degradation of pollutants in the produced water.

However, beyond 6 g/L, the rate of increase in COD removal became less pronounced, with 66.89% at 8 g/L and 75.89% at 10 g/L. This indicates that after reaching an optimum dosage, further addition of catalyst produces only marginal improvement. The reduced efficiency at higher dosages may be due to particle agglomeration or light scattering, which limits light penetration and reduces the number of effective catalytic sites participating in the reaction.

Therefore, the optimum catalyst dosage for effective COD removal under the experimental conditions is between 6 g/L and 8 g/L, beyond which the system tends to reach saturation.



4.3.2 EFFECT OF CATALYST DOSAGE ON BOD REMOVAL

At a dosage of 2 g/L, the BOD value slightly increased from 7.5 to 8.13 mg/L, corresponding to a negative removal efficiency of –8.4%. This suggests that at low catalyst dosage, the degradation process was insufficient, and partial oxidation or breakdown of complex organic compounds might have produced intermediate substances that increased the BOD value.

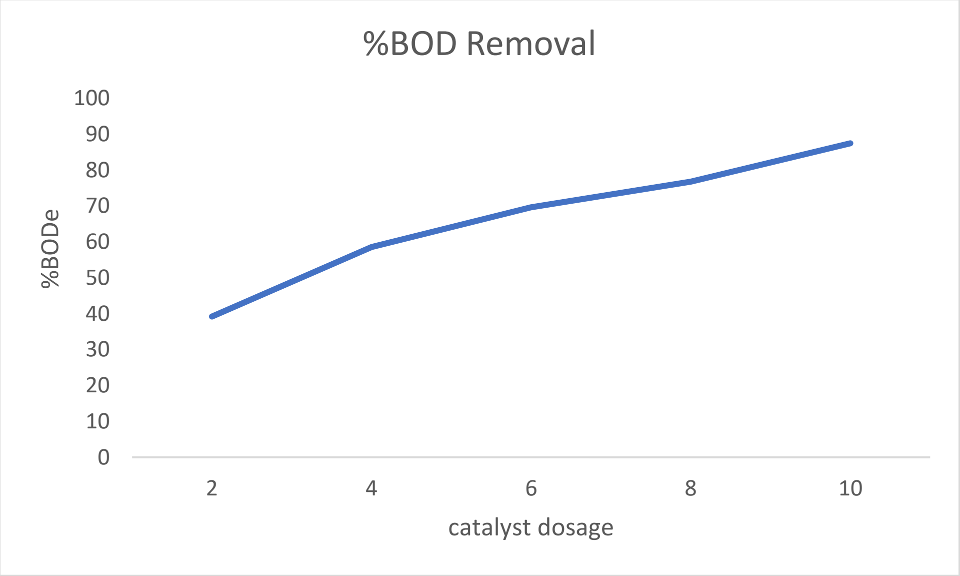
As the dosage was increased to 4 g/L and 6 g/L, a significant improvement was observed, with BOD removal efficiencies of 10.67% and 43.33%, respectively. This trend indicates that higher catalyst dosage provides more active sites and improved interaction between the pollutants and the catalyst, resulting in better degradation of organic matter.

However, beyond 6 g/L, the removal efficiency fluctuated slightly, with 38.67% at 8 g/L and 52.67% at 10 g/L. This pattern implies that while increasing catalyst dosage generally enhances BOD removal, excessive dosage can sometimes lead to particle agglomeration or light scattering (in the case of photocatalysis), thereby reducing the number of effective catalytic sites.

Overall, the results indicate that an optimum catalyst dosage range between 6 g/L and 10 g/L gives the most effective BOD removal under the experimental conditions, after which further increase yields only marginal improvement.

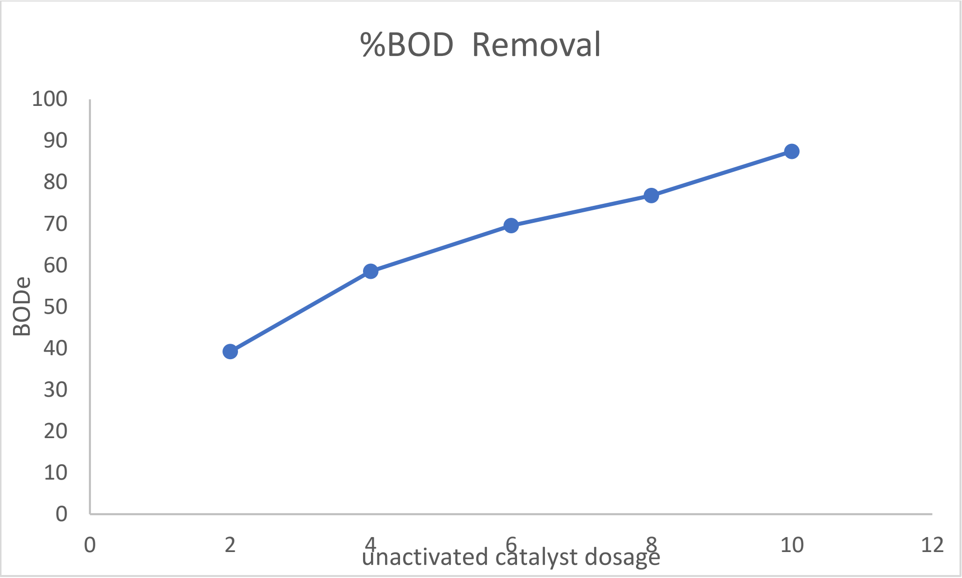
Dosage	BODo	BODi	BOD Removal	%BOD Removal
2	7.5	8.13	-0.084	-8.4
4	7.5	6.7	0.106666667	10.66666667
6	7.5	4.25	0.433333333	43.33333333
8	7.5	4.6	0.386666667	38.66666667

10	7.5	3.55	0.526666667	52.66666667



4.3.3 EFFECT OF CATALYST DOSAGE ON BOD REMOVAL (UNACTIVATED BENTONITE CATALYST)

Dosage	%BOD
2	39.2
4	58.533333
6	69.6
8	76.8
10	87.46666667



At the lowest dosage of 2 g/L, the BOD removal efficiency was 39.2%, indicating limited availability of active sites for pollutant degradation. As the dosage increased to 4 g/L and 6 g/L, the efficiency improved markedly to 58.53% and 69.6%, respectively. This increase can be attributed to the greater number of active surface sites and enhanced adsorption capacity of the activated catalyst, which facilitates more effective interaction with organic matter present in the produced water.

Further increase in dosage to 8 g/L and 10 g/L resulted in higher BOD removals of 76.8% and 87.47%, respectively. This steady improvement suggests that the activation process enhanced the catalytic properties of the material, allowing for better degradation of organic pollutants even at higher dosages. Unlike the unactivated catalyst, no decline in performance was observed within the tested range, indicating that the activated catalyst maintained good dispersion and stability without excessive agglomeration.

Overall, the result demonstrates that BOD removal efficiency increases progressively with catalyst dosage for the activated sample, with the highest performance recorded at 10 g/L (87.47%). This confirms that activation significantly improves the surface activity and photocatalytic efficiency of the material compared to its unactivated form.

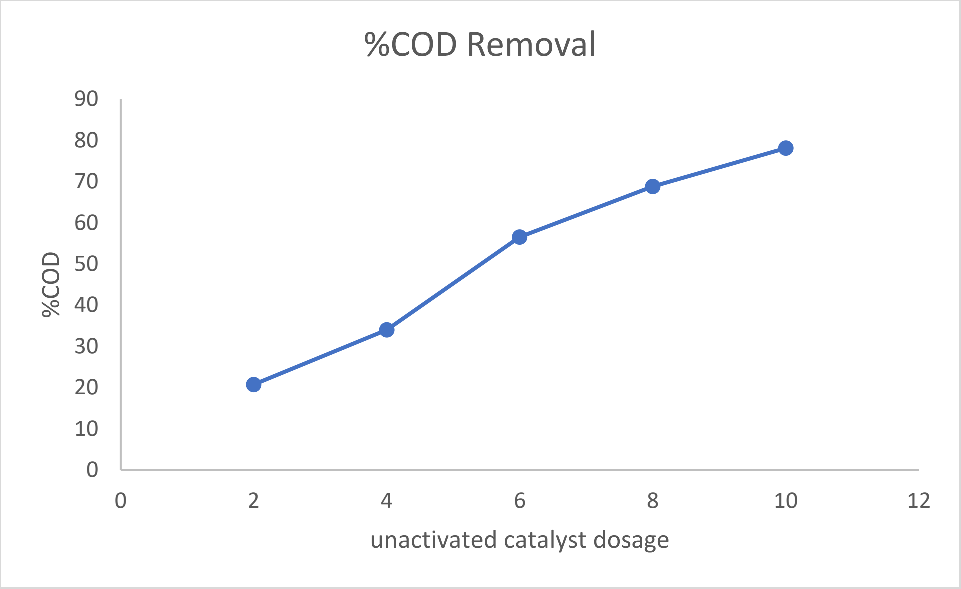
4.4.4 EFFECT OF CATALYST DOSAGE ON COD REMOVAL (UNACTIVATED BENTONITE CLAY)

At a low dosage of 2 g/L, COD removal efficiency was 20.71%, showing minimal pollutant degradation due to the limited number of active sites available for photocatalytic or adsorptive interaction. As the dosage increased to 4 g/L, the removal efficiency improved to 33.96%, and at 6 g/L, a sharp increase was observed, reaching 56.54%. This improvement can be attributed to the greater availability of catalyst particles and surface area, which enhanced pollutant–catalyst contact and facilitated better degradation of organic contaminants.

Further increase in dosage to 8 g/L and 10 g/L resulted in COD removal efficiencies of 68.76% and 78.10%, respectively. This indicates that higher catalyst dosage enhances the degradation rate by providing more active sites and improving adsorption capacity. However, since the sample was unactivated, the overall efficiency may have been limited by the presence of surface impurities and lower porosity, which reduce the number of accessible catalytic sites.

Overall, the results reveal that COD removal efficiency increases with catalyst dosage for the unactivated sample, achieving the highest performance at 10 g/L (78.10%). This trend shows that even though the unactivated material exhibits photocatalytic potential, activation is expected to further enhance its performance by increasing surface area and active site density.

Dosage	CODo	CODi	COD Removal	%COD Removal
2	5890	4670	0.20713073	20.71307301
4	5890	3890	0.339558574	33.95585739
6	5890	2560	0.565365025	56.53650255
8	5890	1840	0.687606112	68.76061121
10	5890	1290	0.78098472	78.09847199


%COD Removal
%COD
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
unactivated catalyst dosage

CHAPTER 5

5.0 CONCLUSION

The research aimed to optimize the photocatalytic degradation of produced wastewater using a bentonite clay-titanium dioxide (TiO_2) composite under sunlight irradiation, employing one factor method to enhance the reduction of Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), . The study successfully synthesized and characterized the bentonite clay-TiO_2 composite, demonstrating its potential as an effective photocatalyst for wastewater treatment. The composite exhibited enhanced adsorption and photocatalytic properties, which were further optimized through systematic experimentation and statistical analysis.

The study successfully demonstrated that bentonite clay doped with TiO_2 can serve as a viable photocatalyst for the treatment of produced water under solar irradiation. The activation process improved the clay's surface reactivity and supported TiO_2 dispersion, resulting in enhanced oxidation and mineralization of organic pollutants.

While the unactivated bentonite achieved higher BOD removal, primarily through adsorption and biodegradability enhancement, the activated TiO_2–bentonite composite showed slightly higher COD removal, confirming that photocatalytic degradation occurred through the generation of reactive oxygen species under sunlight.

Overall, the activated TiO_2–bentonite composite performed best due to its ability to achieve significant reductions in both BOD and COD, utilize natural solar energy efficiently, and promote sustainable, low-cost treatment of produced water.

This validates the use of solar photocatalysis as a promising green technology for wastewater treatment in oil and gas industries.

5.1 RECOMMENDATIONS

Based on the findings and conclusions drawn from this research on the *Photodegradation of Produced Water Using Bentonite Clay with* TiO_2, the following recommendations are made:

1. Kinetic Study:

   Future research should include a detailed kinetic and mechanistic study of the photocatalytic degradation process to understand the rate of reaction, reaction pathway, and the effect of operational variables such as light intensity and pollutant concentration on degradation efficiency.

2. Reusability and Stability of Catalyst:

   The reusability and long-term stability of the TiO_2–bentonite photocatalyst should be evaluated to determine how many treatment cycles it can undergo without significant loss in activity or structural degradation.

3. Optimization of Operating Parameters:

   Additional studies should focus on optimizing process variables such as pH, temperature, catalyst dosage, and contact time to determine the most favorable conditions for maximum pollutant removal efficiency.

4. Scale-Up and Field Application:

   The photocatalytic treatment system should be scaled up and tested under real field conditions using larger volumes of produced water to assess its practical performance and economic feasibility in industrial wastewater management.

5. Integration with Other Treatment Methods:

   The photocatalytic process can be integrated with biological, adsorption, or coagulation techniques to achieve a more comprehensive purification process and improve overall treatment performance.

6. Material Modification and Enhancement:

   Future work may involve doping TiO_2 with other metal or non-metal elements (such as Fe, N, or ZnO) or combining it with other semiconductors to enhance its solar-light absorption and photocatalytic activity.

7. Environmental and Economic Assessment:

   A cost–benefit analysis and environmental impact study should be conducted to evaluate the sustainability, energy consumption, and overall economic viability of employing TiO_2–bentonite photocatalysis for large-scale produced water treatment.

8. Water Quality Monitoring:

   Continuous monitoring of treated water quality is recommended to ensure that physicochemical and microbiological parameters meet regulatory standards for safe discharge or reuse.

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