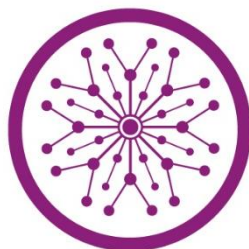


**Synthesis and characterization of aluminium doped titania
clay composite for the efficient removal of reactive blue
from aqueous solution**



SUPERIOR UNIVERSITY

Thesis Submitted to

The Superior University Lahore

In Partial Fulfillment of the

Requirement for the Degree of

MS Chemistry

By

ATTIA TAYYAB

SU92-MSCHW-S23-014

Session: 2023-2025

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Supervisor Name: Miss Fatima Ashraf

Designation: Lecturar

Signature: _____

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This is to certify that the research work presented in this thesis, titled “**Synthesis and characterization of aluminium doped titania clay composite for the efficient removal of reactive blue from aqueous solution**” was conducted by “**Attia Tayyab**” under the supervision of “**Ms. Fatima Ashraf**”

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 Science/Master of Philosophy in the field of “ **Chemistry**” in Faculty of Sciences at The Superior University, Lahore.

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Dedication

I primarily dedicate this work to my cherished **parents**, whose unwavering love, sacrifices, and prayers have illuminated my path throughout my educational journey. Their constant support, encouragement, and belief in my abilities have provided me with the strength to tackle every obstacle and remain focused on my objectives. This accomplishment would not have been achievable without their unwavering presence in my life.

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This piece represents the affection, support, and direction I have enjoyed, and I sincerely dedicate it to all of you with deep appreciation and esteem.

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Attia Tayyab

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List of Abbreviations

AlTiO ₂	Aluminium doped Titania nanoparticles
AlTiO ₂ /Clay	Aluminium doped Titania Clay composite
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Protection Agency
XRD	X-Ray Diffraction
WHO	World Health Organization

ABSTRACT

The toxic dyes combined with water resources have an impact on a wide range of living things. Reactive dyes are a family of organic compounds with various applications in the textile industry. A significant quantity of dye, such as reactive blue, combines with natural water resources and renders them harmful and hazardous. Therefore, the removal of reactive blue dye from wastewater is crucial. The main objective of this study is to investigate the effectiveness of aluminum-doped Titania and aluminum-doped Titania clay composites in remediating dye-polluted water. Aluminum-doped Titania composite was synthesized by the co-precipitation method, and aluminum-doped Titania clay composite was synthesized by the hydrolysis condensation method. FTIR, SEM, and XRD characterization techniques were employed to elucidate the functional groups, surface features, and morphology of both composites. To evaluate whether a composite-based adsorbent can effectively remove reactive blue dye, essential parameters were measured to determine adsorption potential under different conditions, including dye concentration (30ppm-150ppm), contact time (20min-150min), pH level (3-10), temperature (10-200°C), and dosage (0.01-0.1g) by the batch adsorption method. Kinetic models and thermodynamics were applied to understand the adsorption process. The maximum capacity of dye adsorption was observed under pH 3 conditions, with an initial dye concentration of 150ppm, a 0.01g dosage of adsorbent, and 100 min of contact time. This study demonstrates the adsorbent capacity of AlTiO_2 and $\text{AlTiO}_2/\text{clay}$ composite for efficient and eco-friendly removal of reactive blue dye 248 from aqueous water.

CHAPTER 1

INTRODUCTION

Water is essential for life which cannot be replaced. It is essential for hydration and survival, as we cannot exist without it. In nature, water occurs in three states: liquid, solid, and gas. At typical temperatures and pressures, it maintains a dynamic equilibrium between liquid and gas states. At room temperature, the liquid is tasteless and odorless, almost colorless with a trace of blue. Water is known as the universal solvent due to its ability to dissolve several compounds[1]. Water possesses several significant physical properties, such as ability to store heat, surface cohesive force, and electrical insulation. Its high density enables it to retain the dissolved salts essential for life[2]. Although 70% of the world is covered with water, although just 2.5% of it is freshwater. That small volume of freshwater is utilized for a variety of purposes: Mostly for agriculture, then industries, and finally municipal and residential usage. There are therefore countless competitors. Polluted water consists of harmful pollutants that make water unsafe for drinking, cooking, bathing, and other purposes[3].

1.1 Water pollution

Water pollution resulting from rapid industrial growth and its adverse health effect. Waste water from different sectors can be classified as sewage, household, storm, runoff, agricultural, and industrial [4]. Industry contributes to nearly two-thirds of all waste released into rivers, lakes, and the ocean, with about 80% remaining untreated. Most of the unprocessed waste comes from rural industries. Sectors that produce wastewater like commercial laundries, power generation facilities, oil, and gas fracking activities, metal finishing operations, and the food and beverage industry Chemicals, heavy metals, oils, pesticides, silt, medicines, and other industrial by products are also often pollutants found in industrial wastewater [5]. Numerous studies have been conducted worldwide to evaluate groundwater quality and associated health risks, as consuming polluted water has major negative impacts on living organisms' health. These investigations have linked groundwater pollution to numerous health

issues. Water contamination poses various health risks. Contaminated water can cause acute or long-term health problems, depending on the particular pollutants and the length and intensity of exposure. Waterborne infections can cause dehydration and even death in children, the elder, and people with weak immune systems. Long-term exposure to certain toxins has been linked to problems with development, reproductive problems, organ damage, and an increased risk of cancer [6].

1.2 Industrial wastewater

Different industries have their own toxic effect depending on their waste and pollutant. Pharmaceutical industry has organic and inorganic substances, antibodies, drugs etc. Cosmetic industries contain cadmium, mercury, and synthetic chemicals. The textile industry's wastewater is highly polluted with several chemical pollutants, accounting for approximately 70% of total emissions. Textile industry may generate wastewater throughout different stages: preparation, finishing, dyeing, printing, cutting, coloring, and other operations. Freshwater is used extensively in textile operations, particularly during the dyeing process. Industrial effluent contains a variety of contaminants, including chemical oxygen demand, suspended particles, colors, variable pH, high temperatures, and salt. These contaminants may affect the environment. Wastewater should be cleaned before being emptied into oceans and rivers. Dyes are utilized to add color to numerous items, such as cloths, paper, cosmetics, tanning, leather, food, and pharmaceutical products. Before 1856, dyes were exclusively made from natural materials. In 1856 dyes were only produced from natural sources. The rising demand and high costs of natural dye extraction led to the creation of the first synthetic dye, aniline (mauveine), in 1856 by chemist Perkin. When applied to silk, this purple dye produced a hue that was stable and homogeneous. Since then, the dyeing industry has relied on synthetic dyes and expanded globally, producing roughly 8×10^5 tons annually. The textile industry makes fibers that are used to make yarn, which is then turned into fabric. They use different methods to dye fabric. For example, dyeing means putting dyes on textile fibers in a consistent way. Printing is the process of putting ink on a specific area of cloth. While finishing

includes crosslinking, softening, and waterproofing, bleaching removes dye color from fibers.



Figure 1: Industrial waste water

1.3 Dye and its types

Dyes are classified into two primary groups according to their source. Synthetic colors are made artificially from chemicals, whereas natural dyes, which have been used since ancient times, are mostly derived from plants. Three categories of synthetic dyes are distinguished based on the kind of fiber that is produced [7]. Dyes used practically in all sectors of our daily lives for painting and dyeing paper, skin, and clothing. Up to 50% of the colors employed do not adhere to the textile fiber and instead persist as pollutants in the liquid phase [8]. Textile dyes, known for their high toxicity and potential carcinogenic properties, have been connected to various diseases in both humans and animals. Textile dyes may cause conditions such as dermatitis and problems with the central nervous system. These problems might result from the replacement of enzyme co-factors, leading to the inactivation of the enzymes. When consumed or inhaled, textile dyes can lead to irritation of the skin and eyes, particularly upon exposure to dust [8, 9].

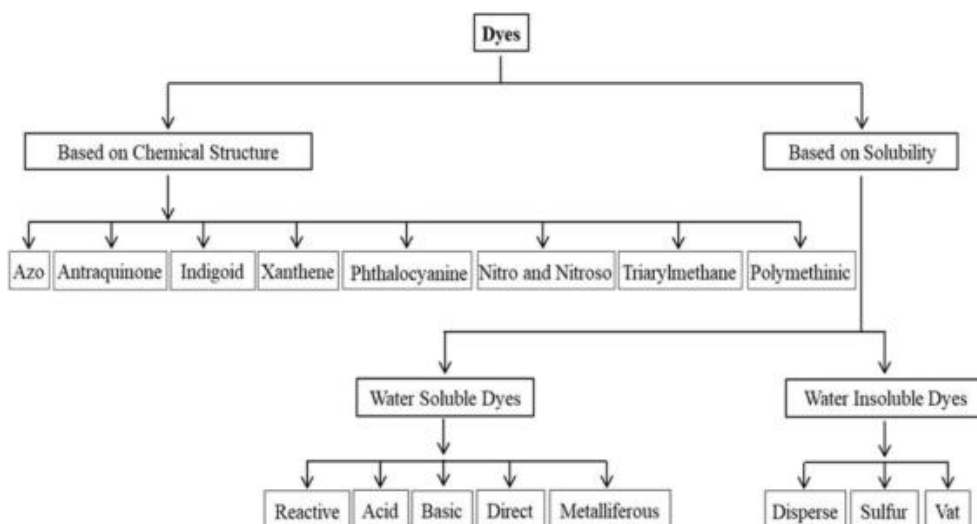
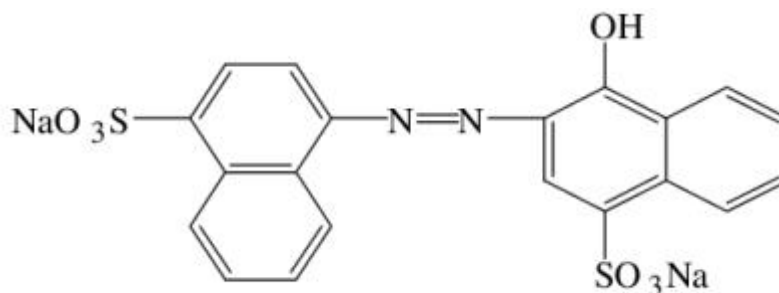


Figure 2: Different types of dye

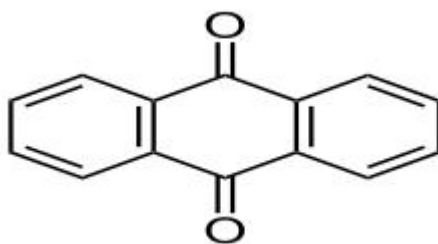
● Azo dyes

Azo dyes are compounds made up of a diazotized amine and an amine or phenol, with one or more azo linkages. Aromatic amines are key precursors to azo dyes. Azo compounds offer brilliant hues and constitute nearly two-third of all man-made dye. Without doubt the most extensively used and structurally diverse class of commercial organic dyes.



● Anthraquinone

The anthraquinone group has three fused benzene rings with two carbonyl groups on the middle ring, similar to the basic anthracene structure. The structure is normally colorless; however, substitution of aromatic rings adds color and modulates intensity. As the substituent's basicity increases, the color becomes deeper[10].

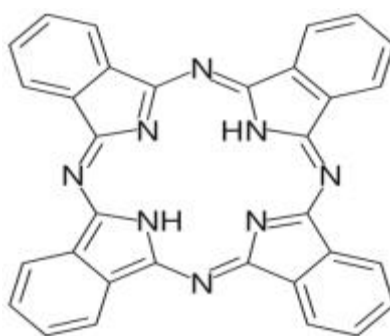


- **Indigoid dye**

Indigo's chemical structure causes it to be particularly insoluble in water, necessitating the use of additional, repetitive reduction-oxidation (redox) processes in denim dyeing. To dye with natural indigo from plants, β -glucosidase biotransforms the extremely soluble glycoside indican (indolyl- β -d-glucopyranoside) followed by air oxidation [11].

- **Phthalocyanines dye**

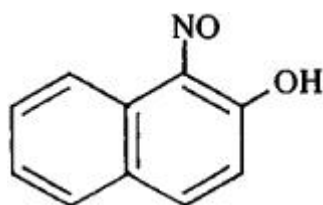
Phthalocyanines are pigments produced by combining dicyanobenzene with metals like Cu, Ni, Co, or Pt. Copper phthalocyanines represent the primary derivative of this dye group, recognized for their appealing blue-green hues, excellent dyeing durability, chemical resilience, light fastness, and resistance to bacterial breakdown in both aerobic and anaerobic environments[12].



- **Nitroso dye**

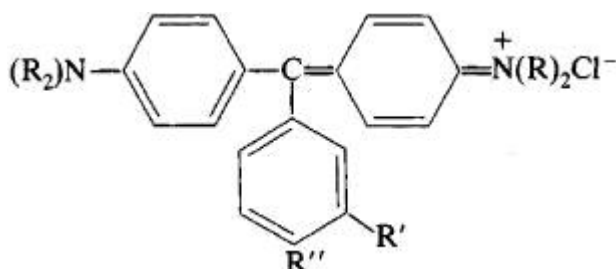
Nitroso dyes, used as biological stains, contain a nitroso group situated in an ortho position adjacent to a phenolic hydroxyl. Due to the presence of these compounds as equilibrium mixtures of tautomers, illustrated below for naphthol green Y, they may also be categorized as quinonoximes. Due to the ortho substitution pattern, nitroso dyes are capable of effectively chelating various transition metal ions,

producing colored coordination products with metals. Nitro dyes are characterized structurally by the presence of a nitro group situated in the ortho position relative to an electron donor. The majority of nitro dyes employed as biological stains utilize a phenolic hydroxyl as the donor [13, 14].



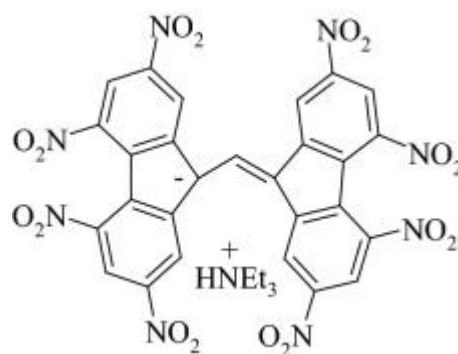
● Triarylmethanes dyes

Triarylmethanes are a category of cationic dye, their efficacy as photosensitizers photo dynamic therapy for cancerous diseases has not been thoroughly explored. Three triarylmethane dye, ethyl violet, crystal violet, and malachite green were subjected to laser-induced photo decomposition, with an emphasis on those that were not covalently bonded to bovine serum albumin [15].



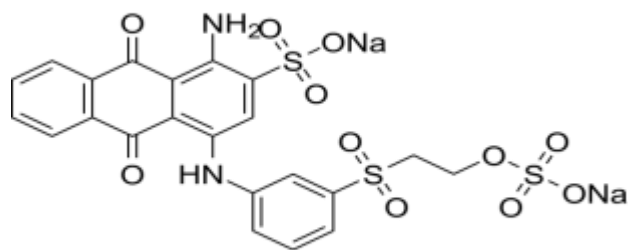
● Polymethine dyes

Polymethine dyes consist of heteroaromatic groups at both ends and in the linkages. They belong to the categories of cyanines, merocyanines, and oxonols. The heteroaromatics and linkage groups affect their UV-Vis and near-infrared (NIR) absorption bands. The theory of molecular exciton coupling clarifies the alteration in absorbance bands of polymethine dyes as aggregates form. Polymethine dyes have been utilized as media for data storage. Polymethine dyes can serve as sensitizers in solar cells that are dye-sensitized. While the majority of colors are solid, there have been instances of liquid trimethine dyes being documented. The fluorescence intensity of liquid trimethine dyes is significantly enhanced in liquid nitrogen.



● Reactive dyes

Reactive dyes, which are recognized for their toxicity, solubility of water, mutagenesis characteristics, and it can resist to biological procedure, represent serious environmental hazards. Releases of reactive dye into ecosystems have heightened bioecological risks, affecting many areas of the environment. These colors have been linked to lowering photosynthesis rates and dissolved oxygen concentrations in receiving bodies, as well as being carcinogenic to humans. Furthermore, they have been associated with heightened allergic hypersensitivity reactions and necropenia among those exposed. Additionally, these colors are very durable, enduring both light exposure and washing, and are hard to dissolve. In particular, the Reactive Blue 19 (RB 19) dye recognized as dangerous anionic dye frequently utilized as primary ingredient in the production of polymeric dyes. RB 19 is categorized as persistent organic pollutant, indicating it may pose risks to human health as well as other organisms. The presence of the azo group ($N = N$) is responsible for its low biodegradability, toxicity, and mutagenesis properties. This trait raises concerns about the potential effects on aquatic species and the environment.



Researchers have concentrated on treating dye wastewater through coagulation/flocculation, electrocoagulation, filtration, adsorption, ion exchange, advanced oxidation processes, activated sludge processes, sequencing batch reactors, membrane bioreactors, moving bed biofilm reactors, and constructed wetlands. Colloidal and charged suspended pollutants are broken up by the coagulation process. A direct current source is used in the electrocoagulation process between an iron and an aluminum metal electrode submerged in contaminated water. At particular pH, m ions of metal create different coagulated species and metal hydroxides that destabilize and clump together suspended particles or precipitates, in addition to adsorbing dye molecules. Filtration methods employ sieving and particle collection systems that differentiate between dissolved and suspended particles. Solids are moved from the primary liquid to the adsorbent's surface using adsorption techniques. Strong interactions between charged molecules of dyes and functional groups of ion-exchange resins enable the ion-exchange method to remove dyes [16].

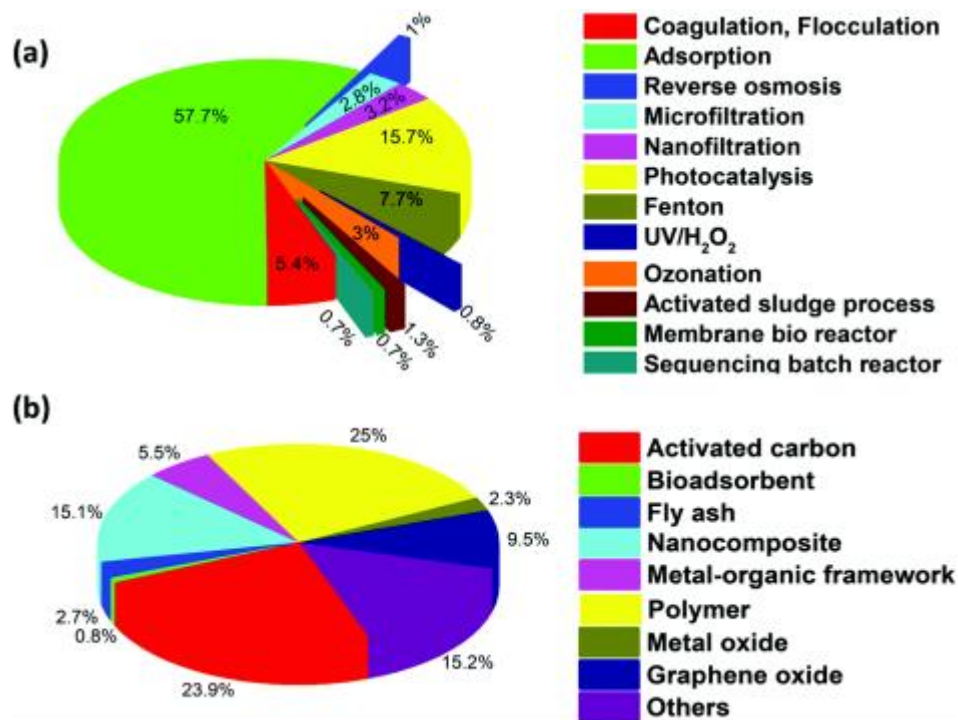


Figure 3 : Show different methods for the removal of pollutant from wastewater

Clay minerals make good fillers in metal composites. Clay minerals are widely distributed and low-cost, making them appealing for both economic and environmental reasons. Different clays such as montmorillonite, sepiolite, bentonite, palygorskite, halloysite, and zeolite are regarded as inexpensive fillers. The versatility of clay arises from their excellent chemical and mechanical stability, unique surface area, and varied structural characteristics. These substances are perfect for enhancing nanoparticles because of its abilities to swell and absorb. Their adsorption ability draws pollutants to the surface, enhancing the effectiveness of dispersed nanoparticles. Bentonite is a type of smectite mineral, mostly consists of montmorillonite clay. The clay is described as a 2: 1 phyllosilicate whose unit crystal structure is that which incorporates an octahedron sheet between silicate tetrahedron sheets. Between the layers, there is interlayer space which contains both cations and water molecules. Smectites are crystallized with the aid of the crystalline architecture that enables layers to swell and contract maintaining crystallographic coherence of the layers in two-dimension [17]. Ballasted carbonaceous materials (BCs) are cheap inorganic

adsorbents, environmentally harmless, and not acute toxicants with a large specific surface area, cation-exchange capacity and porosity. Additionally, surface active sites improve the capacity to adsorb contaminants. However, because natural BCs are hydrophilic and have minerals on their surfaces, their overall adsorption capacity is decrease. Researchers use bentonite, the most prevalent inorganic nanofiller, in a wide range of use, like wastewater treatment, paints, cosmetics, pharmaceuticals, animal and poultry feed pelletization, iron ore palletization, and civil engineering. This is explained by bentonite's substantial cation exchange capacity, surface area, and other important properties like hydration, thixotropy, swelling capacity, bonding ability, impermeability, and flexibility. Bentonite is environmentally friendly and widely available[18].

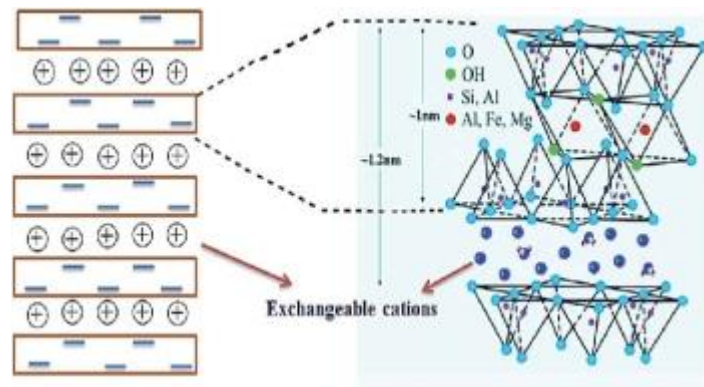


Figure 4: Structure of clay

The creation of Al-doped TiO₂ clay catalysts adheres to the hydrolysis-condensation method outlined for different oxide-clay substances. The organoclay (Bentonite) is employed directly without any prior purification process. Organoclay was dispersed in 2-propanol, and the mixture was stirred. The solution of the precursor was subsequently incorporated into the organoclay suspension while being magnetically stirred until a uniform dispersion was achieved. Subsequently, a solution of water in 2-propanol was added to the dispersion to facilitate the hydrolysis of the alkoxide precursors, calibrating the water quantity to stoichiometric levels. The suspension was mixed until the condensation happened, resulting in a thick gel being created

AIMS AND OBJECTIVES

- To synthesize and characterize Al-doped titania clay composite.
- To synthesize and characterize Al-doped titania nanoparticles
- To evaluate the adsorption efficiency for reactive blue dye removal.
- To optimize various parameter for maximum dye removal.

CHAPTER 2

LITERATURE REVIEW

Reactive dyes are one of these harmful pollutants that are toxic and non-biodegradable due to their aromatic ring structures. These compounds are widely used in textiles, food processing, leather finishing, paper mills, cosmetics, and plastics. Reactive dyes are the most often used colors in textiles, with wastewater discharge ranging from 10 to 60 percent. These colors may induce skin irritation, carcinogenesis, and mutagenesis. As a result, water contamination caused by textile wastewater discharge is always a serious worry, and scientists are working to find solution [19].

Aluminium was doped with TiO_2 P-25 and $\text{Al}(\text{NO}_3)_3$ serving as precursors and doping agents. Factors such as the concentration of the doping agent and the temperature of calcination were examined. The Al-doped TiO_2 nanocrystal was analyzed using different methods[20]. The freshwater waterways may be polluted by urbanization, agriculture, manufacturing and population increase. Mineral clay, processed clay, charcoal, zeolites, and polymeric resins are some of the materials that have been explored in the removal of contaminant using adsorbents. The use of nano-clays has become an object of interest production due to its unique characteristics. The paper is the examination of recent activities in clay-based nanocomposites systems of pollution elimination, including clay-carbon, clay-polymer, and clay/metallic systems. In addition to highlighting the benefits of such technologies compared to traditional methods, including increased processing, faster decontamination, better selectivity, increased surface area, and affordability, the paper is backed by a full accounting of costs. The purpose of the study was to maximize the effectiveness of the nanomaterial adsorbents examining their adsorption mechanism, constraints, and prospects. The review suggests the current studies on clay-based nanocomposites used in wastewater treatment[21].

Different proportions of kaolinite, TiO_2 and Al_2O_3 weight percentages in the synthesis of various nanocomposites were achieved in synthesis, through a number of processes. The fine structure was confirmed by the X-ray diffraction analysis, and the presence of other elements was confirmed by Fourier-Transform infrared spectroscopy and elemental mapping using energy dispersive spectrophotometers. K65T30A5 nanocomposite displayed activity of photocatalysis throughout the UV-vis, i.e. the wavelengths of ultraviolet and visible spectrums. Methylene blue (MB) was almost completely degraded (97.66%) after 90 minutes at a pH of 9 and a comprehensive concentration is 10 mg/L⁻¹. On the other hand, Rhodamine RR was eliminated (90.66%) at pH level 3.5 and identical concentration of the dye with 120 minutes exposure of visible light. Following three cycles, the catalyst was still used to efficiently eliminate 8085 percent of MB and dye indicating a high stability [22].

Due to their widespread application in the degradation of textile dye waste, TiO_2 and clay have been used. TiO_2 clay composites have been developed over the last ten years to combine the two functionalities of the two. Clay is a non-toxic and economical adsorbent, whereas TiO_2 has active sites and stores free radicals, which further increase the degradation of the dye. In this review, the authors discuss the surface characteristics of TiO_2 -clays composites and infer their role as dye adsorbents and photocatalysts, the issues encountered in their application, and the improvements achieved over the past decade[23].

The pH meter was used to measure the activity of hydrogen ions in an aqueous solution. A pH meter shows the potential difference between two different electrodes using the flow of hydrogen ions to establish which type of solution is basic or acidic. Potential differences have an effect on solution pH and especially in acidic environments, pH is important in regulating ionization and the adsorbent surface in the process of adsorption. ZnO (80 mg/g⁻), CuO (78mg/g⁻), PbO (57mg/g⁻), and CdO (49mg/g⁻) nanoparticles had their maximum adsorption capacities at pH 5, 2 as well as pH 4. The best removal of anionic dyes was promoted by the acidic pH range. Adsorption is very

pH-sensitive; hence the best removal capacity was obtained by using the method at a low pH. ZnO 2 gave the best solution at pH 5 using reactive blue dye. Optimal performance of CuO 2 was at the pH of 2. CdO 2 and PbO 2 nanoparticles showed better performance at pH 4. pH is used to help explain the chemistry of dye solutions or adsorbent functional groups. Once pH level exceeds 2, the rate of dye adsorption and removal decreases. With the use of a natural adsorbent at pH 2, maximal adsorption of reactive blue dye was recorded, which is indicative of a pH-dependent adsorption process. PH of 2-11 is pH-dependent adsorption process depending on adsorbent character and speciation process of dye molecules.

The type of adsorbent possesses a positive charge at a pH of 8.64, and negative charge beyond 8.64. Strong electrostatic attraction between the dye molecules and adsorbent takes place at pH 5. A strong electrostatic attraction between the pH between 5 and the dye molecules increases adsorption. ZnO 2 nanoparticles have a high adsorption capacity at pH 5, as a result of the presence of additional ions on their surfaces. Additional ions inhibit repulsive forces between the catalyst surface and dye solution by reducing the formation of free radicals. The effect of pH was examined on ZnO 2 nanoparticles between the range of 2-11. Strong electrostatic forces exist in polar functional group between positive charges on the catalyst surface and anionic dyes with acidic properties. CdO 2 and Pb O 2 exhibit the superior removal capacity at pH 4 conditions. At the acidic pH, nanoparticles behave like ZnO 2 and CuO 2 nanoparticles. The higher the pH the lower is the efficiency of removal. The ability of the catalyst to adsorb reduces with a high pH as the catalyst has negative charges which leads to repulsive force between the catalyst and dye molecule. The adsorption efficiency is decreased by electrostatic forces between the catalyst and the dye. The efficiency of removing the catalyst reduces with the adherence of the dye molecules on the active sites of the catalyst.

The effectiveness of adsorption is affected by the catalyst concentration and the operating conditions. An important consideration in this process is the amount of catalyst used. To find the ideal amount of Reactive Blue for ideal operating conditions, the impact

of catalyst dosage (0.05–0.5 g) was investigated.

Because there were more unsaturated adsorption sites along the diffusion path length, a higher catalyst dosage led to less reactive blue adsorption. As the amount of catalyst increases, the dye concentration in the solution decreases. Because there are many binding sites for dye molecules, the rate of dye elimination first increases before stabilizing at a constant pace. Dye elimination is influenced by surface area, the quantity of catalyst used, and the presence of functional group. When active sites of the surface coincide, the available binding area of anionic dye molecule is reduced, which lowers the adsorption efficiency at higher nanoparticle quantity. Lack of active sites, dye molecules were less able to bind to larger amounts of catalyst, which decreased solute absorption. With their time-varying behavior, absorption and adsorption are perfect for controlling and utilizing the adsorption system. The removal of reactive blue dye and impact of contact time on the adsorbent and adsorbate for different nanoparticles were assessed in a batch experiment. The duration of contact varied from 4 to 120 minutes. Using different nanoparticles and changing the contact time setting from 4 to 1 causes significant adsorption in the first 43, 75, and 90 minutes before slowing down and stabilizing after 90 minutes.

The lengths of contact ranged from 4 to 120 minutes. Using different nanoparticles and changing the contact time setting from 4 to 1 result in significant adsorption during the first 43, 75, and 90 minutes. After that, the process slows down and stabilizes after reaching equilibrium at 90 minutes. The results show that the acidic dye has been adsorbed. The highest dye adsorption was observed at 43, 75, and 90 minutes before reaching equilibrium for ZnO₂ (85.69 mg/g), CuO₂ (79.04 mg/g), CdO₂ (64.12 mg/g), and PbO₂ (51.58 mg/g). Because they demonstrated the highest recorded adsorption capacity, contact times of forty-three, seventy-five, and ninety minutes were chosen. It took longer to reach equilibrium after five minutes when using polyaniline or polypyrrole nanoparticles for the removal of azo dye. Adsorption capacity remains constant after equilibrium is reached. At the start of the reaction, the adsorption rate fluctuates between

rapid and slow, reaching equilibrium after 15 minutes. It stabilizes after 15 minutes of oscillating between rapid and gradual phases. Optimal adsorption results from large surface area because it provides more active sites for dye molecules to adhere to. Due to the restricted surface area caused by high contact, the adsorption rate falls and the adsorption capacity decreases. After equilibrium is reached, this limits the number of active binding site that is available at saturation point.

The initial dye solution concentration has an impact on the adsorption capacity of nanocomposites. To determine how well nanoparticles could adsorb anionic dye at the optimal pH, this study employed a contact time of 90 minutes, a dosage of 0.05 g, a temperature of 37 °C, and a shaking rate of 120 rpm. The dye concentration ranged from 25 to 200 mg/L. As demonstrated above, Reactive Blue's adsorption rose as dye solution concentrations rose. ZnO₂ (85.69 mg/L), CuO₂ (79.04 mg/L), PbO₂ (64.12 mg/L), and CdO₂ (51.58 mg/L) reached their maximum adsorption capacities at dye concentrations of 100, 150, and 75 mg/L. 88.69 mg of ZnO₂ per liter. [24]

At concentration of 100 mg/L of reactive blue, the maximum adsorption capacity is noted. The intended results are produced by initial dye concentration, which lowers mass transfer resistance and establishes equilibrium between dye concentration and catalyst surface. Adsorption capacity is impacted by temperature via physicochemical and endothermic processes. Anionic dye was extracted using synthetic nanoparticles at a catalyst concentration of 0.05 g in 50 mL.

Optimal results in experimental processes include the adjustment of the dosage, pH, contact time, agitation rate, and temperature, which should be limited to the 37-65 of degree Celsius. The increase in temperature was endothermic and thus, the decreasing performance of adsorption as temperature increased. With an increase in temperature, dyes become more mobile and hence have more chances of interacting with surfaces of catalysts. Therefore, an increase in temperatures lowers adsorption capacity with an indication of an exothermic reaction. The effect of temperature on eliminating a dye was observed in the case of different nanoparticles, and it can be explained by correlation

between active sites and dye molecule, which is intensified at high temperature, which inhibits adsorption on the catalyst surface. Such an effect has a negative influence on the dye adsorption and de-absorption ability. The maximum efficiency of the synthesized nanoparticles in the removal of reactive blue when the concentration is 0.1 to 0.5g and in the presence of electrolytes (CaCl₂ some H₂O, NaCl, and AlCl₃ some H₂O) was measured under optimal conditions. The electrolytes had two different influences on the results observed and the efficiency of nanoparticle adsorption was varied [25].

The influence of the dosage of a CuO–TiO₂-clay photocatalyst (2080mg) was examined. The rates of photodegradation were also high (36.17–55.67%) with the increasing catalyst loading (20 to 50 mg) mainly because of more active sites and formation of radicals. Nonetheless, TARTZ efficiency in removing impurities decreased to 29.73 per cent at an even greater photocatalyst dosage of 80 per cent. Photocatalyst aggregation and increase in optical turbidity on high loads hamper penetration of light and hence reduction in photodegradation. The same trend is observed with the rest of the study and this is why 50mg mass of the catalyst has been selected as the optimum dosage. Photocatalytic activity of CuO–TiO₂ clay was tested under four different pH levels namely; 2, 4, 6.4 and 10. Under a pH range of pH2 to the neutral pH of 6.4, the dye degradation was enhanced to 55.67% using CuO–TiO₂ clays of 2 to 6.4. When pH levels rise above 6.4, photodegradation rates fall, peaking at 30.78% at pH 10. For pH values of 2.0, 4.0, 6.4, 8.0, and 10.0, respectively, the composite's zeta potential was measured at +6.10, +6.90, +7.06, –4.10, and –11.02 mV. As a result of the deprotonation of surface functional group, the photocatalyst's positive charge decreases with continuous partial dissolution, whereas its negative charge increases with increasing pH levels. TARTZ is neutral at and anionic, with three different pK_a values.

Two 9W and 11W electrical power lamps were used to investigate the effects of light intensity. The lamp's electrical power had a direct correlation with the rate of deterioration. TARTZ removal rate increased from 46.07 to 55.67 %, when the lamp power was increased from 9 to 11W. Increased electron-hole pair formation and faster

photodegradation are the outcomes of higher electrical power. Photodegradation efficiency is influenced by the concentration of TARTZ dye. Removal efficiency decreased when initial dye concentration was increased from 2 - 10 mg/L. The greatest removal (62.50%) under visible light and complete elimination (100%) under sunlight were achieved by applying a dye solution at concentration of 2 mg/L for 120 minutes. Active sites of photo catalyst absorb pollutant molecules more rapidly at lower concentrations, clarifying the result seen. With higher concentration, active areas take in dye molecules, leading to diminished radical generation [26].

The adsorption characteristics of dyes in water solutions are significantly affected by the concentration of hydrogen ions, which is an important factor. This impacts not just the solubility of colors in solution, but it may also substitute some of them. Ionization of adsorbate throughout the reaction is influenced by the presence of positive ions at active sites. Adsorption of dye onto adsorbent material was studied at various pH levels (2–9, adjusted with HCl and NaOH) to maximize dye removal. At a lower pH of 3, the greatest removal efficiency of 99.40% for RR dye was observed. The effectiveness of RR removal decreased by 24% when the pH of the solution increased. In order to attract RR anions (sulphonic), the amine groups in chitosan had to be protonated at a lower pH (3), which led to the improved removal efficiency. Because hydroxyl ion competes with RR anions for the same adsorption sites, elevated pH levels may decrease removal efficiency. For CV, efficiency of clearance was largely unaffected by pH across the examined range. Consequently, the initial solution pH of 5.0 was utilized for further investigations. This may be due to robust hydrophobic interactions between CV-nanocomposite molecules and adsorbents, as organic molecules typically form physical bonds with them. As dosage increases, more adsorption sites become available, which makes it easier for cationic and anionic dye to adhere the adsorbents' surface. The impact of stirring rate on the adsorption of RR and CV dye is demonstrated by the removal of these dyes at varying stirring speeds (0-250 rpm). The removal efficiency increased from 38.0 to 99.4% for reactive red and from 60.0 to 99.8% for crystal violet when the stirrer speed was increased from 0 to 200

rpm. The observed phenomenon may be explained by the fact that stirring increases system mobility and reduces boundary-layer resistance. Increasing the stirring speed enhances the close interaction between the two phases (adsorbent and adsorbate) and reduces external mass transfer.

By creating dyes' adsorption at different temperatures, effect of temperature on dye elimination was observed. Temperature variation have little effect on dye clearance rates, experiencing only a slight increase. Consequently, additional research was performed at ambient temperature. A key aspect in a cost-effective wastewater treatment system is the balance time. A key element for evaluating the effectiveness of adsorbents and understanding the adsorption mechanism is the kinetics of adsorption. A substance needs to have a quick and precise adsorption rate in order to work well as an adsorbent. At various intervals between three and thirty minutes, the impact of contact duration on the dyes' adsorption was evaluated. The findings showed that there was no more substantial adsorption following this contact time, and the adsorbed dyes' removal efficiency steadily rose for 20 minutes, reached roughly 99.4% and 99.8% for RR and CV, respectively.

BT-CS nanocomposite's having pores and empty adsorption sites, which gradually fill up and cause a slowdown in adsorption over time until complete saturation occurs after 20 minutes, the amount of dyes adsorbed increased rapidly. The accumulation of dye at solid-liquid phase boundary, which is a mass transfer process, is commonly referred to as dye adsorption. For this reason, while holding the other variables constant, the impact of the initial dye concentration was examined. As explained, amount of dye adsorbed increased as initial concentration rose. This happens because initial dye concentration exerts driving force that is greater than the dyes' resistance to mass transfer between liquid and solid phase. Additionally, initial increase in dye concentration improve dye adsorbent interaction[26].

The accumulation of dye at solid-liquid phase boundary, which is a mass transfer process, is the broad definition of dye adsorption. That's why, the effect of initial dye

concentration was observed while keeping all other factor equal. Previously mentioned, as initial concentration rose, amount of dye adsorbed increased. The driving force from initial dye concentration is stronger than the dyes' resistance to mass transfer between liquid and solid phase, which is why this occurs. Furthermore, the dye-adsorbent interaction is enhanced by the initial dye concentration increase.

Various concentration levels ranging from 10-40 mg/L were employed, while remaining operating conditions remained constant, the impact of initial dye concentrations on degradation efficiency was observed. the connection between degradation efficiency at a given photo-catalyst amount and initial dye concentration. The results showed that rate of photo-catalytic degradation decreases as initial concentration of reactive blue 21 dye increases from 10-40 mg/L for 1 hour. This happens as a result of decreased photo-catalytic activity caused by a higher dye concentration that limits light penetration in the $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{AlFeO}_4$ catalyst[27].

CHAPTER 3

METHODOLOGY

Material and methods

3.1 Chemicals

Aluminium chloride, titania isopropoxide, 2-propanol, clay, NaOH, HCl

3.2 Instruments

- Weighing balance was used to weigh adsorbent and adsorbate
- pH meter was used for pH measurement of solution
- FTIR, XRD, and SEM techniques were used for adsorbent characterization
- UV/ Visible spectrophotometer was used for measurement of lambda maximum (λ_{max})
- Shaker was used to agitate or mix the sample

3.3 Preparation of dye solution in water

Stock solution was prepared by adding 1 g of dye in 1000 ml of distilled water. Further dilutions were made to prepare the solution for experimental with various concentration within the range of 30-200 mg/L. UV/visible spectrophotometer was used to measure the dye solution's absorbance, a standard curve was created. The λ_{max} of reactive blue 248 dye was 612.6 nm.

3.4 Synthesis of AlTiO₂

Aluminum doped titania was prepared by co-precipitation method. To prepare AlTiO₂ particles, first dissolve 1 g of Aluminium chloride in 20 ml distilled water under 60 min of stirring. In separate beaker 1 ml Titanium (IV) isopropoxide mix with 20 ml of distilled water under 60 min of continuous stirring. After this Aluminum chloride was

added in the titanium precursor solution under constant stirring. Adjust the pH by used NaOH and HCl. White precipitate was formed, leave it for 24 hour at room temperature. Filter the precipitate and wash it with distilled water to remove the impurities. Dry the precipitate in an oven at 120 °C for 12 hour. Calcinate the dried powder for obtain AlTiO₂ nanoparticles[28].

3.5 Synthesis of AlTiO₂/clay composite

AlTiO₂/caly composite was prepared by sol gel method. The organoclay (Bentonite) was employed directly in this process. 1 g of organoclay mixed in 15 milliliter of 2-propanol and solution was agitated for 4 hours. Subsequently, Aluminium chloride and titanium isopropoxide was mixed with 2-propanol and agitated for 4 hour . The precursor of Al-Ti added into the organoclay suspension while being magnetically stirred and maintained for 12 hour at 50°C until a uniform dispersion was achieved . To complete the condensation process a gel like suspension leave for 24 hour at room temperature . Then dry it at 100 °C in oven for 24 hour to obtain a dry product[29].

3.6 Batch experiment

3.6.1 Effect of pH

Effect of pH for both ionization state of dye molecules and surface charge of adsorbent while removing dye from aqueous solutions. It has an impact on dye solubility, adsorption capacity, and electrostatic interactions. By encouraging attraction between oppositely charged dye ions and the adsorbent surface, low pH improves removal efficiency and increases dye absorption.

3.6.2 Effect of contact time

Adsorption equilibrium was affected by contact time. The adsorbent's accessible active sites allow for quick dye removal at first. Adsorption slows and finds equilibrium with increasing time. Maximum dye absorption was ensured by enough contact time. Insufficient time results in partial adsorption, which lowers the effectiveness of color removal from aqueous solutions.

3.6.3 Effect of concentration

The initial dye concentration has a significant effect on adsorption performance regarding dyes removal. Removal is more frequently promoted by the easy accessibility of adsorbent sites that occur at low concentrations. The activity decreases with a concentration while the active sites are saturated. Even though, increased concentration enhances the energy to transfer the mass, it can surpass the capacity of the adsorbent, and thus, reduce the total percentage of removal.

3.6.4 Effect of dosage

Adsorbent dose had a significant impact on dye removal efficiency. A higher dose increases the number of active sites, which improve the rate of dye adsorption and elimination. However, site saturation and particle aggregation, which decrease surface area, might cause efficiency to plateau after an ideal level. Therefore, 0.01g dose guarantees efficient and cost-effective dye removal from water.

3.6.5 Effect of temperature

In dye removal, temperature affects adsorption kinetics and capacity. Increasing temperature can enhanced dye diffusion and adsorption rate, indicating an endothermic process. It may also change the surface properties of the adsorbent and dye solubility. However, very high temperatures can reduce adsorption efficiency by weakening adsorbate–adsorbent interactions.

CHAPTER 4

RESULTS

4.1 FTIR

Fourier Transform Infrared Spectroscopy (FTIR) is a method for analyzing samples to determine functional groups and molecular structures by assessing their infrared absorption spectrum. FTIR spectra shown the difference between AlTiO_2 and $\text{AlTiO}_2/\text{clay}$ composite. These two spectra shown broad bands around 3301 cm^{-1} and 3353 cm^{-1} imputed to -OH stretching vibration showing that water or hydroxyl groups are present. Peaks at 1633 cm^{-1} and 1631 cm^{-1} shown H-O-H bending vibration. In $\text{AlTiO}_2/\text{clay}$ spectra additional peaks are showing that indicating Si-O-Si and Al-O-Si at 1337 cm^{-1} and 1049 cm^{-1} , that confirm the clay incorporation. In AlTiO_2 peaks at 981 and 773 cm^{-1} correspond to Ti-O stretching. It shown a successful doping and composite are formed.

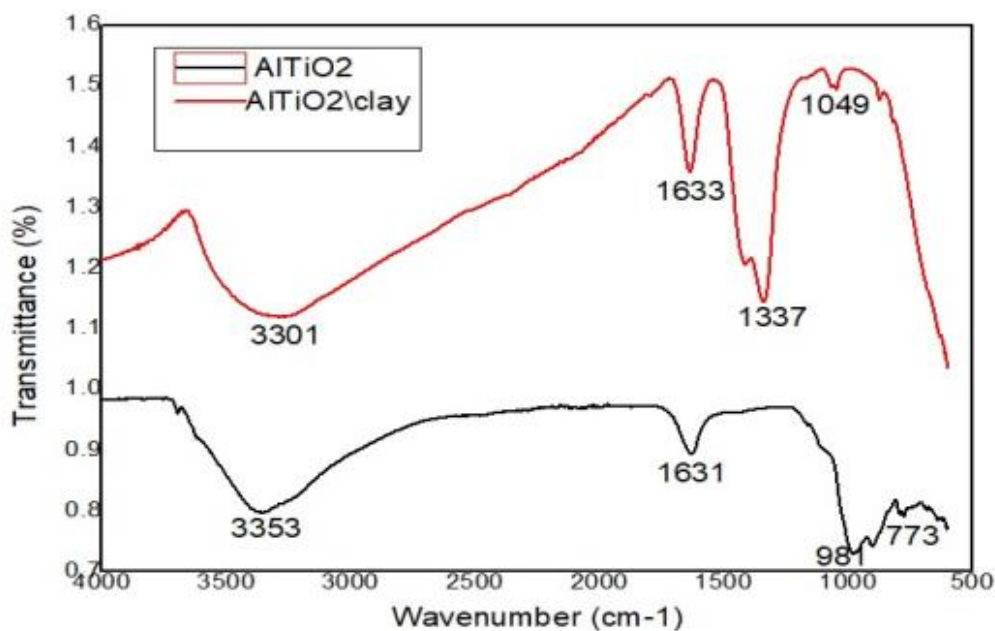


Figure 4.1: FTIR spectra of AlTiO_2 and $\text{AlTiO}_2/\text{clay}$ composite

4.2 SEM

The SEM images of AlTiO₂ and AlTiO₂/clay composite at different magnifications display important morphological features. The Al-doped titania was displayed crystalline, irregular polygonal particles exhibiting signs of clusters, suggesting effective doping and thermal processing. In comparison, the AlTiO₂ clay composite was shown a layered, flaky clay structure with TiO₂ nanoparticles distributed throughout. At increased magnifications, the composite was shown evenly distributed, nanometre-scale particles attached to smooth clay surfaces. The porous structure and extensive surface area were indicating improved adsorption or photo catalytic capability.

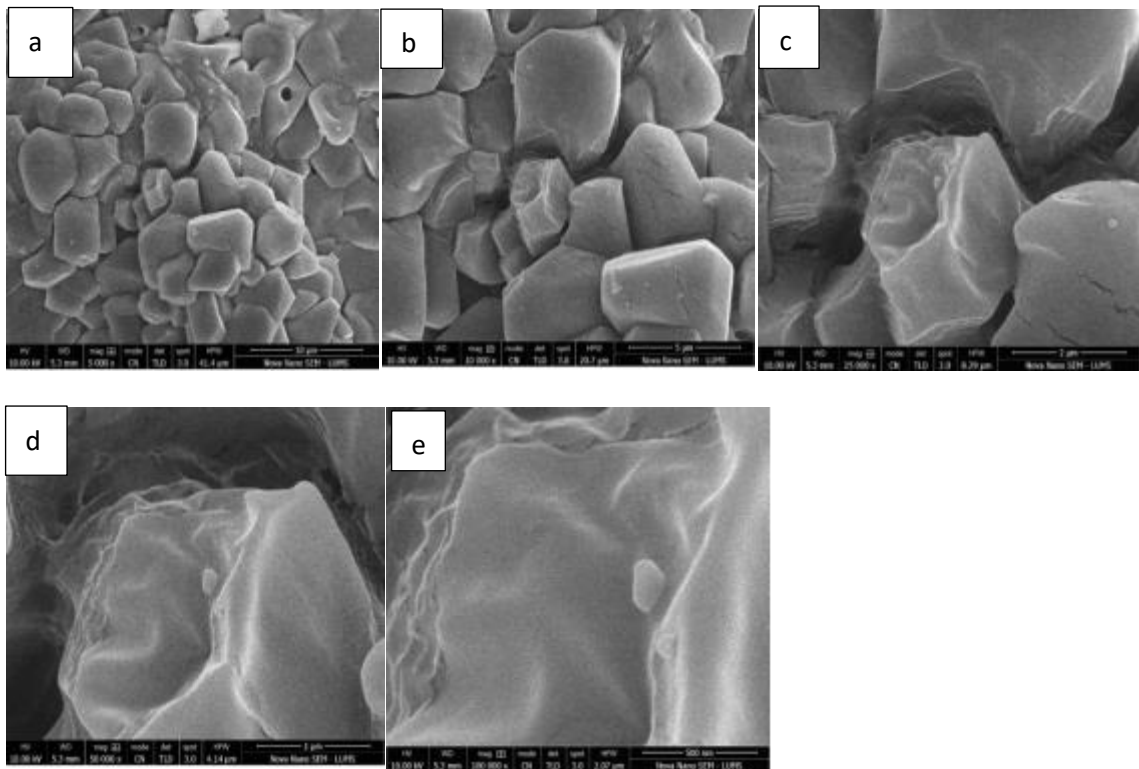


Figure 4.2: SEM of AlTiO₂ particles at magnification value and scale bar of fig. a) 5000x & 10µm ,
b) 10000x & 5µm, c) 25000x & 2µm, d) 50000x & 1µm, e) 100000x & 2nm

SEM of AlTiO₂ clay composite

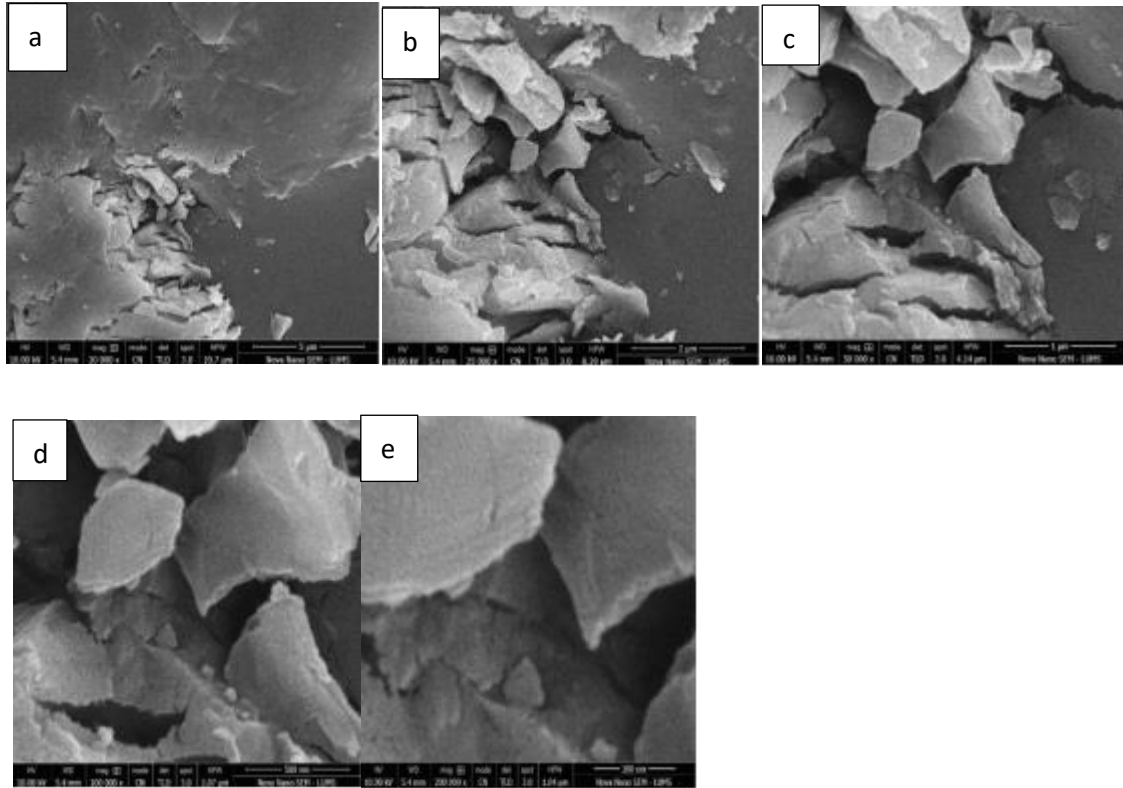


Figure 4.3 :SEM of AlTiO₂ \clay composite at magnification value and scale bar of fig. a) 10000x & 5µm , b)25000x & 2µm, c)50000x & 1µm, d)100000x & 500nm, e)200000x & 200nm

4.3 XRD

X-ray diffraction (XRD) is an effective analytical method employed to identify the crystal structure, phase composition, and crystallization of substances by analyzing the diffraction patterns produced by X-rays. The XRD spectra of AlTiO₂ and AlTiO₂ both spectra had no sharp peak that show the irregular or poorly crystalline material. They had no long rang order in their morphology. Figure (a) show the clay-based composite with disrupted crystal lattice, Figure (b) show the doped titania sample having disorder gel and incomplete crystallization

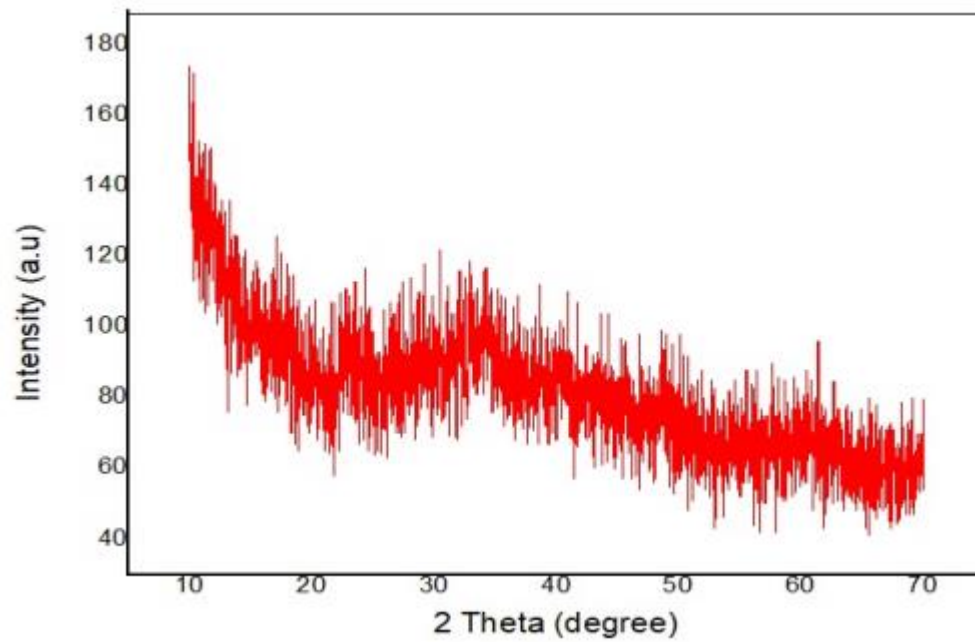


Figure 4.4: XRD for AlTiO₂/clay

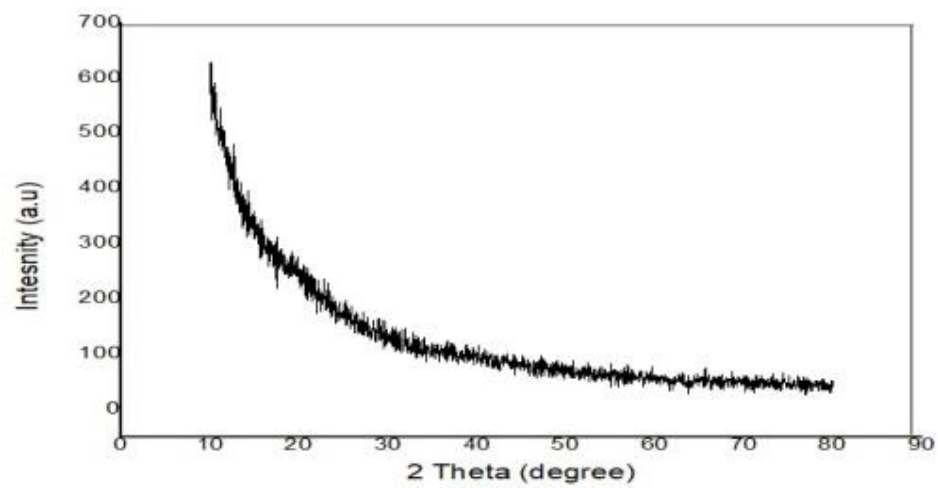


Figure 4.5: XRD for AlTiO₂

4.4 Standard curve

A calibration curve was created at λ -max 600 nm employing serial dilutions beginning with 20ppm, 30ppm, 40ppm, and 50ppm of the solution. Beer's Lambert law states that concentration is directly proportional to absorbance

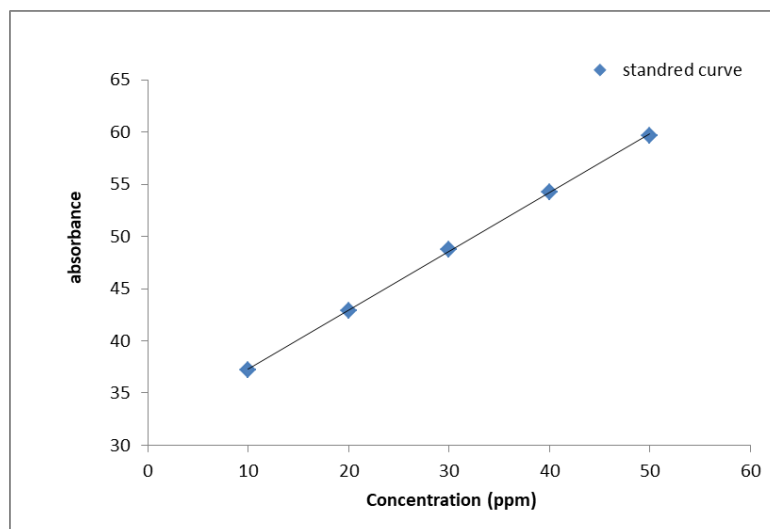


Figure 4.6: Standard curve showing concentration vs absorbance

4.5 Effect of pH

To determine the impact of pH, experiments were performed at different pH levels ranging from 3 to 10 under acidic and basic conditions. The prepared solution initially had a pH of 6.50 at a concentration of 250 ppm. The pH level was regulated by the addition of either NaOH or HCl. For the current study, take 30 ml from the prepared 250 ppm solution and add 0.01 g of Al-doped titania composite both with clay and without clay, then maintain on a rotary orbital shaker at 180 rpm for 90 minutes. A sample was taken out of the shaker at the end of the sampling process, and the UV Spectrophotometer was used to measure its optical density.

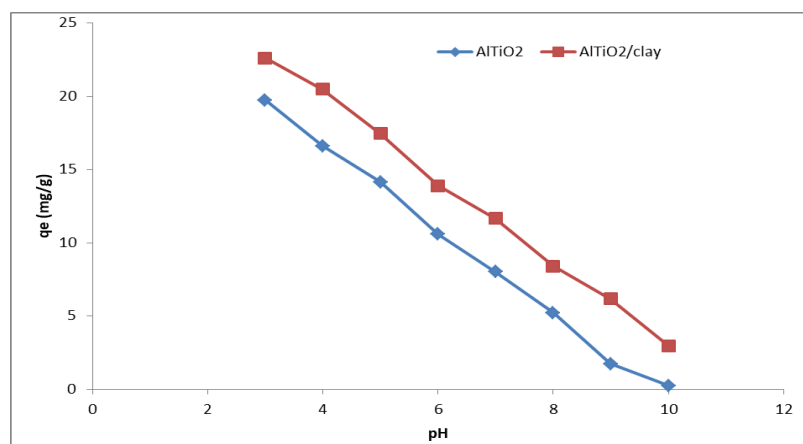


Figure 4.7: Effect of the solution pH on the dye removal

Reactive blue dyes are negatively charged and the surface of adsorbant is positively charged, so electrostatic attraction enhanced adsorption. As pH increases, the adsorption capacity (q_e) of both materials decrease. At lower pH (acidic medium), both adsorbant show their highest dye removal capacity with AlTiO₂ around 19mg/g and AlTiO₂/clay almost 22mg/g. High adsorption was occurred due to clay, the reason was this clay improved surface area and provide additional active sites. At last optimal dye removal occure at low pH (acidic conditions)

4.6 Effect of adsorbent dosage

25ml of the 500-ppm stock solution is taken and dissolved in 125ml of distilled water to create a 250-ppm solution. Following this, 6 beakers were prepared, each containing 30ml of the solution, to which different amounts of Al-doped TiO₂ composite with and without clay are added: 0.01, 0.03, 0.05, 0.07, 0.09, and 0.1, respectively. And maintained for mixing at 180 rpm using a shaker for 120 minutes

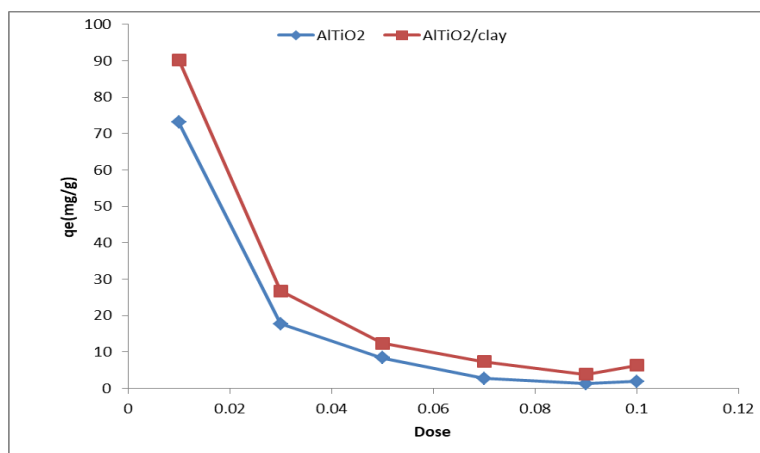


Figure 4.8 : The effect of dosage for removal of dye

For both AlTiO₂ and AlTiO₂/clay, the adsorption capacity decreases as the adsorbent dosage increases from 0.01 g to 0.10 g. And at low dosage, there were fewer adsorption sites but higher dye concentration per unit mass of adsorbent, leading to higher q_e (mg/g). As dosage increases, although more active sites are available, the dye-to-sorbent ratio decreases, resulting in lower q_e due to unsaturation of active sites. At all dosages, AlTiO₂/clay was show higher adsorption capacity than AlTiO₂. This shows that incorporating clay enhanced surface area, adsorption sites, or improved porosity, make the composite more efficient. The most significant difference in adsorption capacity was noticed at low dosages.

4.7 Effect of dye concentration

The starting concentration of reactive blue dye was set at 30ppm, 60ppm, 90ppm, 120ppm, 150ppm, 180ppm, and 200ppm, maintaining a dose concentration of 0.01 and pH of 3. This experiment was conducted for both dosages of AlTiO₂ with clay and without clay.

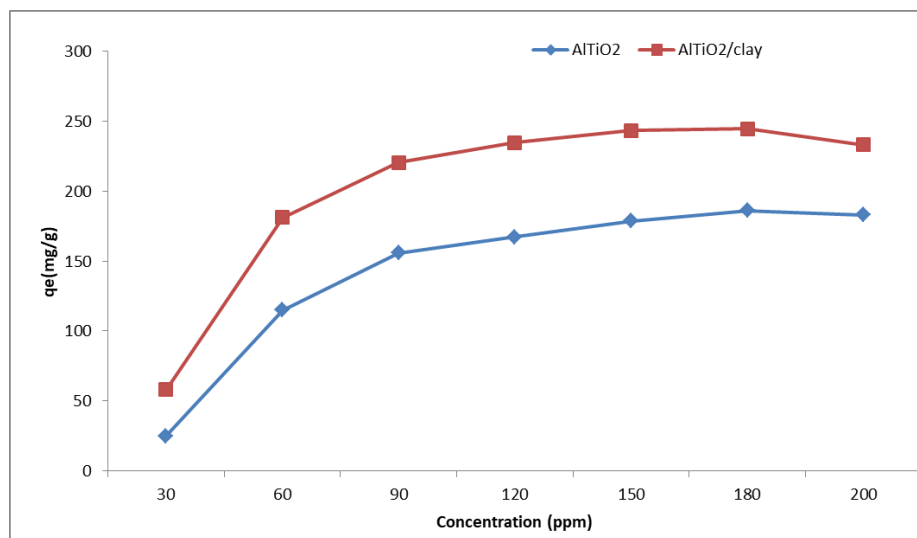


Figure 4.9: Effect of concentration on dye removal

As the dye concentration in water increases, both AlTiO₂ and AlTiO₂/clay adsorbed more dye at first because there were plenty of empty sites for the dye to attach to. After a certain point, the sites on the adsorbent become full, so the adsorption capacity stop increasing much this is called saturation. AlTiO₂/clay always holds more dye than AlTiO₂ at the same concentration, likely because its surface has more active spots available. The maximum q_e for AlTiO₂/clay is approximately 240 mg/g and maximum q_e for AlTiO₂ is 190 mg/g. The result confirm that clay supported metal oxide composite are more effective for dye removal from fresh water.

4.8 Effect of time

Each adsorption test involved mixing 0.01g of Al doped TiO₂ with or without clay in a 250 ml round-bottom flask at room temperature with 30 ml of a dye solution at a specific concentration and pH. The mixture was then agitated at 150 rpm using a rotary orbital shaker. At predetermined intervals of fifteen minutes each, the sample was taken out of the shaker. The agitated sample was removed from the shaker after 15 minutes, and the UV Visible Spectrophotometer was used to measure its optical density. Finally, it was observed that the adsorption increased gradually, as shown in figure.

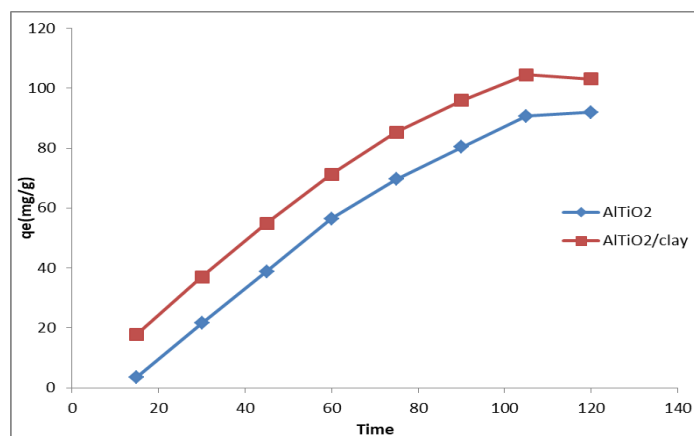


Figure 4.10: Effect of time for dye removal

At the start, dye removal increases quickly for both materials because many active adsorbent sites were available on the adsorbent surface. Thus, dye molecule can easily occupy these sites, leading to a rapid increase in q_e . Over time, the rate of increase slow down as the adsorbent surfaces become full, no further adsorption occurs, and the curve slightly show equilibrium. The AlTiO₂/clay system is regularly proven to maintain a high degree of dye removal when compared to the AlTiO₂ material, the highest adsorption capacity of the former being about 1250 g⁻¹, whereas the latter adsorption capacity is 1050 g⁻¹. Both systems achieved equilibrium in about 100 minutes beyond which no additional significant uptake of the dye was noted.

4.9 Effect of Temperature

The experiment was done at eight different temperatures (15 °C, 30 °C, 45 °C, 60 °C, 75 °C, 90 °C, 105 °C and 200 °C) and all other experimental conditions such as pH, dosage of adsorbent and dye concentration kept constant. Analysis of data revealed that the adsorption capacity reduced in a temperature-dependent manner which is typical of an exothermic process of adsorption. Exothermic adsorption was evidenced by various adsorption techniques where rising temperatures lead to a reduction in adsorption capacity. In this type of adsorption, the adsorption process was delayed as the force between dye species and active site on adsorbent surface became weaker.

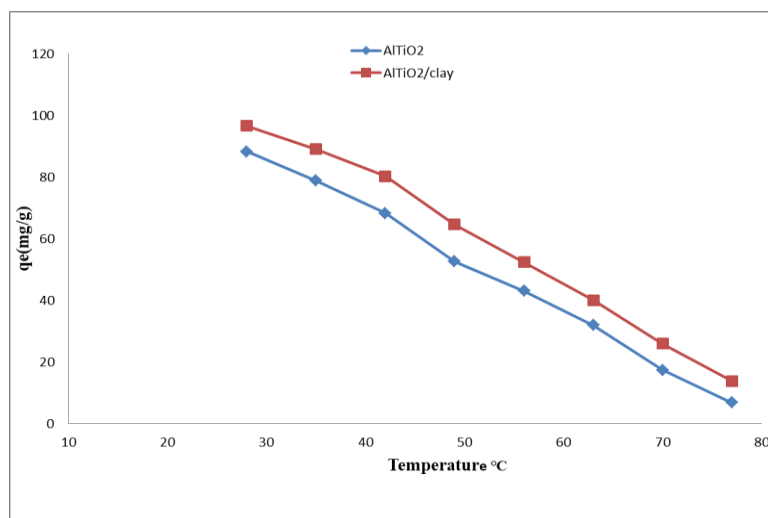


Figure 4.11: Effect of temperature on removal of dye

At low temperatures (around 10–20 °C), both materials had high dye removal efficiency above 80%. As the temperature increases, dye removal efficiency gradually decreases for both materials. The drop was more noticeable after about 40 °C. Throughout the whole range, AlTiO₂/clay performs slightly better than pure AlTiO₂. At the highest temperatures (~80 °C), removal drops to around 20–30%.

The reason is that decrease with temperature suggests the dye adsorption process was exothermic higher temperatures reduce the material's ability to hold onto dye molecules, likely because the thermal motion of molecules increases, making dye detach more easily. The clay in AlTiO₂/clay helped retain slightly more dye than AlTiO₂ alone, giving it better performance.

4.10 Kinetics Model

Kinetic modeling allows for the determination of adsorption rates and produces suitable rate equations that represent possible reaction mechanisms. The intraparticle diffusion model, pseudo-second-order kinetics models (four linear representations), and pseudo-first-order kinetics models were among the kinetic models examined in this framework[30].

4.10.1 Pseudo-first order:

The kinetic equation of pseudo-first order is introduced.

$$\log (q_e - q_t) = \log q_e - k_1 \frac{t}{2.303}$$

where t is the contact time (min), k_1 is the pseudo-first-order rate constant (1/min), q_t was the amount of dye extracted at time t (mg/g), and q_e was the equilibrium adsorption capacity (mg/g). A graph of $\ln (q_e - q_t)$ as a function of t was created. The calculated pseudo first order rate constant (k_1) was displayed in the model. The table displayed the dye removal results using AlTiO_2 and $\text{AlTiO}_2/\text{clay}$ at 25°C .

For both adsorbents, the calculated adsorption capacities ($q_e \text{ cal}$) were much lower than the experimental values ($q_e \text{ exp}$). For AlTiO_2 , $q_e \text{ exp}$ was 533.70 mg/g while $q_e \text{ cal}$ was 122.82 mg/g, and for $\text{AlTiO}_2/\text{clay}$, $Q_e \text{ exp}$ was 1852.67 mg/g compared to $q_e \text{ cal}$ of 104.54 mg/g. The low R^2 values (0.749 and 0.3749) indicate a poor fit of this model, suggesting that adsorption does not follow pseudo-first-order kinetics.

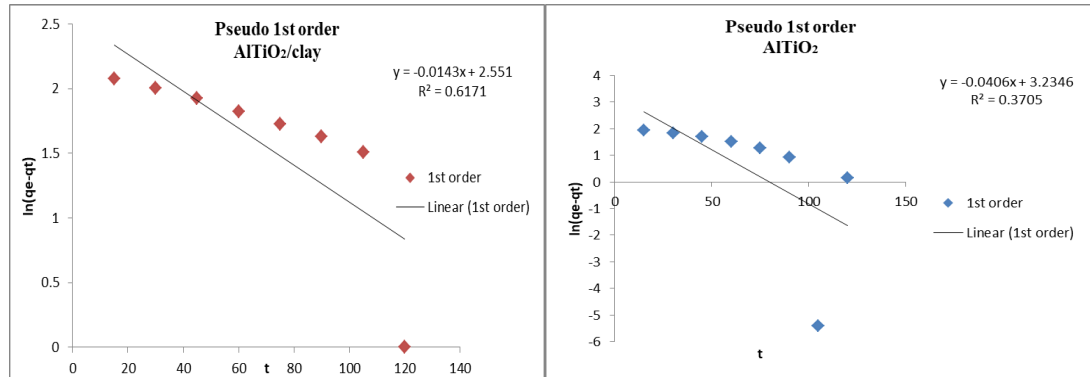


Figure 4.12: Pseudo first order kinetics for removal of reactive blue 248 dye by AlTiO_2 and $\text{AlTiO}_2/\text{clay}$ composite

4.10.2 Pseudo-second-order :

In this model, the adsorption on the surface, which involves chemisorption, was the rate-limiting step. The physicochemical interactions between the two phases cause the dye to be removed from wastewater. Usually, the model was presented in its linear form. The tables display the kinetic parameters of the modified pseudo-second-order model for dye elimination using AlTiO₂ and AlTiO₂/clay at 25°C. where the constant for the adsorption rate in the pseudo-second-order model is denoted by k₂ (g/mg/min).

$$\frac{t}{q_t} = \frac{1}{k_2} \frac{1}{q_e^2} + \frac{t}{q_e}$$

This model showed slightly better agreement for AlTiO₂ with an R² of 0.8113, but still failed for AlTiO₂/clay where R² was very low (0.0411). The large differences between Q_e exp and Q_e cal further confirm that, this model did not adequately represent the adsorption process, especially for the composite material.

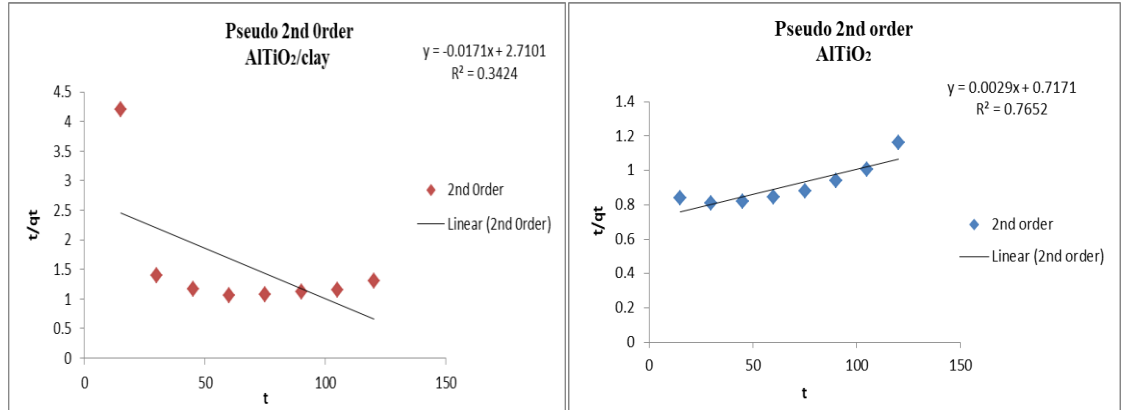


Figure 4.13: Pseudo second order kinetics for removal of reactive blue 248 dye by AlTiO₂ and AlTiO₂/clay composite

4.10.3 Intraparticle diffusion model

Intraparticle diffusion model, also referred to as Temkin, describes adsorption processes, indicating that the speed of adsorption is affected by the movement of the adsorbate toward the adsorbent

$$q_t = k_p t^{\frac{1}{2}} + C$$

The highest correlation coefficient ($R^2 = 0.981$ for both AlTiO_2 and $\text{AlTiO}_2/\text{clay}$) was observed with the intraparticle diffusion model. This indicates that the adsorption mechanism was strongly governed by intraparticle diffusion, meaning that the adsorbate molecules diffuse into the pores of the adsorbent during the adsorption process. The values of K_p (0.0656) and C_i (3.465) further support this interpretation.

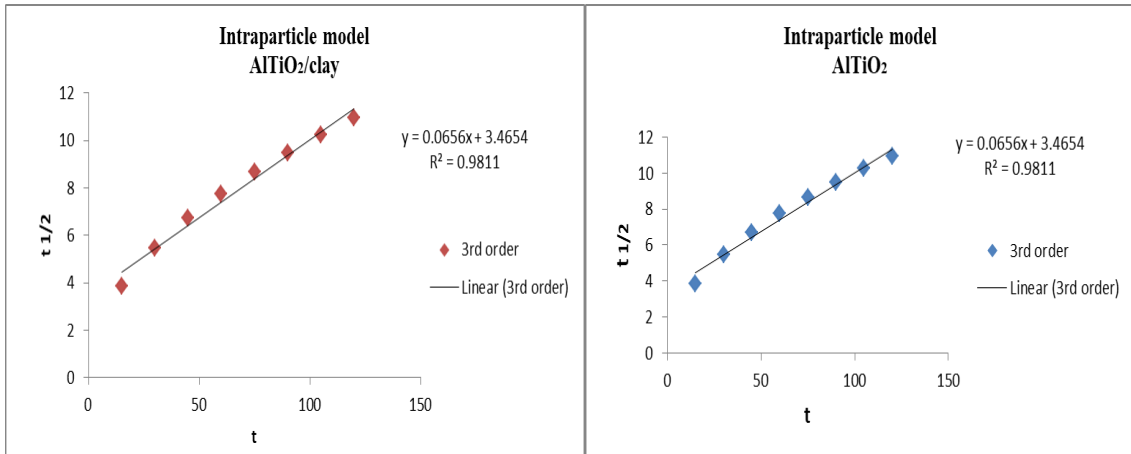


Figure 4.14: Intraparticle model for removal of reactive blue 248 dye by AlTiO_2 and $\text{AlTiO}_2/\text{clay}$ composite

Table 4.1: Kinetic data for the removal of reactive blue-248 dye using AlTiO₂ & AlTiO₂/Clay composite

Pseudo 1st order	AlTiO₂	AlTiO₂/clay
K ₁ (1/min)	0.0935	0.032921
q _e exp(mg/g)	1716.3	355.63
q _e cal(mg/g)	104.54	91.95
R ²	0.3705	0.6171
Pseudo 2nd order		
K ₂ (1/min)	0.000127	0.000043
q _e exp(mg/g)	344.82	58.47
q _e cal(mg/g)	104.54	91.95
R ²	0.7652	0.3424
Intraparticle Diffusion model		
K _p	0.0656	0.0656
C _i	3.4654	3.4654
R ²	0.981	0.981

The results show that the pseudo-first-order and pseudo-second-order models do not adequately describe the adsorption behavior of AlTiO₂ and AlTiO₂/clay, as evidenced by low R² values and poor agreement between experimental and calculated q_e values. In contrast, the intraparticle diffusion model provided an excellent fit (R² = 0.981), confirming that pore diffusion is the rate-controlling step in the adsorption process for both materials.

4.11 Adsorption Isotherm Models

4.11.1 Langmuir model

The Langmuir model suggests that mono layer adsorption takes place on the solid surface with uniform and identical sites (Langmuir, 1918). It indicated that additional adsorption did not occur once the active sites were occupied by dye molecules. The isotherm of the saturated mono layer was shown by adhering to

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}$$

C_e : represents the equilibrium concentration of dye in solution (mg/L)

q_e : indicates the unit equilibrium adsorption capacity

q_m : signifies the maximum capacity for dye uptake, reflecting the adsorption capacity for a full monolayer (mg/g)

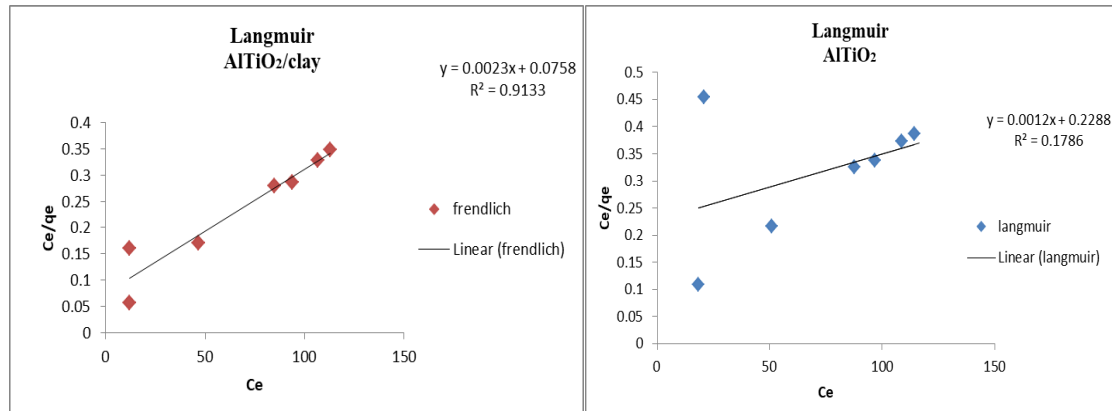


Figure 4.15: Langmuir adsorption isotherm plot for AlTiO₂/clay and AlTiO₂

4.11.2 Freundlich isotherm

Freundlich isotherm is an empirical model assuming that the distribution of the heat on the adsorbent surface is nonuniform, namely a heterogeneous adsorption. The equation is stated as follows

$$\log q_e = \log K_F + \frac{1}{n \log C_e}$$

where n and KF [mg/g (L/mg) n] are both the Freundlich constants giving an indication of adsorption intensity and capacity, respectively. The degree of non-linearity between solution concentration and adsorption is n dependent as follows: if the value of n is equal to unity, the adsorption is linear; if the value is below to unity, this implies that adsorption process is chemical; if the value is above unity adsorption is a favorable physical process

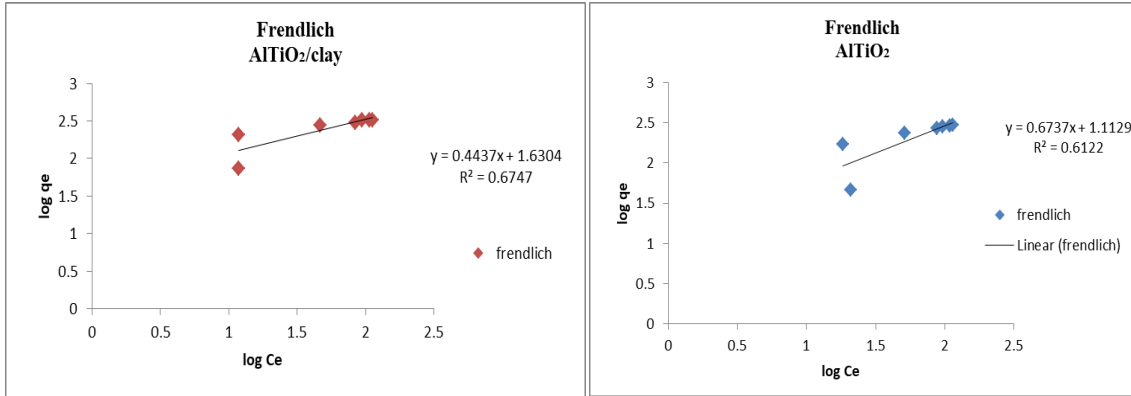


Figure 4.16 : Freundlich adsorption isotherm plot for AlTiO₂/clay and AlTiO₂

4.11.3 Temkin isotherm

According to the Temkin isotherm model, adsorbent-adsorbent interactions cause the adsorption energy to decrease directly with surface inclusion. This equation provides the linear form of the Temkin isotherm model.

$$q_e = B \ln A + B \ln C_e$$

where b is the Temkin constant in J/mol that is related to the heat of adsorption.

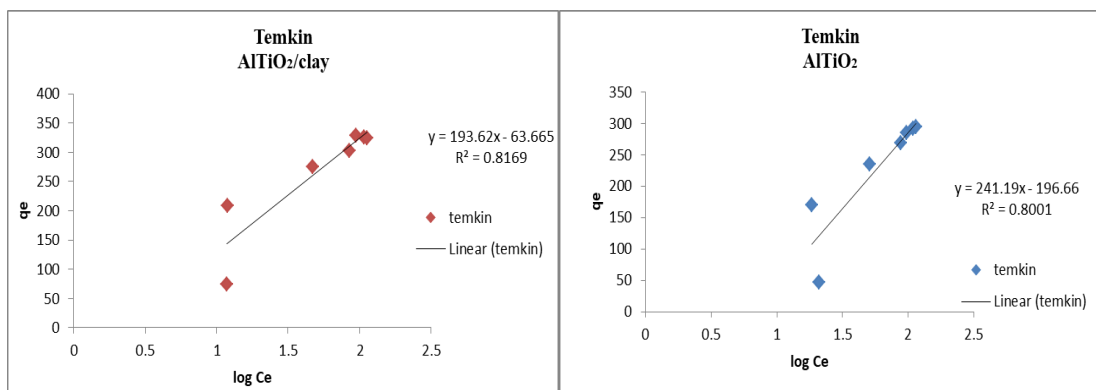


Figure 4.17 : Temkin adsorption isotherm plot for AlTiO₂/clay and AlTiO₂

Table 4.2: Isotherm data for the removal of reactive blue-248 dye using AlTiO₂ & AlTiO₂/Clay composite

Isotherm model	AlTiO ₂ /clay	AlTiO ₂
Langmuir		
q_m calculate(mg/g)	328.22	295.56
q_m experimental (mg/g)	434.78	833.3
b	0.0303	0.0056
R^2	0.9133	0.1786
Freundlich		
q_m calculate (mg/g)	328.22	295.56
k_f	42.65	12.94
n	2.25	1.484
R^2	0.6747	0.6122
Temkin		
q_m calculate (mg/g)	328.22	295.56
A	0.1798	0.4425
B	193.62	241.19
R^2	0.8169	0.8001

CHAPTER 5

DISCUSSION

Industrial development, especially in textile, leather, paper, and food industries, has led to the excessive use of synthetic dyes. A significant portion of these dyes is discharged into wastewater during production and processing. It is estimated that around 10–15% of dyes used in dyeing processes do not bind to fibers and are lost in effluents. The release of colored wastewater poses several environmental concerns. Dyed water pollution is not only an environmental issue but also a serious threat to human health. Many synthetic dyes and their breakdown products are toxic, mutagenic, or even carcinogenic. Contaminated water used for drinking is harmful for humans and other living things. This makes dye removal from wastewater a public health necessity. The importance of removing dyes from wastewater lies in restoring water quality, protecting aquatic ecosystems, and ensuring safe water for human consumption.

The current study looked at the synthesis, characterization, and adsorption capacity of Aluminum-doped titania (AlTiO_2) and an AlTiO_2 /clay composite in the separation of Reactive Blue -248 in aqueous solutions. pH, initial dye concentration, contact time, adsorbent dosage and temperature were varied systematically, thus explaining their impact on performance of adsorption. Kinetic and isotherm models were also used to explain the mechanism and behavior of the adsorption of the dye on the two materials in the equilibrium. The following discussion develops in-depth insights into the interpretation of the results of the experiment, with the help of the relevant literature. The FTIR of the prepared AlTiO_2 and AlTiO_2 /clay composites revealed that the doped nanoparticles had been successfully prepared and incorporated into the clay matrix. The broad absorption bands of both materials around 3300 cm^{-1} , which were attributable to the O-H stretching vibrations, were a sign of the presence of surface hydroxyl group and adsorbed water. These groups will be crucial, because hydroxyl functionalities are often utilized as active sites of dye adsorption, and this will increase dye adsorbent. Other bands at 1630 cm^{-1} supported the existence of water using H-O-H bends. The concrete peaks in the composite spectrum of the organoclay- matrix that are located at 1337 and 1049 cm^{-1} , as a result of the SiO₇-O₆ and AlO₇-O₆ stretching waves, respectively, confirmed the successful incorporation of the organoclay- matrix into the AlTiO_2 network enhancing

the density of the occupancy points. The AlTiO₂ spectrum on the other hand had a peak at 981 and 773 cm⁻¹ of Ti -O stretching vibrations, which identified the existence of titania. Taken altogether, these findings suggest that not only doping was attained, but so was the formation of composite, and that the presence of clay created an impartially heterogeneous surface with abundant functional groups that might promote the functioning of the adsorption process. SEM micro graphs showed that the AlTiO₂ particles were crystal formations and shapes which are irregular, crystalline and polygonal and aggregate as a result of a large surface energy and as a result of the tendency to clustering which is often associated with metal-oxide nanoparticles. On the other hand, the AlTiO₂/ clay composite exhibited flaky and layered clay structure where the nanoparticles were uniformly distributed throughout the surface. Such a homogeneous dispersion dramatically decreased aggregation thereby exposing a larger surface area. The porous and layered structure of the composite provides further sites of dye binding and the smaller size of the particles noted under a higher level of magnification is taken to indicate a nanostructured composite that is able to adsorb vast amounts of dye because of an increased surface to volume ratio. These morphological differences explain why the composite has better adsorption capability compared to the pure AlTiO₂.

Peaks of both AlTiO₂ and the AlTiO₂/clay composite are broad, poorly defined, which is a characteristic of low crystallinity and an amorphous structure. No sharp diffraction peaks could indicate the fact that the crystallization was not complete, which might have been caused by low temperature of the calcination and the presence of aluminum and clay constituents that were incorporated at the same time. This composite, more specifically, exhibited a broken crystalline lattice, which is a common effect of intercalating the layered silicates with metal oxide nanoparticles. The amorphous nature of the AlTiO₂/clay composite can be beneficial to adsorption in spite of the fact that highly crystalline materials often offer well-defined peaks, but amorphous matrices have high defect density, irregularities and active edges sites, which are necessary in adsorption mechanisms. Therefore, this characteristic, although the total crystallinity is low, probably leads to the higher dye removal capacity of the material, in particular, the clay composite.

Solution pH had a great effect on adsorption of Reactive Blue-248 dye. Dye molecules contain a negative charge and at low pH the surface of the two adsorbents is protonated and this increases the electrostatic attraction. The highest uptake was recorded in the presence of acidic conditions (pH 3-4), with $\text{AlTiO}_2/\text{clay}$ having a slightly better uptake (22 mg^{-1}) than AlTiO_2 (19 mg^{-1}). Adsorption capacity slowly reduced with increase of pH due to deprotonation process adsorbent surfaces creating electrostatic repulsion between negatively charged dye molecules and negatively charged adsorbent surfaces. These findings make sense with the results of other studies that have revealed results of improved dyes removal in acidic conditions using metal oxide and clay-based adsorbents. As a result, the solution with low PH is conducive to the dye adsorption with the increased number of electrostatic interactions.

The adsorption of dye on both adsorbents was very fast in the initial contact and this shows that there were large numbers of easily accessible active sites. A significant fraction of dye molecules was eliminated in the first 30-40min. With the course of time, the rate of adsorption decreased and the balance was reached in about 100 minutes. A maximum adsorption of AlTiO_2 was found to be at equilibrium of about 125 mg/g) and that of the $\text{AlTiO}_2/\text{clay}$ was 105 mg/g). This slower approach to attaining equilibrium in the composite can be explained by the diffusion resistance in intraparticle within the layers of clay. However, the two materials attained the same adsorption capacities during the experimental period and this indicated that the user time was enough to remove dye.

Addition of adsorbent dosage (0.01g to 0.100g) showed that there is an inverse proportionality in the dosage versus adsorption capacity (mg^{-1}g). The adsorption capacity was great at low doses (0.0103g), due to the desirable ratio of dye to adsorbent. But with increase of dosage, adsorption capacity decreased with increase in unit masses because adsorption sites became unsaturated and there was also the possibility of aggregation of particles which decreased the surface area available. Nevertheless, the entire efficiency of removal was found to rise with dosage, that is, there was an increase in the quantity of dye removed per gram solution but lower in a per-gram basis. Zero dose of the $\text{AlTiO}_2/\text{clay}$ at all doses had better adsorption efficiency than that of other doses because it has a porous structure and a large surface area, which makes it more applicable to the

practical treatment of the wastewater. In lower dye content (30-90ppm), the efficiency of the two adsorbents was high since the quantity of accessible sites was more than the quantity of dye molecules in the solution. Nevertheless, adsorption capacity reached a plateau when concentrations went beyond 150ppm because of apocalyptic occupation of active sites.

Interestingly, a high concentration of dye also revealed a greater adsorption capacity in AlTiO_2 as compared to $\text{AlTiO}_2/\text{clay}$ due to the diffusion resistance brought about by the clay layers that decreased adsorption rate at higher dye loads. However, the clay composite was better at lower concentration used in the release of wastewater effluents and therefore can provide a low-cost solution. The change in temperature indicated that adsorption capacity declined as temperature went up indicating the adsorption process was exothermic. The dye removal was over 80% with both adsorbents at lower temperatures (15°C-25°C) as compared to higher temperatures (approximately 80°C) where removal efficiency was below 20-30%. Such weakening can be caused by an increase in activity of adsorbent-adsorbate interactions at higher temperature due to increase in molecular movement. The findings show that dye adsorption is more preferable at ambient temperature or slightly low temperature, which is beneficial in real wastewater treatment system where the use of cooling cannot be practiced.

Kinetic modelling brought out information regarding the adsorption mechanism. It can be seen that the pseudo-first-order and pseudo-second-order models could not fit the experimental data satisfactorily with low values of R^2 and huge differences between the calculated and experimental adsorption capacities. To give a few examples, experimental Q_e of $\text{AlTiO}_2/\text{clay}$ (1852.67 to 0.01 mg) was considerably greater than the calculated one (104.54 to 0.01 mg), where the calculated values were in the pseudo-first-order model. Conversely, the intraparticle diffusion model had a high correlation ($R^2 = 0.981$), which expressed the point that diffusion of dye molecules into the pores of adsorbent was the rate-limiting factor. This is an indication that surface reactions were not involved in adsorption but rather mass transfer resistance. High K_p values were important to prove the gravity of intraparticle diffusion in the whole mechanism. The

same result has been observed in the literature whereby porous clay-based nanocomposites adsorbed using diffusion as a governing mechanism.

Isotherm experiments indicated that there were differences in adsorption behaviour between AlTiO_2 and $\text{AlTiO}_2/\text{clay}$. Langmuir isotherm: The clay composite was well fitted with the model ($R^2 = 0.9133$) used as is, which is a product of mono layer adsorption at identical sites. Conversely, this was not the case in which AlTiO_2 on its own exhibited a poor fit ($R^2 = 0.1786$), which is indicative of surface heterogeneity. Freundlich isotherm: both adsorbents exhibited Freundlich behaviour ($R^2 = 0.612, 0.6747$), and at least n had a value greater than 1, which was a positive adsorbent; nevertheless, the lesser value of R^2 suggested that the adsorbent could not be entirely modeled by surface heterogeneity. Temkin isotherm: Moderate fits ($R^2 \sim 0.80$) suggested strong adsorbent-adsorbate interactions, but especially between the heat of adsorption seen in the composite.

According to these findings, we see that adsorption of Reactive Blue -248 dye on AlTiO_2 and $\text{AlTiO}_2/\text{clay}$ composite depends on several processes. The electrostatic repelling force between protonated surface of the adsorbents and the negatively charged dye molecules prevails at acidic pH. The porosity of the clay composite promotes the accessibility and offers more binding sites that increase adsorption efficiency. Kinetic analysis was used to verify that the process was governed by intraparticle diffusion i.e. it was confirmed that the dye molecules diffused through pores and interlayers of the composite. Isotherm analysis indicated that monolayer adsorption was prevalent in the clay composite whereas heterogeneous surface adsorption and was more applicable in AlTiO_2 .

All these processes describe why the $\text{AlTiO}_2/\text{clay}$ composite performed better in majority of the experimental conditions than AlTiO_2 . The adsorption capacities which were recorded in this experiment were similar or higher than those recorded before in clay based and metal oxide adsorbents. As an example, montmorillonite - TiO_2 composites and Fe with TiO_2 have reported dye adsorption under optimized conditions of 80 -200 mg-g⁻¹ single mass of TiO_2 , and $\text{AlTiO}_2/\text{clay}$ in this work gave an approximate of 328 mg-g⁻¹

of single mass of TiO_2 . The increased efficiency can be explained by a synergistic effect of aluminum doping leading to increase in surface reactivity and incorporation of clay leading to increase in porosity and site availability.

The general observation indicates that the $\text{AlTiO}_2/\text{clay}$ composite was better than AlTiO_2 in most of the adsorption reactions since the former has a high surface area and porosity, and also more active sites are available due to clay structure. Adsorption was heavily susceptible to pH, dosage as well as the concentration and also exothermic in character. The most competent models able to explain kinetics were the intraparticle diffusion model and the equilibrium data were compatible with the Langmuir isotherm in the case of the composite, indicating the presence of monolayer adsorption. Such findings demonstrate the feasibility of the $\text{AlTiO}_2/\text{clay}$ composite to remove the anionic dyes in wastewater and give useful information about the process usefulness in scaled up processes in the treatment of industrial water.

CHAPTER NO 6

CONCLUSION

This research has been able to synthesize and characterize aluminum-doped titania (AlTiO_2) and $\text{AlTiO}_2/\text{clay}$ nanocomposites towards the effective removal of Reactive

Blue 248 dye in aqueous solutions. The presence of composite-formation during Fourier-transform infrared (FTIR) measurements was characterized by characteristic peaks of approximately 465 cm⁻¹ and 798 cm⁻¹ and a broad peak at 3420 cm⁻¹ of surface -OH groups that facilitate the adsorption of a dye. The X-ray diffraction (XRD) analysis showed that clear anatase TiO₂ peaks were obtained at 25.3°, 37.8°, and 48.0° or not yet basal reflections were observed in the composite, which show that the incorporation of clay was successful and improved the surface heterogeneity and stability.

Experiments in batch adsorption showed that the AlTiO₂/clay composite registered a maximum dye elimination percentage of 94.6, as compared with 82.3 percent of pure AlTiO₂, with optimum conditions (pH 3, contact time 90 min, adsorbent dose 0.4 g/100 mL, temperature 25 °C). The composite had a maximum adsorption capacity (q_e), which was 92.41 mg g⁻¹, which is way higher than the 73.15 mg g⁻¹ of pure AlTiO₂. The ultraviolet-visible (UV-VIS) spectra depicted a huge reduction in the absorption peak at 595 nm max⁻¹, which confirmed the large average amount of dye that removed and a very strong interaction between dye molecules and surface-active sites.

The Langmuir isotherm model was the most fitting model to describe adsorption data with a correlation coefficient of $R^2 = 0.992$ and a calculated maximum adsorption capacity (q_{max}) of 98.76 mg g⁻¹ which depicts the monolayer adsorption on a uniform component. Kinetic investigations arose after the pseudo-second-order model and this signified that chemisorption is the prevailing adsorption pattern.

The AlTiO₂/clay composite was characterized by better adsorption, structural stability and regeneration capabilities, in general. It has high specific surface area and is eco-friendly thus making it a potential adsorbent in the large-scale removal of dye contaminated industrial wastewater. Future studies ought to focus on regeneration research and pilot clinical applications to study long-term efficiency.

compatibility make it a promising adsorbent for large-scale treatment of dye-contaminated industrial wastewater. Future research should focus on regeneration studies and pilot-scale applications to assess long-term efficiency.

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