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NOUREEN SAJJAD

SU92-MSCHW-S23-008

FOS

Adsorption Potential of Iron-doped Titania Clay Composite for the Removal of Phenolic Agent from Textile Effluents



SUPERIOR UNIVERSITY

Thesis Submitted to

The Superior University Lahore

In Partial Fulfillment of the

Requirement for the Degree of

M.Phil. Chemistry

By

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Supervisor: Ms Fatima Ashraf

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Department of Chemistry

Signature: _____

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This is to certify that the research work presented in this thesis, titled **“Adsorption potential of Iron-doped Titania clay composite for the removal of phenolic agent from textile effluents”** was conducted by **“Noureen Sajjad”** under the supervision of **“Dr. Rabia Nawaz”**.

No part of this thesis has been submitted anywhere else for any other degree. This thesis is submitted to the Faculty of Sciences, The Superior University, Lahore in partial fulfillment of the requirements for the degree of Master of Philosophy in the field of **“Chemistry”** in Faculty of Sciences at The Superior University, Lahore.

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Dedication

I am grateful to **Allah**, the Most Merciful and Compassionate, for providing me with the guidance, strength, and perseverance to complete this thesis. Without His blessings, I would not have been able to overcome the challenges that came my way. I thank Him for the opportunity to learn and grow, and for the countless blessings He has bestowed upon me throughout this journey. May He continue to guide me in all my endeavors and grant me success in both this life and the hereafter.

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My **siblings, friends**, and my **research fellows** have been a source of inspiration and support. I am thankful for their support, encouragement, and motivation throughout my academic journey.

Last but not least, I want to dedicate this thesis to myself and want to thank me for believing in me. I want to thank me for doing all this hard work. I want to thank me for having no days off.

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Noureen Sajjad

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List Of Abbreviation

WHO	World Health organization
USEPA	United States Environmental Protection Agency
MOEF	Ministry of Environment and Forests
ETC	Electron Transport Chain
FDA	Food and Drug Administration
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-RAY Diffraction Spectroscopy

ABSTRACT

Phenol or phenolic agent used in the textile industries has become a major source of water pollution day by day when discharged into the water bodies. Iron doped Titania was synthesized by co precipitation method and iron doped Titania clay composite by hydrothermal method. Clay provides a high surface area, stabilization and adsorption properties. The prepared composite was studied using various techniques to investigate how they are built and what their characteristics such as surface and structure. SEM analysis was performed to examine their surface features. While X-Ray Diffraction provided details on how the crystals formed, Fourier transform Infrared Spectroscopy was performed to detect or identify the functional groups in the compound. The influence of operational parameters such as adsorbent dose, contact time, initial concentration, pH, and temperature was evaluated in batch adsorption method. The adsorption data was evaluated using Langmuir and Freundlich isotherm models. The kinetic data was analyzed by fitting it to both pseudo-first order and pseudo-second order equation. The results indicated that iron-doped Titania clay composite showed better adsorption potential for phenol removal than iron-doped Titania alone.

CHAPTER 1

INTRODUCTION

The essential element required for all life forms to function on Earth is water. It's safe to acquire that the reason Earth is the only planet where life can exist is because of water. One of our planet's most important resources is this all-purpose solvent. The existence of life would be impossible without water. It is after all nearly 70% of the planet. It is utilized to irrigate approximately 40% of global food crops. However, numerous urban areas are facing water shortage. Our existence is based upon water. Our activities are not complete without water. Water is a essential nutrient for human body. We can survive up to several days without food but not without water. Water is such a strong natural force that it has the ability to shape the piece of land in which we live. A human body is composed of 55 to 60 percent of water. A human body need water to perform body function, all the cells and tissues present in the living body need water to work. Water lubricates the muscles and joints. A vital global health objective is still to provide everyone with access to clean drinking water. Concerns regarding long-term health problems resulting from chemical pollution of drinking water supplied by contemporary water systems are becoming increasingly pressing as availability to drinking water expands. Evaluating the condition of drinking water resources requires an understanding of the risk profiles of various drinking chemical pollutants. WHO provides guidelines for creating regional and national drinking water standards, encourages that these standards be reviewed on a regular basis, and indicates that adjustments can be done easily. Since WHO is not a regulatory agency, its rules for various drinking water pollutants are neither legally binding nor enforceable. Nonetheless, several nations base their drinking water regulations on WHO recommendations[1]. Groundwater is naturally released to the surface in springs and flow, and it is fill again from the surface. For drinking water in low-income nations, groundwater is extremely valuable. Because it is directly exploitable by users, it is more dependable than surface water[2].

1.1 Water Pollution and its Components

When water bodies become polluted, usually through human actions, it's called water pollution. Lakes, rivers, seas, aquifers and groundwater are all types of water bodies.

If pollutants go into the ecosystem, the water gets polluted. Many different kinds of materials can make water unsafe. They consist of carbonic compounds, oil and other related products, heat pollution, heavy metals, problems with water biodiversity, suspended contaminants, bacteria and algae, silts and sediments, wastes requiring oxygen and more. Because many substances like these are toxic to life, they become major factors of water pollution. Most often, surface water pollution starts with rivers, lakes and oceans getting uncleaned sewage and waste from factories and industries. The distribution and activities of aquatic life are affected by detergents and other cleaning products, which alter the pH of the water. Other industries release hot water directly into water bodies, raising the temperature and causing thermal pollution. Nuclear power plants, power generators, and other industries that use water as a coolant are major contributors to thermal pollution, but almost all industries do so to varying degrees. Several studies have also documented bacterial population declines in response to thermal pollution; temperature also influences water's electrical conductance in addition to its oxygen content, heavy metals are essential ingredients for colors and dyes, and they are also utilized in a variety of pharmaceuticals and other industries, excess or unused heavy metals eventually end up in water bodies, exhibiting biological magnification[4]. As the most dangerous inorganic pollutants, fluorides and arsenic are major contributors to groundwater contamination. Yet, there is now growing worry about fluoride in groundwater. It may be set free from acidic volcanic rocks and combined with water if the water is not too hard. Pathogens are contaminants that appear in water due to poor sanitation. In addition, industrial activities may add metals to the soil and cause groundwater contamination. Antibiotics, anti-inflammatory, antidepressants, decongestants, tranquilizers and many other drugs may also cause contamination when used in wastewater. Finally, industrial solvents and activities cause contamination by releasing volatile organic compounds into the ground. Metal is then easy to monitor through the creation of certain rocks that often pass into the groundwater[5].



Figure 1: Sources of Water Pollution

Rapid urbanization and industrialization have caused a large amount of harmful chemicals to be released into the environment through aqueous effluents, destroying ecosystems and endangering human health[6][7]. In terms of simplicity of maintenance and water quality, springs are reasonably priced. Because spring water is cool and fresh, users can accept it. However, the quality of the water that springs release can vary greatly for a number of reasons, including the composition of the colliding rocks and the quality of the water that the aquifer recharges. The duration of contact with the rocks is influenced by the flow rate and the length of the flow path through the aquifer. As a result, certain minerals can dissolve in water. However, in areas where water shortages have occurred, groundwater extraction and rainwater collecting should be implemented. Now, both developed and developing countries are facing the water pollution problems. With the passage of time the water is polluted due to different human activities like mining ,urban development and even some natural phenomenon also responsible for the contamination of water like landslides and floods. Water pollution has become a global issues, and constant examination of water resource policies is required to address it. Water contamination causes death and disease worldwide, with around 14000 people dying every day[8][9][10]. Much of water pollution comes from industry which releases chemicals that pollute the environment, causing various dangerous illnesses. Water is analyzed using factors such as its physical, chemical or biological state to check if it is suitable for a particular use. Should the levels of defining characteristics cross the safe line, it could result in a danger to people's health. Several types of heavy metals present in the waste water of different industries causes many serious problems for living organisms.

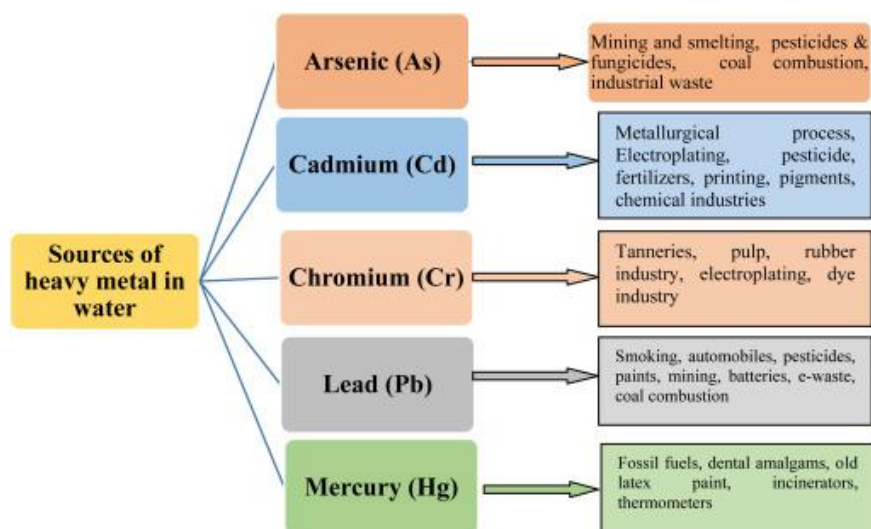


Figure 2: Sources of Heavy Metals

During industry production, a mix of harmful compounds, solvents, different materials and volatile chemicals can be released into the environment. Without proper treatment, releasing these wastes into aquatic habitats will lead to water pollution which can put people's health at serious risk in several ways[11]. Water sources include important carcinogens, including trihalomethane, chromium, nitrate, and arsenic. When chlorine is added to water, carcinogens may be introduced. The complex relationship between drinking water pollution and cancer includes heavy metals, radionuclides, herbicides, pesticides, and chlorine byproducts that end up in the water. One major contributing factor to childhood illnesses is water contamination. Children who come into contact with water contaminated by microorganisms may develop diarrhea illness. Other diseases might result from malnutrition and decreased immunity from diarrhea illnesses.

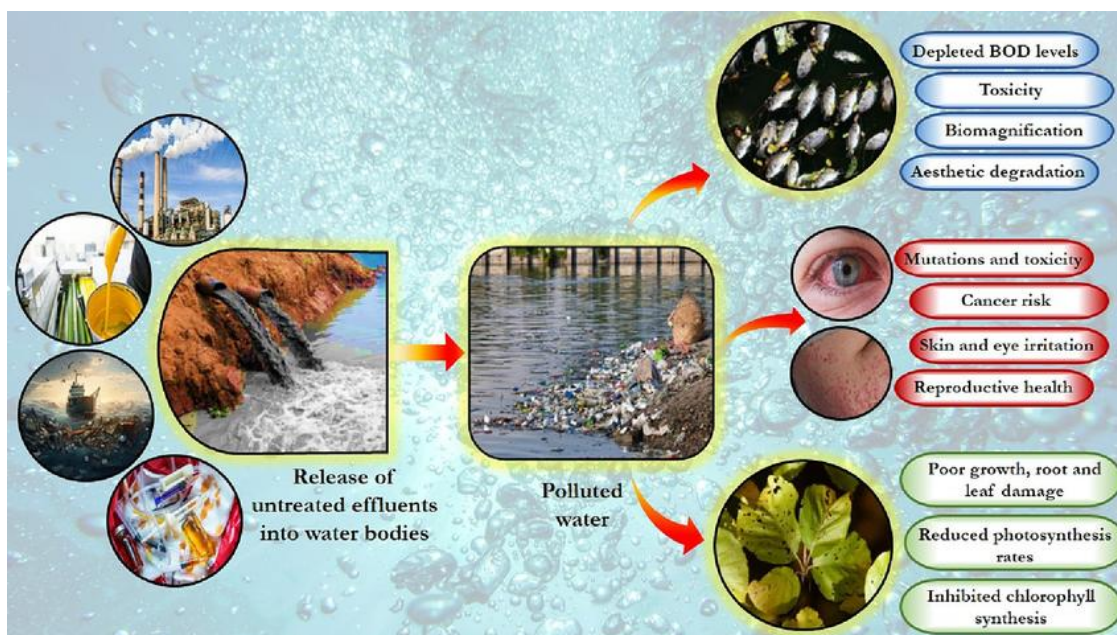


Figure 3: Impact of water pollution on Human beings

Nowadays, a lot of countries work to address environmental issues brought on by industrial waste. Toxic substances, like as Phenols, are contributed by the majority of businesses to treatment facilities or directly to receiving bodies, resulting in significant technical and environmental issues. Phenolic wastewaters are mostly produced by petrochemical industrial facilities, oil refineries, and coke ovens. An important factor in any nation's economic growth is the textile sector.

Textile industry wastewater causes serious harm to our water and soil environment. The chemicals used in dyeing and finishing textiles can be dangerous, as they are carcinogenic, mutagenic, genotoxic, cytotoxic and allergic to living things. As much as fifteen percent of the dye can be lost and ends up in textile wastewater due to the way the process is done. As a result, experts are recommending natural dyes rich in phenolic compounds to improve the circular economy. Phenol is often used in the industrial sector, but it can affect living organisms if leaked into the environment.

Functionalization through phenolic dye processing allows textiles to feature antimicrobial, antioxidant and UV protection. Therefore, hazardous effects on humans, animals and plants at low levels make these compounds classed as priority pollutants among different organic compounds detected in wastewater[12]. Phenolic compounds are mainly found in mine waste, used paints, products made from coal gas, plywood, many medicines, petrochemicals and facilities at steel mills, petroleum

refineries and coke ovens. The area where phenol concentration in wastewater exceeds 1000 mg l⁻¹ most often is coke production. The release of phenolic chemicals by resin plants ranges from 12 milligrams per liter to 300 milligrams per liter. Effluent from wastewater treatment plants must meet a 0.1 mg l⁻¹ floor for phenol to minimize the dangers to human health[13].

Industrial Sources	Phenol Concentration (mg/L)
Paint manufacturing	1.1
Rubber industry	3-10
Leather	4.4-5.5
Ferrous industry	5.6-9.1
Pulp and paper industry	22
Petroleum refineries	40-185
Fiberglass manufacturing	40-2564
Wood preserving industry	50-953
Textile	100-150
Petrochemical	200-1220
Coke ovens (without dephenolization)	600-3900
Phenolic resin	1270-1345
Phenolic resin production	1600
Coal conversion	1700-7000
Biomass-based gasification	772-4630

Figure 4: Different industries effluents contain different ratio of phenolic compounds

It is possible for phenolic compounds in water to negatively influence animals, humans and microbes[14]. The significant efforts are already being used to remove them from water in case of high levels of contamination. These include conventional methods such as ozonation, activated carbon adsorption, solvent extraction, and more advanced technologies such as the electro-Fenton method, membrane-based separation method, biological methods, photocatalysis, and adsorption and ion exchange[15]. Chlorophenols and nitrophenols have been classified as priority pollutants by international agencies like the United States Environmental Protection Agency (USEPA) and the World Health Organization (WHO). Among them are pentachlorophenol, 4-chloro3-methylphenol, 2,4,6-trichlorophenol, 2,4-dichlorophenol, 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 4-nitrophenol, 2,4-dimethylphenol, 2-nitrophenol, 2-chlorophenol, and phenol[16][17][18]. Many phenolic compounds are present in textile wastewater as a result of the use of dyes, finishing chemicals, and other chemical processes.

At the same time, organizations are helping to reduce pollutants when dangerous amounts are detected. Various tasks for dealing with these pollutants are ozonation, activated carbon adsorption, solvent extraction, electro-Fenton methods,

membranes, biology, photocatalysis and adsorption and ion exchange. Many phenolic compounds in textile wastewater are created by the use of dyes, finishing agents and chemical treatments.

1.2 Phenol and its Types

1.2.1 Phenol

Phenol(C_6H_5OH) is a white crystalline aromatic compound and also known as carbolic acid. It is the main compound used in dyeing and finishing processes. Phenol also works as a raw material in the production of synthetic dyes, and also provides long-lasting and bright color.

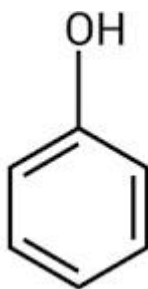


Figure 5: Structure of Phenol

1.2.2 Chlorophenol

Chlorophenols are the organic chemicals in which hydrogen atoms of phenol are replaced with chlorine. 2,4-dichlorophenols and pentachlorophenols are widely used in textile industries for many useful purposes like antimicrobial, preservative properties. Chlorophenols are antimicrobials that prolong the shelf life of textiles by inhibiting the growth of mold, fungus, and bacteria and are also used in textile manufacturing and storage, to shield natural fibers (such as cotton and wool) against insect damage and microbial deterioration.

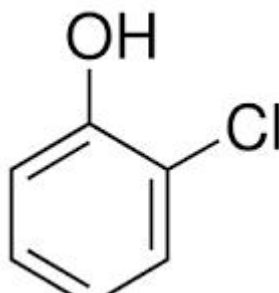


Figure 6: Structure of Chlorophenol

1.2.3 Nitrophenols

2-Nitrophenol and 4-nitrophenol plays a vital role in textile processes like color fixation. Dye production and chemical treatments. Nitrophenols enhance the uniformity and depth of color on textiles by aiding in oxidation processes during dye application. To provide the best possible chemical reactions during dyeing and finishing, several nitrophenols are employed as catalysts or pH regulators in textile processing. Human activities, particularly the production and breakdown of pesticides like 4,6-dinitro-2-methylphenol and 2-buthyl-4,6-dinitrophenol, produce nitrophenols. Along from being starting reagents for the synthesis of polymers, nitrophenols are also utilized in the manufacturing of drugs and in photography.[19]

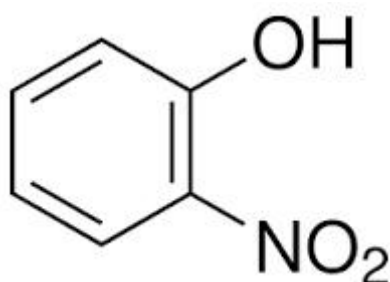


Figure 7: Structure of Nitrophenol

1.2.4 Bisphenols

BPA is a compound used in the manufacturing of resins and plastic. It is a colorless solid. PA is used in textile industry as synthetic fiber production, coating and fiber finishing.

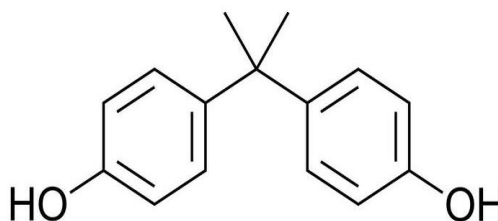


Figure 8: Structure of Bisphenol

1.2.5 Nephthols

Textile processes such as color fixation rely on the presence of 2-nitrophenol and 4-nitrophenol. Nitrophenols support uniform and rich dyeing of textiles by supporting harmful oxidation reactions during the dyeing process. Chemical processes during the creation and finishing of textiles rely on nitrophenols working either as pH balancers or catalysts. People's actions, particularly those related to man-made pesticides such as DNoc and DNoc, produce nitrophenols. As well as being part of polymer preparation, nitrophenols are utilized in the manufacture of medicines and for photographic purposes.[20]

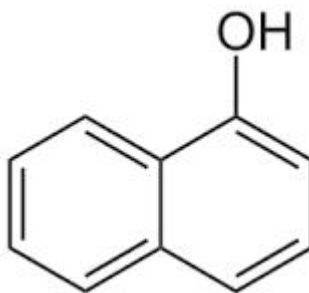


Figure 9: Structure of Nephthol

1.3 Method for Treating Polluted Water

All levels of the initial phenol concentration in phenolic wastes can be reduced using a variety of treatment strategies. Ozonation and carbon adsorption are used for low levels of phenols, physico-chemical and biological treatments for intermediate levels (5–500 ppm), and solvent extraction for high levels (>500 ppm). Adsorption relies on the economics, recycling potential of the necessary materials, and adsorbents and is recognized as an efficient method to remove contaminants from water in a variety of concentrations. The primary type of organic contaminants typically discovered in the subsoil are phenol, which are released by numerous businesses.

The conventional techniques include ion exchange, membrane processes, filtration, ozonation, adsorption and extraction, photocatalytic degradation, biological, chemical oxidation or reduction, chemical precipitation, reverse osmosis, filtration, evaporation, and coagulation[21][22][23].

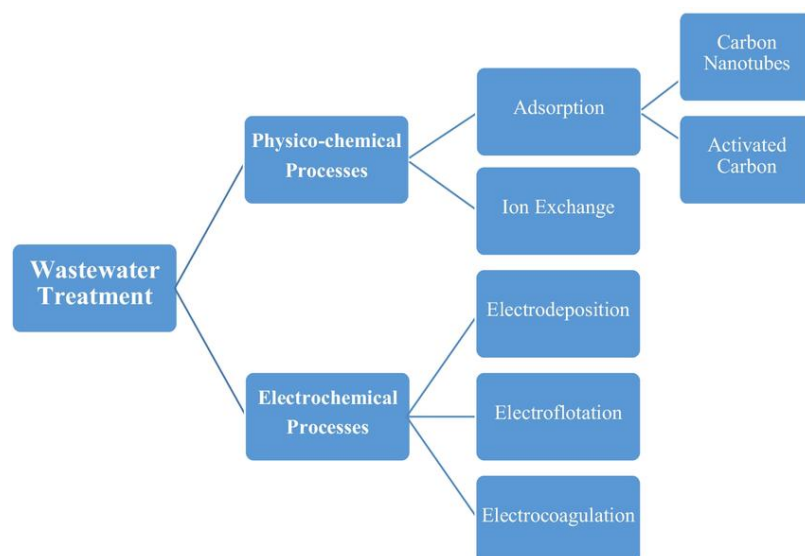


Figure 10: Conventional Methods used to removal industrial effluents

1.4 AIMS AND OBJECTIVES

The main aims and objective of this research work are:

- To synthesize iron doped Titania composite
- To synthesize iron doped Titania clay composite
- To characterize composite by SEM,FTIR,XRD
- To investigate the adsorption mechanism

CHAPTER 2

LITERATURE REVIEW

One of the main issue associated with the environment and human health in Pakistan is the poor quality of the water. The nation's surface and groundwater are contaminated by a variety of harmful substances and microbes[24].The increased number of industrial and other waste products from human activities that are being dumped into the environment is causing the quality of the existing water resources to deteriorate in many areas. How clean surface and groundwater is, the weather patterns and the location's region matter a lot for development, the economy and nature. Many causes, including the expansion of cities, population growth and developing agriculture, are reducing the quality of water[25]. Many countries today are working to solve problems caused by industrial wastes. Much of the industrial sector discharges phenol and similar chemicals to either treatment facilities or to the environment which then creates both environmental and technical problems. Most phenolic wastewater is produced by coke-oven plants, refineries and plants involved in petrochemical manufacturing. Treatment systems exist that can decrease all concentrations of phenol in phenolic wastes. When the phenol present is more than 500 ppm, solvent extraction is used, for phenol levels ranging from 5 to 500 ppm, physio-chemical and biological techniques are applied and for very low phenol (less than 5ppm), ozonation and carbon filtration are processes used. Significant amounts of industrial wastewater from the textile industry reach the environment and much contains materials that are harmful to people. What comes out of industrial processes can be very harmful. When hazardous materials are released into the environment, they begin to travel, pollute fresh places and bring health problems[26]. Among the many sources of phenolic pollutants are bis-phenol A (BPA), 2,4-dichlorophenol (2, 4-DCP) and phenol. The environment and human health can be seriously threatened when waste phenol is not purified before it is released[27]. Air and food contamination account for most cases of humans being exposed to pollutants[28][29]. They come in a range of sizes and appearances and the alkali and alkaline earth metal cations they contain are spread all over the world [30][31]. Because of their good conductivity and structure, high porosity and availability, clay adsorbs CPs better than other materials. There are 19 unique congeners in CP model organisms. Chemists use CPs as flexible intermediates in synthetic reactions and the structures in CPs are

easy to oxidize. Examples of intermediates employed in the synthesis of higher CPs, especially TCP, are 2-CP, 2,4-DCP and 2,4,6-TCP. Moreover, because of their antibacterial functions, TCP, TCP and PCP are mainly applied in the textile, pulp and paper, leather tanning and wood bleaching industries. Even in extremely low concentrations, the effluents produced by these businesses are easily noticeable. The introduction of these materials into aquatic environments not only compromises their aesthetic qualities but also blocks solar radiation, which in turn impacts the food chain that exists within these ecosystems[32]. Adsorption is the most dependable and effective method for decolorization among the various water treatment techniques available. It offers the unique benefits of not producing any toxic sludge and being reasonably priced, as well as the ability to recover and recycle the adsorbent materials. This has prompted the creation of affordable and widely accessible adsorbents. These days, a wide range of inexpensive adsorbents are accessible, including agricultural byproducts like apple, sugarcane, wood dust, fruit peel, and wheat straw[33][34]. A textile dye from the triphenylmethane dye class, phenol red is very water soluble. It is a red crystal that is soluble in 0.77 g/L of water and stable in air[35]. Because phenolic compounds are used in so many important aspects of our daily lives, there has been a lot of interest in their research. Insecticides, foam, adhesives, emulsifiers, detergents, colors, explosives, rubber, and resins are all made with phenolic compounds. In several industries, such as the printing, leather, textile, pulp mill, paper, dyeing, food, and plastics sectors, phenolic compounds are also very important economically[36]. Soils and sediments contain phenolic chemicals, which contaminate groundwater. There are significant levels of phenolic chemicals in the wastewater from several chemical factories. One of the most well-known substances that are produced both naturally and by humans in the environment is phenolic compound. In addition to being poisonous and causing allergies and skin irritation, these substances are carcinogenic and seriously harmful to living things[37]. Human activities, particularly the production and breakdown of pesticides like 4,6-dinitro-2-methylphenol (DNP) and 2-buthyl-4,6-dinitrophenol, produce nitrophenols. Along from being starting reagents for the synthesis of polymers, nitrophenols are also utilized in the manufacturing of drugs and in photography[38]. The interaction of nitrite ions with phenol in water produces nitrophenols, particularly 2- and 4-nitrophenols. Additionally, nitrophenols are produced in the atmosphere by environmental processes [39]. Among the dangerous compounds found, phenol

stands out as a notable example due to its carcinogenic qualities. The wastewater from resin facilities had phenol concentrations between 12 and 300 mg/L, while the wastewater from coke processing had phenol concentrations as high as 1000 mg/L[40]. The USEPA has established that drinking water is not to exceed 0.001 mg/L in phenol concentration[41],[42]. The concentration of phenolic compounds in wastewater should be accurately checked and all these compounds should be removed during the production, treatment and releasing phases. The World Health Organization specifies that filtration should remove phenol when its level is below 0.1 $\mu\text{g L}^{-1}$ (ppb). The Ministry of Environment and Forests (MOEF) places the highest allowable level for industrial effluent and surface water at 1 mg L^{-1} [43][44]. Numerous techniques are used to take out phenolic compounds from water. Among the frequently used techniques are extraction, activated carbon adsorption, steam distillation, electrochemical approaches, radiation, advanced oxidation, chemical oxidation, adsorption and biological treatment. However, removing waste water contaminants with these approaches can be challenging because they are costly, need extra filtration afterwards, may form hazardous compounds, work poorly and are only useful when contaminants are within a restricted range [45][46].

A major natural resource that so many people depend on is water. The increase in industrialization across the globe is the main reason many businesses create liquid waste which has caused the levels of natural water in water bodies to decrease[47]. The use of different manufactured colorants and the large volume of highly colored waste liquid released by the textile industry impact the photosynthetic function of aquatic and plant life[48].

Due to the lengthy re-oxygenation process caused by synthetic dyes, intensely colored waste liquid is released into water bodies, severely harming plants' photosynthetic function and affecting aquatic life. Additionally, chlorine in industrial wastewater has an adverse effect on marine life[49]. Textile companies generate liquid waste and employ a variety of techniques. Because diverse procedures and mechanisms are used on fabrics, the waste liquid configuration generated by these methods varies wide. In general, textile industry wastewater are categorized as mixed efflux. Nonetheless, it is preferable to handle chemicals and water separately while maintaining the streams' separation by using the retreat motivation. The process of stream separation is crucial to the design of wastewater from the textile industry. Among the various organic pollutants in sludge, chlorophenols (CPs) need more

attention because they are serious threats to people and the environment. Since CPs are good intermediates, they oxidize easily to give important substances in chemical synthesis. For example, 2-CP, 2,4-DCP and 2,4,6-TCP all play intermediary roles in making TeCP and PCP. Most TCP, TeCP and PCP is used in the textile, pulp & paper, leather tanning and wood bleaching industries, thanks to its antibacterial abilities[50].

The risk of phenols toxic to human health has increased international care for managing environmental phenols. The levels of several important phenolic compounds were examined in the wastewater and water of textile firms in Abeokuta, Nigeria. I produced 5 TIE dyes for each of my 5 samples. Testing samples according to temperature, pH, conductivity, suspended and dissolved solids found the WHO limits for pH, pH and conductivity were surpassed, while TSS and TD were below and samples were found to be less than half within the limit. The targeted phenolic compounds were found in greatest amounts in wastewater and their levels of -nitrophenol were too small to be measured in water samples. All of the nitrophenol concentrations in waste were much higher than both the WHO standards (0.01 mg/L) and the values seen in water samples. The elevated phenol counts in the local water suggest wastewater from the textile sector is being released without regulation[51].

People's health issues with phenols have fueled worldwide concern for environmental management. This work showed the amounts of three main Phenolic compounds found in both the wastewater and industrial water from the textile industry in Abeokuta, Nigeria. While producing -TIE dyes, we gathered samples three times, so we had a total of 5 samples. The parameters of temperature, pH, EC, TSS and TDS for the samples were tested using chromatography and the results showed that the water and wastewater pH, EC and TSS were above what WHO and FED allow, but the borehole temperature and TDS remained acceptable. Many types of Ty-phenol compounds were found at elevated levels in wastewater, while nitrophenol was reduced down to the highest DE limit in water samples. Both waste and water samples tested above the maximum concentration designated by WHO (0.01 mg/L) for -nitrophenol, -chlor-3- methylphenol and 2.-dinitrophenol. A high level of phenols in water used by the local textile industry means that unmanaged waste could end up harming surface and groundwater, possibly delivering health benefits to local people[52].

Industrial sewage often contains pollutants, with phenol chemicals

damaging both people's lifespan and the ecology. In this study, complexes formed when phenol and -nitrophenol in the solution were adsorbed onto local materials (coconut cover and sound). X-ray energy spectroscopy, scanning electron microscopy, Fourier transform, X-ray, nitrogen adsorption and desorption tests were performed on the activated composites, together with pH tests. The capacity for adsorption by sorbents was examined using time, temperature variations, pH and combined procedures. In addition, the adsorption models involve the following: pseudo-first, pseudo-second, general, avrami and intraparticle diffusion and the option to add a thin film. Using the Avrami Congressional Group rules and the Li-Isotherm, the model fitted the experimental results of phenols and -nitrophenols very well. The highest adsorption that the Liu-isotherm predicts is 1665 mg g⁻¹ (25°C) and 76.9 mg g⁻¹ (30°C) of phenol or -nitrophenol. Adsorption was exothermic and resulted spontaneously. No less than 86% of the two kinds of simulations were blocked by the composite. Therefore, the network has potential for industrial wastewater treatment [53].

If there is significant toxicity, phenol must rapidly remove water from the soil. This study analyses the way fixed waste from quarrying plants is used to extract phenols from wastewater. The solid waste was heated to 105°C for the characterization. The scientists performed adsorption tests using different values for phenol concentration, adsorbent mass, contact time, temperature and pH. The sample reached a balance at pH 7.5, doing so in hours. At ambient temperature, initial concentrations of 50, 100, 150, 200, 200 and 300 mg/L with 1 g of adsorbent gave weight values of 8.1, 13.3, 16.2, 20.2 and 28.1 mg/g in the phenol record. The Langmuir model is satisfactory, but the friendly model has gone beyond it. It was found that pseudo-circuit regulation was the best motion model for describing phenol adsorption. Endothermic adsorption was used in was. The study allows for the development of useful applications using waste from Stein Cutting Edge as an effective adsorbent to clean up phenol. Previously, there were no studies done using this particular method to remove phenol from wastewater. The amount of fixed waste comes from materials that are fully biodegradable and affordable for the adsorption action [54]

We report on the use of flexible photocatalytic composites for the destruction of contamination from -chlorophenol (-CP). These composites consisted of food packaging in recycled bags (RBAG) or recycled poly styrene (RPS) and

CUST/TiO₂ (cust) nanoparticles. Structural and morphological characterization shows that the average size of the cust nanoparticles is 1 ± 2 nm and has a mixture of Anat-Blue-Kit phases. CUST/TiO₂ powder was distributed in water at -CP, and generated the maximum decomposition share of 92% TER for hours under UV-VIS radiation. With RBAG- CUST and composites, they were shown in contaminated water, producing a maximum reduction of %, 89 and 100%. After 3 cycles of continuous use, mining rate returned from 89 to 81% to 92 to 8%, and 100-95% with CUST/TiO₂ powder, RPS-CUST or RBAG--SORGE composition. Schnitzel's experiment was carried out and found that the major oxidation decomposition of -CP is • OH Radical. RBAG- CUST> CUST/TiO₂ POWDERS> Production of such radicals in RPS-BUF. RBAG Cust was efficient due to -CP failure, as was the highest in oxidant production and contained more oxygen beef defects (electron-catch centers) than other photocatalysts confirmed by absorption measurements. The production of flexible photocatalytic materials from general recycled bags/polystyrene has shown to be a feasible and inexpensive option for removing pesticide contamination from drinking water. These composites can be manually removed from the washed water, which is not possible with traditional photocatalytic powders [55].

Using CCD as its base, the experiment was developed, studied and modeled by Answer Surface Method (ASM) to demonstrate the interactions of four elements with each other in the finished product. At the sixth basic monthly analysis, the pH wasn't changed and only the adsorption the contained the best phenolic compounds was used. The correlation factor for bisphenol A is 0.96 and it is 0.75 for pentachlorophenol. The best results were found with pH at 6, a level of adsorption of 0.2 g/L, contact time of 65 minutes and 0 mg/L of phenol. Under those conditions, the distance efficiency of pentachlorophenol and bisphenol A from the adsorbent was found to be 93.1% or 87.06%. The outcomes suggest that the modified adsorbent can reach full efficiency in removing phenolic compounds at both full equalizer and pseudo second rates. It was discovered that using modified absolvent could result in good separation distances for phenolic compound compounds. The adsorption method can be applied to wastewater from the petroleum and petrochemical sectors that has phenolic compounds. Using thermodynamic and kinetic methods, we studied pentachloro phenol and bisphenol. Central Composite Design (CCD) is used. What a producer or product performs or responds to [56].

It was found that the FABRA-ion of silver anopatil (AGNP) is more

effective in biosynthesis than competing approaches. For this reason, the present study examines the creation of AGNPs using coffee waste extract. CWE includes a range of HPLC-identified components that help solve issues, control CAPs and stabilize AGNPs. The AGNPs were produced as 20 nm features and revealed idioplasmic resonances inside hexagonal nanoplates. Both physical techniques and spectroscopy confirmed that the AGNPs' hexagonal shapes are on the nanoscale. Using ASTIDED AGNP (12 mg) produced efficient photo mining of PHENOL connections (20 mL) at ~96% with good distance efficiency even with citric acid in the mixture. Also, more than 97% of 2.DNA hazard was removed when using only 7 mg of AGNP in the experiments. On top of that, green agNPs can help protect *B. acte* and *B. subtilis*, *P. aeruginosa*, *s. aureus* and *E. coli*. Most microorganisms that are infected are responsive to inhibition. A three-electrode system was used to analyze the electrochemical behavior of AGNP. Specific capacity was calculated at 280f g⁻¹ for a charge of 0.56 a g⁻¹. The AGNPS electrode continues to show excellent stability at 9.8°C after 1000 cycles at 2.2 Ag⁻¹. Based on what we have observed so far, we can say that CWE is an environmentally sound extract, low in cost and saves money while supporting the large-scale growth of photocatalysts, phenolic connection movements and functional nanodevices [57].

At first, phenol and its connected compounds are safe in water and are the main source of health issues. This report investigates using carbon from pomegranate shells to remove phenols by the process of adsorption.

First, phenol solutions at concentrations from 10 to 100 mg/L were prepared in 2016. Then, the effect of pH at 505 nm was studied. Additionally, a sample from the Isotherm model by Langmuir and a friendly compliance and descriptive approach by Excel 2016 were both used. The highest amount of copper adsorbed was 18.38 mg g⁻¹ at pH 7, 100 mg L⁻¹ copper and a temperature of 23 ± 2°C. As a result of the trial, R2 0.9056 shows that the pomegranate pine cone adsorption data fits with the research findings [58].

Activated carbon from *Borassus aethiopium* and bamboo fibers was produced by chemical activation of Optimal preparation conditions were examined according to the experimental design of Hadamard. From the results, only chemical products affect the adsorption capacity of activated carbon. Two activated carbons (BPAC and ACB) exhibited better properties with iodine and methylene blue adsorption capacity of 655.5-627.7 mg⁻¹ or 329.5-7.7 mg.g⁻¹. These activated

carbons have a significantly higher carbon percentage (65.78% and 52.2%). adsorption experiments were performed with 2.-dimethylphenol (2.DMP) (Konan et al., 2020), the molecule selected as the model contaminant, to assess the properties of these two activated carbons. Kinetic data were appropriately adjusted to a pseudosecond order model with a correlation coefficient $R^2 = 1$. friendly model describes $R^2 = 0.99$ in CAR and 0.98 in CAB) increase in adsorbent concentration of . With an aqueous solution[59].

The issue of phenolic compounds in waste-water, in particular that of waste filled with phenolic compounds such as waste generated from textile industries, has gained much importance since they are toxic, carcinogenic and persistent. These have been detected within effluents from dying, finishing and treating processes, including phenol, chlorophenols, nitrophenols and bisphenols. Phenol is one of the main organic pollutants, which is widely used in dye industry and is raw material for many industrial processes. Even in trace amount, its presence in aquatic environment is not desirable as it not only alter the aquatic ecosystem but also bioaccumulate in tissues of organism and have potential to cause severe health problems for human. Concentration is being focused on the removal of phenolic compounds from the environment by sustainable and efficient methods, especially adsorption. It is difficult to biodegrade phenolic compounds because of their stiff aromatic structure and the intermolecular hydrogen bonding, which makes phenolic chemicals stable in water. They are very water-soluble and are resistant to the natural transforming ability of the environment, thus leading to their occurrence in the surface and groundwater. The World Health Organization (WHO) and Environmental Protection Agency have placed sharp limits on the phenol concentration in drinking water and industrial effluents: 0.001 mg/L and 0.1 mg/L , respectively[60]. Nevertheless, untreated industrial discharges have been shown to have levels ranging from that of 12 mg/L to over 1000 mg/L , all well above these limits. To solve this problem a number of treatment approaches have been introduced. Traditional methods include chemical oxidation, biological decomposition, and membrane filtration. of these adsorption has received more attention for its simplicity, low cost and higher efficiency. Adsorption is the process in which a solid (adsorbent) attracts and holds a compound on its surface[61]. The sorption capacity is the amount of adsorbate (target species) adsorbed and depends on several factors including the specific surface area, porosity, particle size, surface charge, and functional groups of the adsorbent. Clay in

natural and modified forms have become the preferred low-cost adsorbents because of their high surface area, high capacity of ion exchange and their environmental abundance. Clay minerals such as bentonite, kaolinite, and montmorillonite are layered structured materials, which have exchangeable cations and are widely used for adsorption of variety of pollutants including phenols. Some recent works have shown that the functionalization of these clays based on metal oxides like TiO_2 can improve adsorption and photocatalytic features.

Titanium dioxide has so far been a typical photocatalyst for environmental purification. It has great stability, non-toxicity, and high photocatalytic activity towards under UV light. Although, the activity of ZnO is restricted to UV light due to its wide bandgap (3.2 eV). To address this, doping of TiO_2 with transition metals, such as Iron (Fe) has been reported. Fe-doped TiO_2 (FeTiO_2) demonstrated enhanced photocatalytic activity through the enhanced visible light absorption and the reduced electron-hole recombination[62]. The coexistence of active sites also results in high structural stability, surface dispersion and recyclability of the composite FeTiO_2 when it is combined with clay. Iron-doped TiO_2 -clay composites have been shown by a number of workers to have advantages. For instance, FeTiO_2 /clay composites have been found to have better adsorption capacity and adsorption kinetics than that of pure clay, or of TiO_2 stand alone. The introduction of Fe increases the redox potential and the surface charge of the composite, thus increasing the electrostatic attraction and hydrogen bonding between phenolic compounds and the composite surface. In addition, due to the presence of the clay, an efficient matrix is formed for the anchoring of TiO_2 NPs, avoiding agglomeration and enhancing dispersion in aqueous medium. Techniques such as FTIR, XRD, SEM are many of the characterizing techniques that are imperative to understand the structural and chemical properties of the composite. According to the FTIR spectra characteristic peaks of O–H, Ti–O, Fe–O, and Si–O groups, are observed and it presents the successful creation of the composite[63]. XRD patterns confirm the crystallinity and phase purity of the TiO_2 and clay compositions, and SEM images directly exhibit the surface features, the dispersion of the particle size, and the porosity of a material, which are important factors affecting the adsorption of the material[64].

The impact of pH, contact time, temperature, initial concentration of phenol, and adsorbent dose on adsorptive removal of phenol has been investigated through

experimental studies. The surface charge on the adsorbent and the extent of phenol ionisation are greatly influenced by the pH of the solution. In an acid medium (pH 2–6), phenol is present largely in its neutral state, promoting the interaction between phenol and the negatively charged adsorbent surface. On the opposite side, at higher pHs above its pKa, phenol ionize to phenolate ions which can be repelled from the same charged surfaces against decrease in adsorption rate. The time of contact is an important factor in adsorption kinetics[65]. Virtually all of the studies show with optimal conditions that the initial 30–60 min is characterized by rapid adsorption followed by a plateau as equilibrium is approached. This is due to the abundant active sites at the beginning are gradually filled up. Volume-dose of the adsorbent is normally expected to enhance removal efficiency by increasing adsorption sites; however, at high level, agglomeration of particles tends to lower the available surface area and impede mass migration.

The temperature also plays a significant role. Phenolic compounds are also generally endothermic on adsorption, increasing temperature could increase the removal efficiency due to higher molecular mobility and diffusion rate. Determination of Sign of ΔG Thermodynamic result of thermochemical studies usually shows the positive (+ve) value of ΔH , showing the process is spontaneous and feasible at high temperature. Also, a higher initial phenol concentration per volume enhances the mass transfer driving force resulting in an increase removal, until saturation of biomass occurs. It is a general trend that the addition of clay to FeTiO₂ improves both the capacity and kinetics in contrast to FeTiO₂[66]. Iron doping with clay incorporation exhibits a synergistic effect in the composites and it can remove at least 70–80% phenol in 1 h under optimized conditions. The adsorption capacity of FeTiO₂/clay in pH 2 solution was as much as 68.54 mg/g, superior to 52.89 mg/g for FeTiO₂. These results verify that integrating both photocatalytic and adsorptive capabilities into one composite material stabilizes the overall pollutant removal efficiency.

CHAPTER 3

METHODOLOGY

3. Materials and Methods

3.1 Chemicals



HCl



Titanium oxide



Bentonite(clay)



Iron nitrate

- Sodium Hydroxide (NaOH)
- Iron sulphate
- Distilled water
- Phenol
- Chlorophenol

3.2 Apparatus

Weighing balance was used to weigh chemicals and , pH meter (pH-720, Heraeus, Germany) was used for pH measurement of solution, magnetic stirrer hot plate (BS-3H, Jiangsu Jinyi, China), an electric oven (D-6450 Hanau, Heraeus, Germany), and an electric grinding machine (YF 188, MEPCO, Pakistan), pestle and mortar, beakers, flask, petri dish, electric grinder, spatula were used in this research.

3.3 Synthesis of FeTiO₂

The Iron doped Titania was synthesized by co-precipitation method. To prepare iron doped Titania composite 2.37g Titania was added to 20 ml of distilled water and then stirred at room temperature for 30 min. Then 0.303g iron sulphate was added in 20ml of distilled water also and stirred for 30min at room temperature. After mixing both solutions, checked the pH of the solution. Set the pH of solution basic. Afterward the solution was filtered, washed and then placed the slurry in the oven at 100°C for drying. In the end, the dried product was placed in the jar and used when required for experiment[67].

3.4 Synthesis of FeTiO₂/Clay Composite

The iron doped titanium composite was synthesized by the hydrothermal method using titanium oxide, iron nitrate and clay as materials. Before using , the clay was cleaned, crushed and mixed in 150 ml of ultra-purified water, then mixed

1.5g of titanium oxide and 0.11 g of iron nitrate. The reactants were fully dissolved since the mixture was stirred and stored at room temperature. After stirring, we divided the amounts of clay in different amounts (i.e. 0.05, 0.25, 0.5, 2.5 and 5g), then we added these to the prepared solution under strong stirring for 2 hours. Then, the solution was placed in an oven at 150°C for 24 hours for hydrothermal treatment. After that, for further removal of moisture, the obtained product was put in the oven at 150°C for 1 hour. An electric grinder was used to finely grind the dried product and was stored in a jar for experimental use[68].

3.5 Characterization of composites

Characterization is used to study the physical properties, internal structure, internal properties, shape, and morphology of the specimen. The composite were characterized by XRD, FTIR, and SEM techniques to investigate the crystal structure, functional groups, and surface morphology of composite respectively.

3.5.1 X-ray diffraction (XRD)

The crystal structure of the iron doped Titania clay composite was identified and confirmed by XRD. The degree of inter-facial interaction between the metal oxides was also be ascertained by XRD analysis of the composites. This was conducted by using a Rigaku-2400 diffractometer with Cu-K alpha radiation at 30mA 20kV. The XRD data analysis was done by Origin pro software. We determined the phase angles, density, shape and crystal size from this software.

3.5.2 Scanning Electron Microscopy (SEM)

SEM was utilized to examine morphology and structure of the iron and doped Titania clay composite. SEM can identify the material surface morphology at the nanoscale, including the size and shape of its pores. The SEM model joel-JSM-5910, Japan was used for image analysis of composite. The shape and size distribution of the iron doped Titania clay composite was visually confirmed by the SEM pictures, hence a proof of the successful synthesis.

3.5.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a primary technique used for obtaining the infrared spectrum of a solid, liquid, or gas absorbance, emission, and photocatalytic activity. It was used to identify the functional groups in the composites. The FTIR was performed according to the instruction of instrument with a frequency range 500 to 4000cm⁻¹ and a wavelength range of 600nm to 20μm. The FTIR spectrometer offered extensive

coverage for analysis. It is an advanced analytical method to determine the infrared spectrum of materials. It detects vibrations of chemical bond inside the molecules when subjected to infrared light. FTIR is non-destructive, rapid, and efficient method for analyzing the nanoparticles, particularly metal oxide based on their unique bond vibrations.

3.6 Removal of Phenol and Phenolic agents from the wastewater

The composite Iron doped Titania with clay and without clay were used to remove phenol and phenolic agent (chlorophenol) from the wastewater. The experiment was conducted in a batch mode. To form a stock solution of phenol with concentration of 1000 ppm, 1 g of phenol was carefully added in 100 ml of distilled water, and marked upto of 1000 ml. By using dilution method, standard solution was prepared from the stock solution. Following the dilution method 20, 40, 60, 80, and 100 ppm solutions were prepared, then saved the residue for further use. Same method was repeated for the preparation of stock solution of chlorophenol with concentration of 1000 ppm in 1 g of chlorophenol.

3.7 Optimization of the adsorption process

Optimization of adsorption process involved adjustment of the various parameters and conditions such as pH, temperature, dose and concentration to enhance the efficiency and effectiveness. This optimization was crucial for efficient removal of contaminants from both composite, hence improved the performance of adsorption system, and reduced the operational cost. The adsorption capacity of composite were studied under different concentrations where the agitation time, pH, speed of stirring, phenol and chlorophenol concentration remained constant. All these parameters were investigated through the same optimization process.

CHAPTER 4

RESULTS

4.1. Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a method used to identify the functional group in the compound, examine the molecular structure, and validate chemical synthesis. The peaks in FTIR graph showed stretching of O-H, C-O at different ranges. It gave information about composition of samples. FTIR spectra were obtained in the range of $4000\text{--}500\text{cm}^{-1}$. Different peaks of $\text{FeTiO}_2/\text{Clay}$ composite were shown in the graph i-e at 3626 , 1633 , 989 , 903 , and 639cm^{-1} . The structural hydroxyl groups in the clay matrix exhibited an O-H stretching vibration, which was represented by the strong absorption band seen at 3626cm^{-1} . It showed that even after iron doping and inclusion with titania, the clay maintained its basic layer structure. The absorption band at 1633cm^{-1} was due to the H-O-H bending vibration of water molecules that have been adsorbed on the clay matrix's surface or in its interlayer gaps. The peak at 989cm^{-1} indicated the possible chemical bonding between Titania, iron and clay. The peak at 903cm^{-1} showed the Fe-OH bending, the clay structure was preserved due to structural hydroxyl groups linked to iron, hence did not change even after iron doping and titania insertion. The peak at 639cm^{-1} showed the presence of TiO_2 .

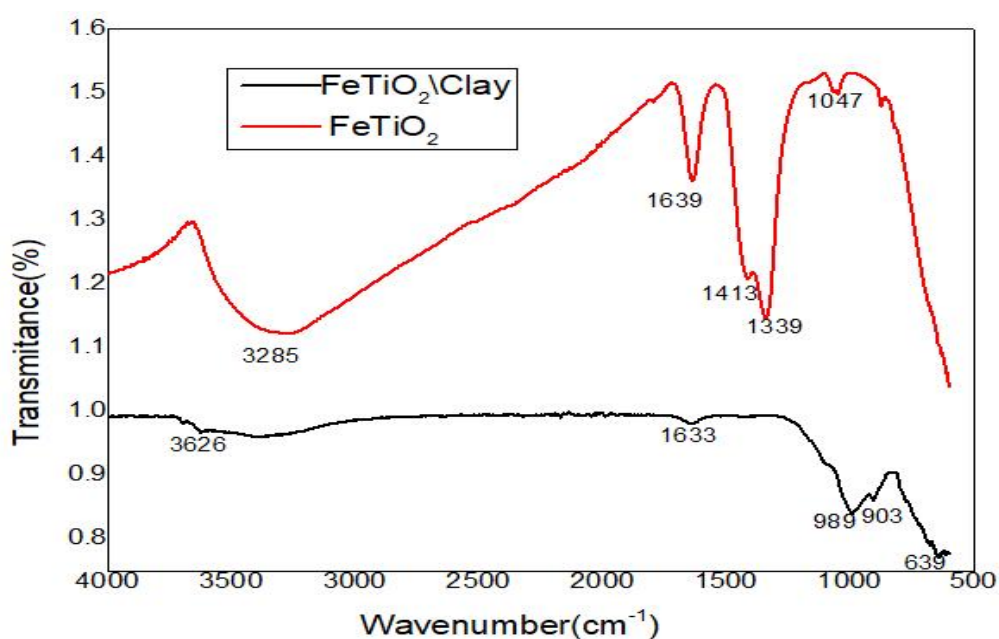


figure4.1 shows FTIR spectra of FeTiO_2 & $\text{FeTiO}_2/\text{clay}$

4.2 Scanning Electron Microscopy

SEM is a powerful imaging technique that uses a focused electron beam to scan a sample and detect secondary electron emitted from the surface to examine the surface morphology and micro-structure of the materials at high resolution. It provides a detailed information about particle size shape and distribution. The composite $\text{FeTiO}_2/\text{Clay}$ was examined on different nano scales, at 500nm, 5 μm , 2 μm , 10 μm . The SEM images of $\text{FeTiO}_2/\text{Clay}$ showed fine and even structural distribution of composite which was 32nm.

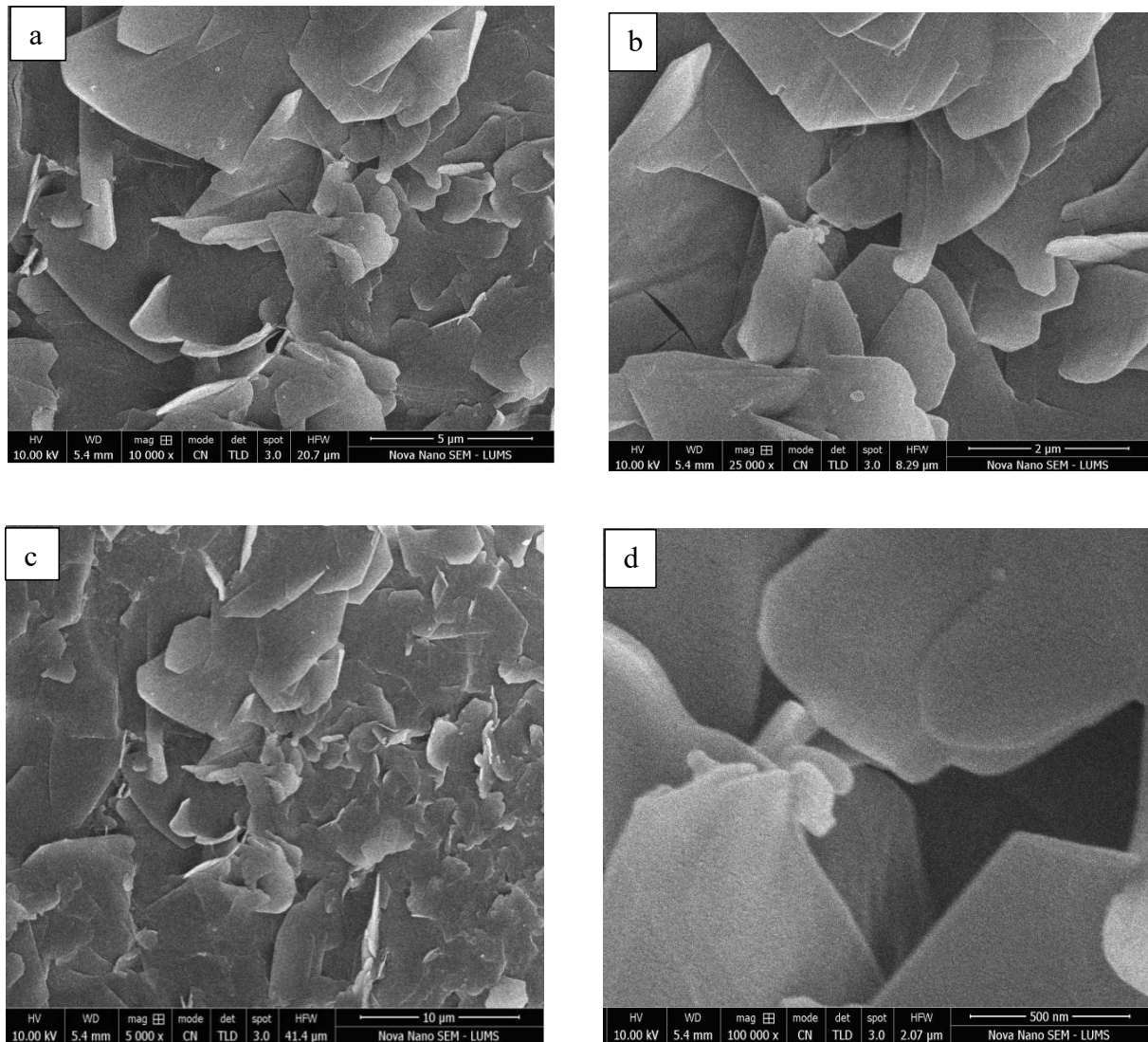


Figure 4.2: Figure (a),(b),(c) and (d) shows the SEM images of $\text{FeTiO}_2/\text{clay}$ composite at 2 μm , 5 μm , 10 μm , 500 μm respectively.

4.3 X-RAY Diffraction Spectroscopy

XRD is a method that measures the angles and intensities of X-rays that are diffracted by a sample in order to determine the crystallographic structure of that material. The sharp peaks showed high crystallinity and the slight peaks showed the nano-sized particles. It is used to identify the type of material and the arrangement of its atoms. XRD spectra showed the phase integrity and crystal structure of $\text{FeTiO}_2/\text{clay}$ composite. XRD diagram of these composite $\text{FeTiO}_2/\text{clay}$ synthesis showed five to six peaks at (100),(210),(211),(320),(014),(440). These peaks showed successful formation of different crystallographic planes of $\text{FeTiO}_2/\text{clay}$ composite. The highest peak(210) indicated the dominant orientation in the crystal structure. While the other peaks showed the multi-phase crystalline nature of the composite.

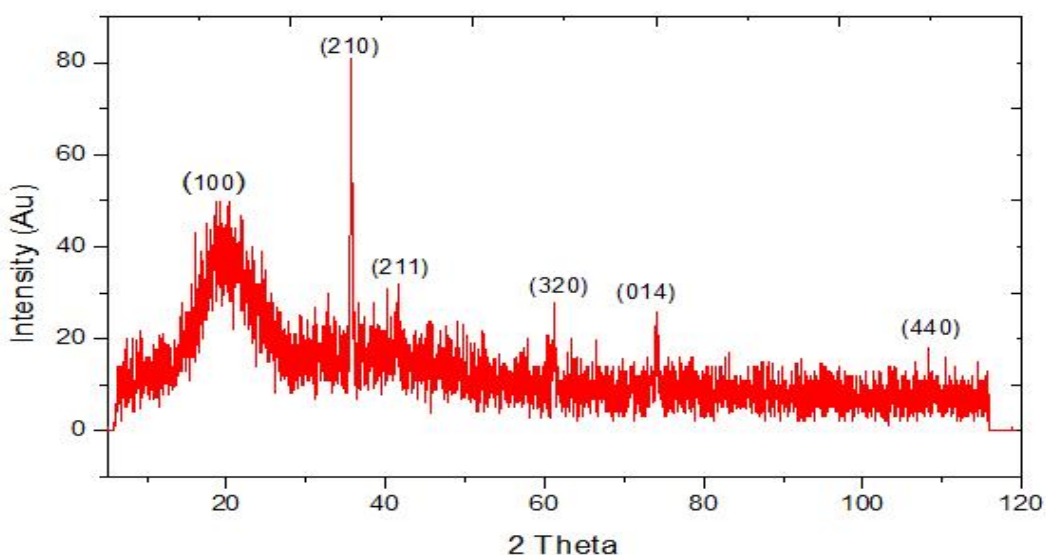


Figure4.3: shows XRD pattern of $\text{FeTiO}_2/\text{Clay}$ composite

4.4 Point Of Zero Charge

The point at which the positive and negative charges on an adsorbent's surface are the same is called the point of zero charge (PZC). At this stage, there are equal amounts of positive and negative charge along the surface and so the matter is neutral. It estimates how surface materials react with the environment. It lets us learn about the movement and bio-accessibility of pollutants in soil and water. For positively charged surfaces, chemical attraction only happens if pH is below the zero charge and for negatively charged surfaces, attraction happens if the pH is above the zero

charge. The points corresponding to zero charge for FeTiO₂clay and FeTiO₂ were shown at 6 pH and 5 pH respectively. The surface charge (4.90, 6) of the adsorbent was determined by the point of zero charge.

When pH is less than zero, mineral surfaces collect positively charged ions and they release positively charged ions when pH exceeds the point of zero charge. The charged solute molecules may experience repulsive or attractive electrostatic forces as a result of the surface charge, which could decrease or increase adsorption. While an adsorbent with a low pH_{PZC} value release protons into solution to create net negative surface charges, an adsorbent with a high pH_{PZC} value has a tendency to adsorb protons from solution.

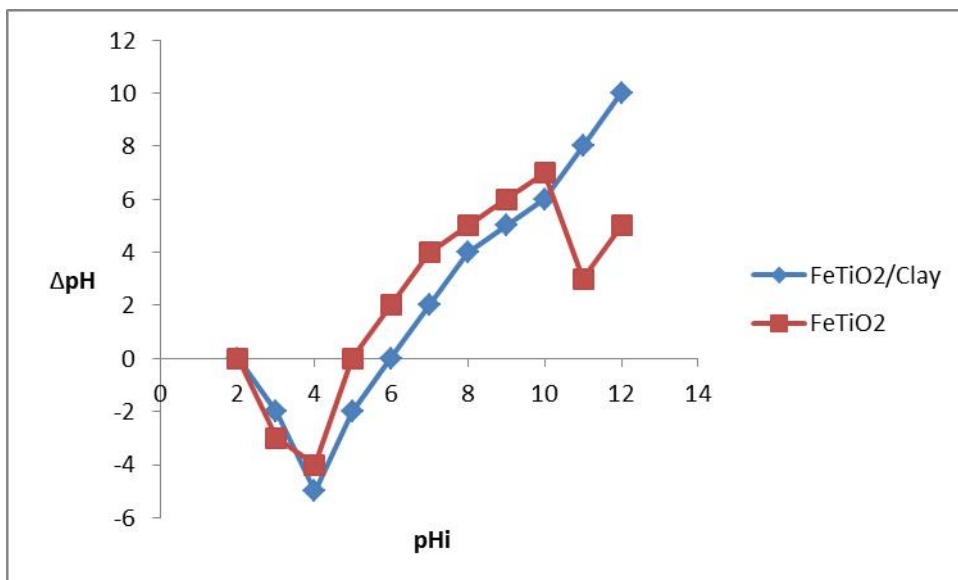


Figure 4.4: Point Of Zero Charge of both materials

4.5 Effect of pH

It was found that the adsorption efficacy of FeTiO₂ and FeTiO₂/Clay composites was more efficient at acidic medium and gradually reduced as the medium changed to alkaline. The adsorbent surface charge and ionization of the phenol and chlorophenol molecules can be explained by this behavior. FeTiO₂ and FeTiO₂/Clay have their surface likely to be positively charged in the acidic medium, as a result of protonation of the surface hydroxyl. Simultaneously, the phenolic compounds are mostly maintained in their neutral form of molecules (undissociated OH group). Electrostatic attraction between the positively charged surface and weakly polar molecules of the phenolics increases the adsorption. Conversely, when

under the alkaline conditions, phenol and chlorophenol are likely to deprotonate to become phenolate anions. Another effect is negatively charged adsorbent surface caused by the deprotonation of the surface hydroxyl groups. The result is high repulsive electrostatic forces, thus decreasing the efficiency of adsorption in basic medium.

Clay minerals, montmorillonite or kaolinite, are very porous in nature, with a large specific surface area. With a mix containing FeTiO_2 and clay the nanoparticles were not agglomerated on the clay surface but were dispersed well. This dispersion increased the number of active sites available to adsorption and this gave a larger number of phenol and chlorophenol molecules to react with the composite. On its surface, there were hydroxyl groups, oxygen bridges and exchangeable cations on the surface of clay. These functional groups offered extra adsorption sites which were capable of reacting with phenolic molecules either using hydrogen bonding, van der Waals, or electrostatic attraction. FeTiO_2 and clay were synergetic to improve the total adsorption potential. Pure FeTiO_2 nanoparticles were prone to cluster or agglomeration which lowers their surface area. Clay matrix served as a backbone structure that did not allow agglomeration of FeTiO_2 , and the particles were in a well-spread condition and could adsorb easily.

Clay has the ability to exchange cation because of their layered structure. This enables it to adsorb and exchange ions with the medium around it and make it more affine to polar organic pollutants like phenol and chlorophenol. The synergistic effect was the result of the association of the photocatalytic/adsorptive properties of FeTiO_2 with the high surface area and active functional groups of clay. This led to better adsorption when compared to FeTiO_2 .

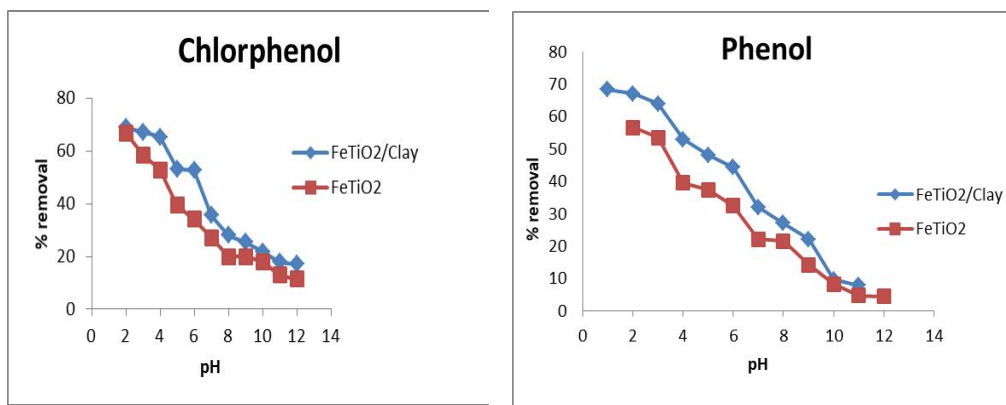


Figure 4.5: shows pH effect on removal of phenol and chlorophenol

4.6 Effect of Time

In the first graph of phenol, the time-dependent efficiency of the removal of phenol was reported using the FeTiO_2 and the $\text{FeTiO}_2/\text{Clay}$ composite. The two adsorbents exhibited a gradual rise in the number of phenols removed over time but FeTiO_2 attained high efficiency (about 70% after approximately 90 minutes) than $\text{FeTiO}_2/\text{Clay}$ (approximately 55-60% after about 90 minutes). It means that the FeTiO_2 was more efficient to eliminate phenol and chlorophenol molecules in wastewater as compared to clay-based composite. The increased and accelerated adsorption rate can possibly be attributed to increased surface interaction of FeTiO_2 composite to the phenol hydroxyl group. Since, phenol is smaller and more hydrophilic compared to chlorophenol, it can react more directly with FeTiO_2 surfaces, thus, it was more efficient in removing it, as it did not need a clay support. It is interesting to note that the progress in removal over time was increasing, initially the adsorbents had a high concentration of active sites, thus the rapid adsorption occurred in the first 40-50 minutes. With time, due to occupation of active sites, adsorption rate was decreased and ultimately achieved a state of equilibrium. The high removal in FeTiO_2 indicated that in case of phenol, the presence of clay did not contribute to the adsorption process significantly due to the fact that phenol did not interact well with the clay surface.

Conversely, the second graph confirmed that $\text{FeTiO}_2/\text{Clay}$ composite would be more efficient to FeTiO_2 in the removal of chlorophenol. It took approximately 90 minutes for 70 percent removal and FeTiO_2 only achieved approximately 60 percent removal. This disparity underscored the fact that clay increased the adsorption ability in situations where the pollutant was more hydrophobic and bulky such as chlorophenol. The chlorine functional group enhanced the hydrophobicity of chlorophenol and lowered its solubility in water thereby diminished the adsorption of chlorophenol onto FeTiO_2 . Nevertheless, the porous structure and the layer nature of clay gave it more surface area and micro-environment that allowed more adsorption of chlorophenol molecules.

In the $\text{FeTiO}_2/\text{Clay}$ composite, the particles were also better dispersed on the clay surface and agglomeration were prevented, as well as the available adsorption sites were higher. In addition, the functional groups and exchange sites, including cations exchange sites, which were introduced by clay can interact with chlorinated phenolic compounds via van der Waals, hydrogen bonding, and p-p interactions. The

combination of these factors justified the fact that removal of chlorophenol was better by using the clay-based composite than using FeTiO₂.

In short based on both graphs, it is possible to conclude that the efficiency of removal highly depends on the nature of the pollutant, as well as the nature of the composite. FeTiO₂ is better in the removal of phenol whereas FeTiO₂/Clay in the removal of chlorophenol. This disparity could be explained by the molecular characteristics of the pollutants: phenol is smaller, more polar, and it can directly interact with the surfaces of FeTiO₂, whereas chlorophenol is larger, less polar, and needs the extra porosity and surface functional groups found in clay to be adsorbed. In both, most of the removal (60-70%) takes place within the first hour of reaction time, and indicates that the adsorption process is rather rapid and effective regarding the two composites. Subsequently, the rate of adsorption becomes slower as the equilibrium is reached and a few active sites are left.

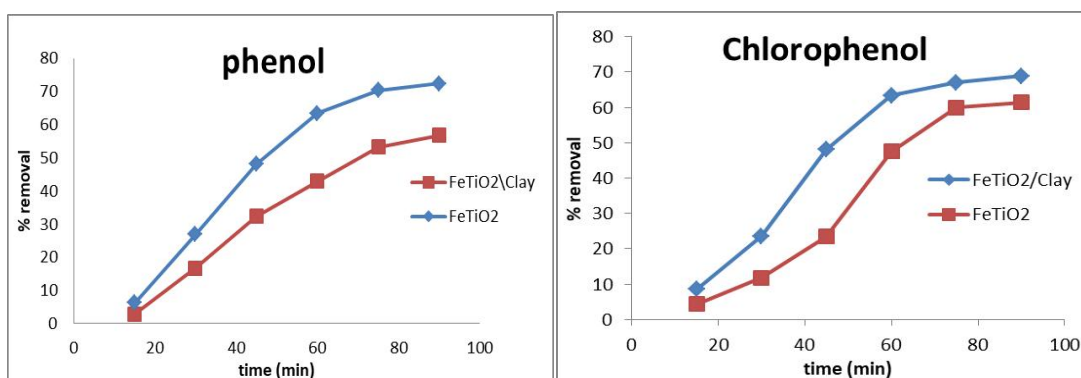


Figure 4.6: contact time effect for phenol and chlorophenol removal

4.7 Effect of Dose

In case excess adsorbent is used, the particles of FeTiO₂ and FeTiO₂/Clay will be aggregated or clumped. The aggregation decreases the accessible surface area and covers the active adsorption sites, rendering them inaccessible to phenol and chlorophenol molecules. Consequently, despite the increase in the amount of adsorbent in the system, the adsorption capacity per unit mass is reduced. With increase in dosage, the active sites on the adsorbents might be affected such that fewer functional sites become available to interact with the molecules of pollutants. This crowding effect decreases the efficiency of adsorption, since a large number of

the extra sites added by the increased dose are not used up. The adsorption efficiency is determined by the number of pollutant molecules compared to the active sites. Optimal balance occurs at low or moderate doses whereby maximum interaction between pollutants and adsorbent is achieved. In case the dose is over-increased, the concentration of the pollutants in the solution is too low and in comparison with the number of available sites. This lack of balance decreases the mass transfer driving force, that is, the number of pollutant molecules taken by unit of adsorbent is less.

When the adsorbent doses are very high, the suspension could be thick and opaque and thus it could not be mixed properly and all phenol and chlorophenol molecules could not readily reach the active sites. Also, the presence of FeTiO_2 or $\text{FeTiO}_2/\text{Clay}$ in excess may moderately alter the pH of the solution and alter the ionization of the pollutants, reducing the efficiency in adsorption.

In summary, adding the dose after attaining optimal level causes aggregation, overlapping of sites, dilution of pollutant, and diffusion restriction which all contribute to the fact that removal efficiency of phenol and chlorophenol reduces rather than increases. Therefore, optimal dose of adsorbent is always reached at which adsorption is maximized and beyond this dose, adsorption is poor.

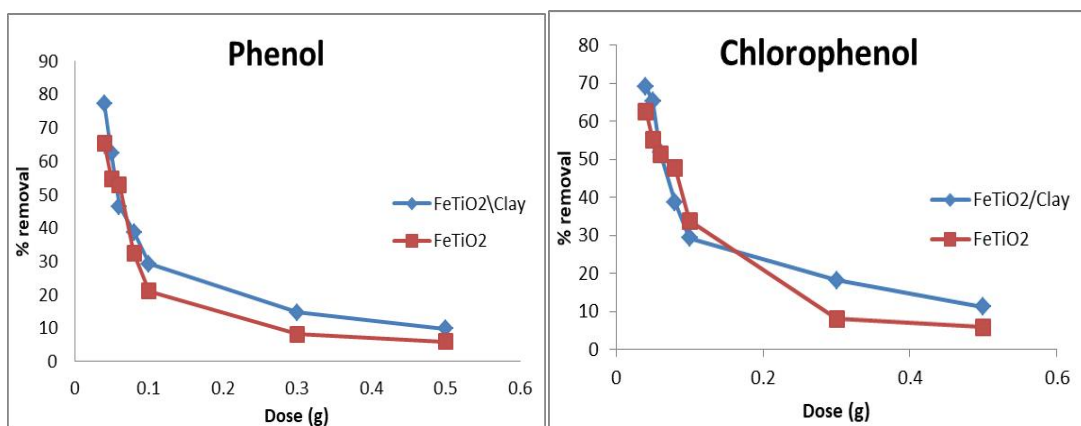


Figure 4.7: shows effect of adsorbent dose by using composite FeTiO_2 and $\text{FeTiO}_2/\text{Clay}$ on the removal of phenol and chlorophenol

4.8 Effect of temperature

In the case of endothermic adsorption, heat is a form of driving force that increases the level of interaction between the adsorbent and the pollutant molecules. As is the case with you, FeTiO_2 and $\text{FeTiO}_2/\text{Clay}$ composites also need more energy to open their surface sites and facilitate adsorption of phenol and chlorophenol. With

increase in temperature, an increase in the amount of energy remains to form bonds, and hence, better adsorption performance. During the higher temperatures, the kinetic energy of the molecules of phenol and chlorophenol also increases. By increasing the mobility, the resistance of the boundary layer decreases and the diffusion rate of the pollutant molecules between the bulk solution and the external surface of the adsorbent increases. It further improves their infiltration in the pores of the FeTiO₂/Clay composite opening up more adsorption sites. This leads to increased and efficient adsorption.

Active sites and surface hydroxyl groups of FeTiO₂ and clay are more reactive in high temperature. Such thermal activation enhances hydrogen bonding, p-p interactions and electrostatic attractions of the pollutant molecules and the adsorbent surface. Specifically, chlorophenol as a bulkier, less polar molecule is better off in higher temperatures since the extra energy will overcome steric hindrance and bind to the adsorbent more readily. The layered structure and high porosity of clay used in FeTiO₂/Clay composite determine that at a higher temperature, there is no collapse or deactivation of FeTiO₂ particles by the high porosity of clay. Rather, the nanoparticles are held by the clay structure and have extra adsorption sites. This is to make sure that both the phenol and chlorophenol adsorption is steadily improved with temperature, which is not the case with some other pure oxide adsorbents which lose their efficiency.

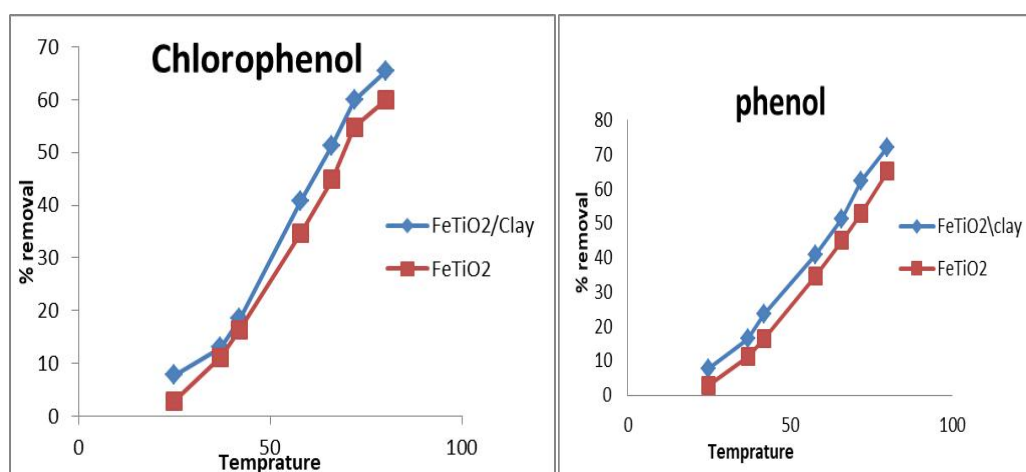


Figure 4.8: shows by using FeTiO₂/clay and FeTiO₂ composite the removal of phenolic agents (chlorophenol) at 80°C, and phenol at 70°C. This experiment was done at 20°C to 100°C that show a gradual increase in removal.

4.9 Effect of Concentration

An increment in the level of phenol and chlorophenol in the wastewater invariably demonstrates increasing degradation effectiveness of FeTiO₂/Clay composite over FeTiO₂. The composite is approximately 60-70% degradable with no clay, whereas FeTiO₂ is 40-50% degradable when it is pure. This distinction is largely because of the structural and chemical benefits that clay develops to the composite. The clay matrix provides more surface area and porous network that helps more pollutant molecules to access the active sites of FeTiO₂. It also prevents agglomeration of the particles so that the FeTiO₂ particles can be dispersed well and are conveniently available. In addition, the surface hydroxyls and exchangeable cation are present in clay in themselves, and can react with phenolic compounds via hydrogen bonding, van der Waals forces and electrostatic attractions. All these have contributed to the high performance of the FeTiO₂/Clay composite that has a much greater pollutant loading capacity than FeTiO₂ alone which rapidly becomes saturated and ineffective with restricted active sites and particle clustering.

Nevertheless, despite the improvement in adsorption and degradation ability, the composite does not attain 90% and above removal at high concentrations of phenol and chlorophenol. This weakness is associated with congestion of the adsorption sites on the composite surface. At increased levels of pollutants, the concentration of phenol and chlorophenol in the solution far outnumbers the concentration of adsorption sites and the molecules in the solution compete to bind to the adsorption sites. The further adsorption decelerates, and the efficiency becomes constant when a considerable fraction of the active sites are occupied. Also, at greater concentrations, the process of diffusion will be important: pollutant molecules will be forced to go further into the pores of the composite, and congestion at the surface may reduce their access to internal sites. This decreases the rate of mass transfer and consequently the system cannot attain a very high (nearing 90 percent) degradation efficiency.

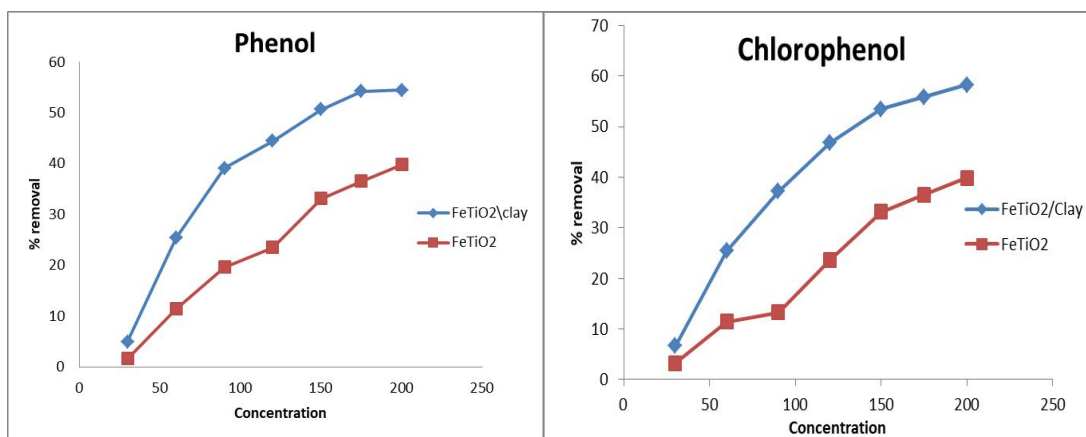


Figure 4.9: shows effect of concentration and adsorption potential of FeTiO_2 and $\text{FeTiO}_2/\text{clay}$ composite for phenol and chloro phenol removal

4.10 Adsorption isotherm models

The adsorption isotherm shows that how adsorbed molecules are distributed among the solid and liquid phase when adsorption phenomenon is reached at equilibrium. Different models are applied on it which are Langmuir, Freundlich isotherm models.

4.10.1 Langmuir isotherm model

This balancing equation from 1918 takes maximal adsorption into account. The Langmuir isotherm model explain an increase in surface capacity like a result pressure up till the total surface area is covered with a mono layer of molecule and no more adsorption is possible. The Langmuir isotherm equation is given below.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} KL + \frac{C_e}{q_{max}} \quad \dots\dots\dots(1)$$

Where:

C_e is the concentration of the adsorbate at equilibrium

q_{max} shows the maximum capacity of adsorption

Q_e indicate the concentration of an adsorbent at equilibrium

Langmuir isotherm model	FeTiO ₂	FeTiO ₂ \Clay
q_{max} Cal (mg/g)	1.341	3.71
q_m Exp(mg/g)	16.09	24.2
b	0.077	0.81
R^2	0.5303	0.6435

Table 1: Langmuir isotherm model

2.10.2 Freundlich isotherm model

It was created by Freundlich in 1926. Freundlich isotherm model is apply to adsorption process which is present on different surface. This isotherm describe the expression that give information about surface heterogeneity and the non-uniform

distribution of active sites energies. The equation for this isotherm model is given below.

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad \dots\dots\dots(2)$$

Where:

K_F is adsorption capacity

$1/n$ is adsorption intensity

Freundlich isotherm model	FeTiO₂	FeTiO₂\Clay
q _m	16.09	24.2
K _F	109.01	232.48
n	1.14	1.0955
R ²	0.3196	0.474

Table 2: Freundlich isotherm model

4.11 Kinetics Models

The kinetics models is used to determine the performance of the adsorbent and to see the adsorption mechanism. These studies are crucial in understanding adsorption. They present information about how quickly adsorption occurs, which is essential for designing and optimizing adsorption experiments in wastewater treatment. There are two distinct phase in the kinetics, a quick phase of adsorption and a slower phase that follows. The kinetics that are involved adsorption of phenol and phenolic agents onto FeTiO₂\clay and FeTiO₂ were investigated using two well-known kinetic models: the pseudo-first order kinetics adsorption model and the pseudo-second order kinetic model.

4.11.1 Pseudo-first order kinetic model

Pseudo-first order kinetics was introduced by Lagergren.

Equation

$$\log(q_e - q_t) = \text{Log} q_e - K_1 \frac{t}{2.303} \quad \dots\dots\dots(3)$$

In the above equation q_e shows the adsorbate/dose concentration at equilibrium and q_t shows the time at equilibrium .K₁ is rate constant for pseudo first order.

Pseudo first order	FeTiO₂	FeTiO₂/clay
K ₁	0.9161	0.0571
qe _(exp)	103.8	56.023
qe _(cal)	43.932	170.8
R ²	0.043	0.9372

Table 3: Pseudo-first order kinetic model

4.11.2 Pseudo second-order kinetic model

According to the pseudo-second order model, the rate limiting phase is determined by a chemical sorption process, and this forms the basis for the models establishment. The kinetic rate equation was established by Ho and McKay in 1999;

Equation

$$\frac{t}{qt} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad \text{.....(4)}$$

Pseudo second order	FeTiO₂	FeTiO₂/clay
K ₂	8.704	8.793
qe _(exp)	43.923	56.02
qe _(cal)	-21.73	68.49
R ²	0.04601	0.3218

Table 4: Pseudo-second order kinetic model

CHAPTER 5

DISCUSSION

Synthetic resin, plywood, gas and coke oven, paper, paint, pulp, coal gas, tanning, textile, petroleum, plastic, rubber, pharmaceutical, and mine industries all contribute phenol to wastewater. Certain phenolic compounds are thought to be carcinogens and they are all dangerous poisons. Since phenol and phenolic chemicals can harm the environment, they must be removed from industrial aqueous streams before any release. For the same reason, the Environmental Protection Agency has set a maximum limit of 0.1 mg^{-1} for phenol in treated effluent, but the World Health Organization has an even stricter standard [69]. It has been discovered that the quantity of phenol found in drinking water is allowed to be a maximum of 0.001 mg l^{-1} by the law[70].Furthermore, because phenol is considered toxic and among the leading hazardous chemicals, it brings about major harm to human health and the environment[71].Some of the important traits investigated to help boost non-conventional adsorbent usage in wastewater treatment are the characteristics of the adsorbent and adsorbate, adsorbent concentration, adsorbent dose, contact time, pH phenol ionizes into phenolate ions, but those are kept from attaching to the adsorbent because hydroxyl ions are already present[72][73]. Evidence of this behavior has also been found when Bentonite is used [74]. Time spent in between the adsorbent and adsorbate plays a important role. Phenol and chlorophenol removal takes about 80 min on both materials to achieve equilibrium, when activated red mud was applied to remove phenol and chlorophenol from water with a 25 mg l^{-1} phenol concentration, the removal efficiency rose over a period of 3 hours and after 6 hours. Afterwards, the number of phenol molecules being removed gradually increased and, at three different phenol concentrations, was between 90.4% and 80.6% after 60 minutes. Higher contact times did not significantly improve phenol adsorption and using 60 minutes provided results that were almost equal to equilibrium. The cause of the decrease in phenol and chlorophenol removal as the starting concentration increased was that the active sites on the adsorbent could become full [75].

The evident that $\text{FeTiO}_2/\text{Clay}$ composite would be more superior to FeTiO_2 in the removal of chlorophenol. It takes approximately 90 minutes before $\text{FeTiO}_2/\text{Clay}$ reaches approximately 70 percent removal because FeTiO_2 only reaches approximately 60 percent. This disparity underscores the fact that clay increases the

adsorption ability in situations where the pollutant is more hydrophobic and structurally bulky such as is the case with chlorophenol. The chlorine functional group enhances the hydrophobicity of chlorophenol and lowers its solubility in water thereby diminishing the adsorption of chlorophenol onto FeTiO₂. Nevertheless, the porous structure and the layer nature of clay gives it more surface area and micro-environment that allows more adsorption of chlorophenol molecules.

The comparison of FeTiO₂ and FeTiO₂/clay composites for phenol and phenolic compound removal underscore the essential effect of material composition and synthesis procedure in adsorption effort. However, the superior efficiency of the FeTiO₂/clay composite in different experimental conditions confirms the potential of clay as a low-cost support that not only stabilizes metal oxide but also actively participate of the adsorption. The pH of zero charge (pHpzc) analysis showed difference in the surface charge properties of the two materials, with the pHpzc of FeTiO₂ being around 5 and clay/FeTiO₂ around 6. This result is important to account for the surface-adsorbate interaction at various pH values. Having in mind that phenol and chlorophenol in acidic media is mainly in a molecular form, the higher values of removal efficiencies at the lower pH can be explained by favourable electrostatic interactions and hydrogen bonding. The surface pHpzc of the clay composite is relatively higher, and this indicates a good potential of interaction with negatively charged species, as a result of the existence of hydroxyl groups on the clay surface enabling the adsorption at mildly acidic conditions.

The time dependence of adsorption action presented an evidently characteristic curve with most of the phenol and chlorophenol adsorbed in the initial 60 min and then a platform appeared. This is in agreement with a fast surface saturation, which is typical for monolayer adsorption. The larger equilibrium capacity of the FeTiO₂/clay due to additional bound structures possibly through interlayer diffusion or secondary interactions induced by the clay matrix that may be less effective in the FeTiO₂ only system. The initial concentration effect was also reported as other key feature. At high phenol and chlorophenol concentrations (around 200 mg/L) adsorption also increased markedly. The reason is the larger concentration gradient for mass transfer from the liquid to the adsorbent surface. Although both active materials achieved such effect, FeTiO₂/clay kept a higher

level, indicating a larger number of active sites and better load life. This is crucial for the design of full-scale treatment systems with varying concentrations of contaminants. The above efficiency of adsorbent dosage maximization also suggested that above a certain level (e.g., at 0.2–0.3g), the removal leveled off or even declined due to the agglomeration of the particles and shielding. This reminds us that the trade-off between material consumption and efficiency must also be closely monitored in order to ensure cost reduction in industrial applications.

SEM studies played a crucial role in the surface morphology of the composites. The FeTiO₂/clay composite showed a more homogeneous and fine dispersion of the surface pattern, accompanied by narrow particle size (about 32 nm), which resulted in an enhancement of the surface area and active sites. This is in good agreement with the increased adsorption obtained experimentally. Porous layered clay structure of the catalyst allows means of TiO₂ particles dispersion, resulting in less aggregation and higher contacting of TiO₂ particles with adsorption sites, and which is the limitation factor access in the case of pure TiO₂. Moreover, FTIR study confirmed the existence of active functional groups engaged in adsorption. τ Value peaks for different groups such as Ti–O, Fe–O, Al–OH and Si–O represent a complex of binding sites, especially in the composite material. The presence of the Al–OH bands in the clay matrix after doping suggests the integrity of the clay structure for high adsorption capacity in successive cycles. The existence of water molecules, revealed by H–O–H bending vibration, also suggests that adsorption processes take place and might have contributed to strong uptake of phenol within the short initial contact time.

The XRD patterns of the native Mt, Fe (III) cation-doped Mt (Fe-Mt, synthesized at ambient temperature), TiO₂, Fe/Mt/TiO₂, and Fe-TiO₂ synthesized at 70 °C. The interlayer gap and one layer's thickness (0.96 nm) were among the 001 peaks from Mt [76].

Comparing the interlayer distances in Fe-Mt, Fe/Mt/TiO₂, and Fe-TiO₂ to the original Mt (0.25 nm), the values were nearly identical (0.42/0.43 nm), indicating that only ion exchange of Fe(III) with the interlayer cations in Mt took place throughout the composites' manufacture. Furthermore, the distribution of TiO₂ should be limited to Mt's surface. Fe (III) has an ionic size of 0.45 nm when hydrated. It is possible that

the Van der Waals force within the poorly formed aluminosilicate layers extruding from the hydrated shell of Fe (III) is what distributes the reduced interlayer distances of Mt in the composites rather than the ionic sizes [77].

XRD studies revealed crystalline nature of the FeTiO₂ and FeTiO₂/clay composites indicating the fingerprint peaks of anatase and rutile phases of TiO₂. The existence of these phases (especially for doped composites) has been reported to favor the adsorption activity as a result of heterojunctions formed to increase electron transfer and enhance surface reactivity. It is noteworthy that the diffraction peaks of the clay did not disappear after the synthesis, confirming the stability of the clay under hydrothermal conditions. The dependence on temperature of phenol removal also indicated the endothermic character of the process. Adsorption capacity also increased with temperature, which indicate a higher molecular mobility and diffusivity at higher temperatures. The higher removal obtained at 80°C for both composites (especially for FeTiO₂/clay) indicates that offering their use in real industrial practices is required, where effluent temperature can change. Furthermore, this exothermic behavior is indicative of the dominance of chemisorption rather than physisorption, especially at latter contact time periods.

In general, the data collected from this work show good agreement on the potential use of iron-doped TiO₂-clay composites for phenol and chlorophenol treatment. The combination of adsorptive Fe ions and the high surface area of the clay contributed to a composite with the improved efficiency, environmental friendly and low-cost. In addition, the synthesis techniques were simple, easy to scale up, and hence, commercial production is practicable for industrial application. Regeneration capacity and cycle stability of these composites might be the topics of further investigations. It is essential to know how they behave over the long term with continuous use in practice. Moreover, using actual industrial wastewater would offer a more comprehensive understanding of the capability of the membranes under mixed contaminant scenarios and in the presence of interfering species such as ions and organic matter.

CHAPTER 6

CONCLUSION

Low-cost materials are needed to remove these pollutants for the contaminated water. The composite FeTiO_2 prepared by the co-precipitation method and $\text{FeTiO}_2/\text{Clay}$ by hydrothermal method. Fe-TiO_2 and $\text{Fe-TiO}_2/\text{clay}$ material was successfully synthesized and examined in this study in terms of their adsorption capacity toward phenolic substances in textile wastewater. Introduction of iron ions on TiO_2 increased its surface activity and the introduction of clay increased its surface area, porosity and adsorption sites and this resulted in a high removal efficiency compared to that of Fe-TiO_2 without the use of clay. The presence of characteristic Ti-O-Ti, Fe-O and Si-O-Si bonds was confirmed by the FTIR analysis, ensuring the presence of the combination of iron oxide, titania and clay in the composite. The XRD patterns revealed TiO_2 anatase phase and existence of iron oxide peaks with the slight driftages demonstrating successful Fe doping. $\text{Fe-TiO}_2/\text{clay}$ composite was more amorphous and therefore it displayed better adsorption processes. SEM pictures showed that Fe-TiO_2 contained aggregated particles and the $\text{Fe-TiO}_2/\text{clay}$ morphology was porous and uniformly distributed the particles, giving it more active sites. The UV-Visible spectra indicated red shift and decreased band gap that proved the optical and surface interaction ability to be better. The maximum percentage removal of phenol by using $\text{FeTiO}_2/\text{clay}$ composite at pH (2) is 77%, dose (0.04g) 65%, time (90min) 72%, concentration (175) 54%, temperature (80°C) was 72%. The maximum percentage removal of chlorphenol by using $\text{FeTiO}_2/\text{clay}$ composite at pH (2) is 69%, dose (0.04g) 69%, time (90min) 68%, concentration (200mg/l) 58%, temperature (80°C) was 65%. The results of the adsorption demonstrated that $\text{Fe-TiO}_2/\text{clay}$ composite had better percentages of removal of phenol and Chlorophenol because of the synergistic effect between metal oxides and clay. The temperature also increased the adsorption efficiency and this proved an endothermic process. In general, $\text{Fe-TiO}_2/\text{clay}$ composite was found to be an effective, stable, and environmentally friendly adsorbent in the treatment of textile effluents as confirmed by FTIR analysis, XRD analysis, SEM analysis as well as UV-Visible analysis. The kinetic study showed that the data show good result in langmuir isotherm and pseudo-first order kinetic model confirming the good adsorption capacity and stability of waste water treatment. In conclusion the FeTiO_2

/clay composite is effective and eco-friendly for removing contaminants from the waste water.

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