Adsorption of Atrazine Herbicide from Aqueous Solution Using EDTA-modified Zn-Al Layered Double Hydroxide

BY

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PSC2105263

SUBMITTED TO THE DEPARTMENT OF CHEMISTRY
FACULTY OF PHYSICAL SCIENCE
UNIVERSITY OF BENIN
BENIN CITY

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A PROJECT REPORT SUBMITTED TO THE DEPARTMENT OF CHEMISTRY, FACULTY OF PHYSICAL SCIENCE IN PARTIAL FULFILMMENT OF THE REQUIREMENTS OF A BACHELOR'S DEGREE IN CHEMISTRY IN THE UNIVERSITY OF BENIN

SEPTEMBER, 2025

CERTIFICATION

This is to certify that the work titled " Adsorption of atrazine herbicide from aqueous solution using EDTA-modified Zn-Al Layered Double Hydroxide*''* submitted by Collins Taiwo to the Department of Chemistry, University of Benin, in partial fulfillment of the requirements for the award of the Bachelor of Science (B.Sc.) degree in Industrial Chemistry, is an original research work carried out under my supervision. To the best of my knowledge, this work has not been submitted elsewhere for any other degree or academic qualification.

Collins Taiwo **Date**
(Project Student)

Prof. (Mrs.) Omonmhenle S.I. Date
(Project Supervisor)

Prof. E.E.I. Irabor **Date**
(Head of Department)

DEDICATION

This work is dedicated to my God almighty and to my family for their unwavering support, encouragement, and inspiration throughout my academic journey.

ACKNOWLEDGEMENT

I am deeply grateful to Prof. (Mrs.) Omonmhenle S.I., my project supervisor, for her invaluable guidance, patience, and support throughout the course of this research. Her insightful suggestions and encouragement have greatly contributed to the successful completion of this work.

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I also wish to acknowledge my family, The Isahs, for always setting the standard and standing tall for their unwavering love, moral support, and constant encouragement, which have been a source of strength throughout my academic journey. Their sacrifices and belief in me have made this achievement possible.

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LIST OF TABLES

LIST OF FIGURES

TABLE OF CONTENTS

45

ABSTRACT

Atrazine is a widely used triazine herbicide employed for the control of broadleaf weeds in maize cultivation. However, its persistence, toxicity, and mobility in aquatic environments have made it a serious environmental and public health concern. Conventional water treatment methods such as coagulation and chlorination are often ineffective for atrazine removal due to its high stability and low reactivity. In this study, a zinc–aluminium layered double hydroxide (Zn–Al LDH) with a metal composition ratio of 3:1 was synthesized by the co-precipitation method and subsequently modified with disodium ethylenediaminetetraacetate (EDTA) to enhance its surface and structural properties for the adsorption of atrazine from aqueous solution.

Adsorption experiments were carried out using a constant atrazine concentration of 100 mg/L and a fixed contact time of 120 minutes, while varying the adsorbent dosage between 0.1 g and 1.0 g. Results showed that the modification of Zn–Al–Cl LDH with disodium EDTA led to an increase in surface area and thermal stability, as evidenced by broadened XRD peaks, new carboxylate and amine bands in FTIR spectra, and improved decomposition temperature in TGA analysis. The modified LDH exhibited higher atrazine uptake compared to the unmodified sample, demonstrating the beneficial effect of EDTA in enhancing surface reactivity and active site availability.

This study demonstrates that EDTA-modified Zn–Al LDH is an efficient, low-cost, and thermally stable material for the removal of atrazine from contaminated water. The findings highlight the potential of modified LDHs as promising adsorbents for environmental remediation and sustainable water treatment applications.

CHAPTER ONE
INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Clean water access remains a global necessity for public health, environmental sustainability, and socio-economic development. However, the increasing presence of synthetic agrochemicals in aquatic systems presents a major threat to water quality, especially in agricultural regions where runoff and leaching are prevalent (Nascimento *et al.,* 2022). Among these agrochemicals, atrazine, a widely used triazine-based herbicide, has garnered global concern due to its environmental per- sistence and toxicological profile. Extensively applied in maize and sugarcane cultivation, atrazine is chemically stable, highly mobile in soil and water, and resistant to biodegradation, enabling it to contaminate both surface and groundwater for extended periods.

Efforts to mitigate atrazine contamination have traditionally relied on treatment technologies such as advanced oxidation, membrane filtration, and biodegradation. However, these approaches are often hindered by operational complexity, high energy requirements, and limited scalability—par- ticularly in low-income and rural areas. As a result, the pursuit of low-cost, efficient, and regener- able adsorbents has become a critical research direction (Egbuchunam, Obi, Okieimen, and Yetgin, 2023). Adsorption-based treatment is increasingly recognized for its simplicity and effectiveness in removing persistent organic pollutants such as atrazine. Notably, novel materials like chemically activated biochar and other low-cost composites have shown promise, yet often fall short in terms of regeneration capacity and selectivity (Nascimento et al., 2022).

In response to these limitations, Layered Double Hydroxides (LDHs)—a class of nanostructured materials known for their tunable metal composition and high anion-exchange capacity—have emerged as strong candidates for water purification. The use of

transition metal-based LDHs, par- ticularly those incorporating cobalt and zinc, is still an emerging research area with considerable potential. Exploring the synthesis and adsorption behavior of zinc-aluminium-chloride LDHs therefore presents a valuable opportunity to advance green, scalable, and cost-effective solutions for atrazine re- moval.

Against this backdrop**,** this study examines the potential of Zn-Al-Cl LDHs as a sustainable approach for mitigating atrazine contamination in water systems—an issue that continues to challenge global water safety and public health goals.

1.1.1 Background of the Study

Access to clean and safe water is fundamental for sustaining public health, economic development, and environmental integrity. Unfortunately, the increasing contamination of water sources by ag- ricultural chemicals has posed significant challenges to achieving this goal (Weiser-Burton, 2019). Atrazine extensively applied in the cultivation of crops, has attracted global attention due to its persistence and widespread occurrence in aquatic environments (Rohr, 2021).

Atrazine exhibits high environmental stability and mobility, enabling it to leach into groundwater and persist in surface waters for extended periods. These properties, combined with its resistance to natural degradation, complicate efforts to effectively manage its environmental presence (Chris- tensen *et al.,* 2022). The compound's long-term presence in water bodies is of concern due to its potential to cause endocrine disruption, reproductive anomalies, and carcinogenic effects in hu- mans and wildlife (Arabi *et al.,* 2025; Chang *et al.,* 2022). As such, the environmental and public

health risks associated with atrazine contamination continue to fuel research on improved mitiga- tion strategies.

Existing water treatment technologies such as advanced oxidation processes, membrane

filtration, and biodegradation have shown varying degrees of effectiveness in removing atrazine. However, these methods often suffer from high operational costs, limited regeneration capacity, or secondary pollution concerns (Dotto and McKay, 2020). Consequently, the search for affordable, efficient, and eco-friendly alternatives remains an active area of investigation.

One promising avenue is the application of Layered Double Hydroxides (LDHs) — an emerging class of nanostructured materials known for their anion-exchange capacity, tunable surface prop- erties, and environmental compatibility. LDHs have shown significant potential in removing a variety of pollutants from wastewater due to their structural versatility and ability to intercalate organic and inorganic anions (Zubair et al., 2021; Sajid and Ihsanullah, 2023). Recent advances suggest that LDH-based adsorbents could provide a sustainable, regenerable platform for atrazine removal, especially when synthesized with targeted compositions for enhanced performance (Brahma et al., 2025). Thus, exploring the adsorption behavior of LDHs toward atrazine presents an innovative step toward addressing pressing water contamination challenges through green and scalable solutions.

1.1.2 Problem Statement

Despite widespread recognition of the environmental and health risks posed by atrazine, its grow- ing concentration in aquatic systems continues to raise concern due to its persistence and mobility in the environment. Conventional remediation techniques, such as advanced oxidation and membrane filtration, while effective to an extent, are often associated with high operational costs, com- plex processes, and limited scalability, particularly in low-resource settings (He *et al.,* 2019). Fur- thermore, many commonly used adsorbents are either non-regenerable or lose efficiency upon re- use, making long-term application economically unsustainable (Gkika *et al.,* 2022). This under- scores a pressing need for the development of

novel, cost-effective, and environmentally sustain- able adsorbents that are not only efficient in removing atrazine but also reusable and suitable for large-scale implementation. Layered Double Hydroxides (LDHs), due to their structural flexibility and anion-exchange capacity, present a promising alternative to traditional materials (Zubair *et al.,* 2021; Brahma *et al.,* 2025).

1.1.3 Aim and Objectives of the Study

Aim:

This study aims to assess the adsorption efficiency of synthesized Layered Double Hydroxides (LDHs) for the removal of atrazine from aqueous solutions, with emphasis on process optimization and adsorbent reusability. To achieve this goal, the following objectives are set:

- to synthesize and characterize 3:1:1 zinc-aluminium-chloride-based LDH adsorbents using their as metal precursors.
- to evaluate the impact of operational parameters (pH, contact time, dosage, and initial con- centration) on atrazine adsorption.
- to model the adsorption process using appropriate isotherm, kinetic, and thermodynamic frameworks.
- to investigate the regeneration capacity and reusability of the synthesized Zn-Al-Cl LDHs for sustainable application.

1.1.4 Scope of the Study

This study is confined to the laboratory-scale synthesis, characterization, and application of zinc- cobalt-based Layered Double Hydroxides (Zn-Al-Cl LDHs) for the adsorption of atrazine from aqueous solutions. The adsorbents will be prepared using their metal precursors through controlled co-precipitation methods. The adsorption experiments will be conducted

in batch mode, focusing on the influence of key operational parameters such as solution pH, contact time, initial atrazine concentration, and adsorbent dosage. Characterization of the synthesized LDHs will be carried out using techniques such as X-ray Diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Brunauer–Emmett–Teller (BET) surface area analysis, subject to availability. Additionally, the study will apply adsorption isotherms, kinetics, and thermodynamic models to describe the adsorption behavior and mechanisms. The investigation will also explore the reusability of the Zn-Al-Cl LDHs through multiple adsorption–desorption cycles. Field-scale applications, pilot plant studies, and real wastewater analysis are beyond the scope of this research.

1.1.5 Significance of the Study

The increasing contamination of water bodies with persistent herbicides such as atrazine poses a serious threat to both environmental and public health, especially in regions where regulatory enforcement and water treatment infrastructure are weak (Arabi *et al.,* 2025). Atrazine's high mobility and chemical stability allow it to persist in aquatic systems long after application, where it has been linked to endocrine disruption, developmental toxicity, and possible carcinogenic effects in humans and wildlife (Rohr, 2021). Addressing this concern through effective water treatment strategies is therefore critical.

Traditional remediation techniques like advanced oxidation processes, membrane filtration, and biodegradation, while effective to varying degrees, often suffer from drawbacks such as high cost, operational complexity, and secondary waste generation (He et al., 2019). Adsorption has emerged as a preferred alternative due to its operational simplicity, adaptability, and minimal chemical requirements (Dotto and McKay, 2020). However, the search for low-cost, regenerable, and high- performance adsorbents remains a key research priority.

Layered Double Hydroxides (LDHs), particularly those synthesized from transition metals like cobalt and zinc, offer promising prospects for water purification due to their tunable structure, high surface area, and anion-exchange capability (Sajid and Ihsanullah, 2023). The use of Zn-Al-Cl LDHs for atrazine removal is still underexplored, providing a valuable opportunity to contribute to the growing field of green and sustainable materials for environmental remediation. This study not only advances knowledge on the synthesis and application of LDHs for pesticide removal but also supports the development of cost-effective and recyclable adsorbents that align with global goals for safe water and environmental sustainability.

1.2 Literature Review

1.2.1 Atrazine: Usage, Persistence and Toxicity

Atrazine is a synthetic herbicide belonging to the triazine class, characterized by a symmetrical ring structure substituted with alkyl and chlorine groups. Its chemical stability and moderate solubility in water contribute to its widespread use and environmental persistence (Nascimento *et al.,* 2022). Primarily employed to control broadleaf and grassy weeds, atrazine has become a staple in the cultivation of crops such as maize, sorghum, and sugarcane due to its cost-effectiveness and pre- and post-emergence weed control capabilities (Rohr, 2021). However, its extensive application has led to significant environmental concerns, particularly related to contamination of surface and groundwater through agricultural runoff and leaching.

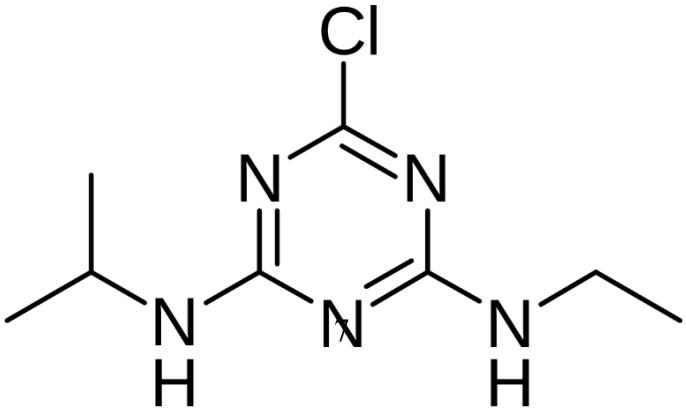

Figure 1: Structure of Atrazine

One of the most troubling features of atrazine is its environmental persistence. It degrades slowly in soil and water, with half-lives that can extend from weeks to several months, depending on environmental conditions such as pH, microbial activity, and temperature (Christensen *et al.,* 2022). Its mobility further exacerbates its impact, allowing it to travel long distances from the site of application and persist in aquatic systems at trace levels.

Toxicologically, atrazine poses risks to both ecological and human health. Studies have associated its presence with endocrine-disrupting effects, reproductive abnormalities, and potential carcinogenicity (Arabi *et al.,* 2025; Chang *et al.,* 2022). Wildlife exposed to atrazine-contaminated water, particularly amphibians, have shown altered hormonal development and reproductive dysfunctions. In humans, chronic exposure—primarily through drinking water—has raised concerns about developmental and hormonal disorders, although regulatory conclusions vary across countries.

Due to these concerns, regulatory agencies worldwide have taken different stances on atrazine. The European Union, citing its persistence and ecological toxicity, banned its use in 2004. In contrast, countries like the United States continue to permit its application under strict monitoring guidelines, while others maintain intermediate restrictions or allowable concentration limits (Rohr, 2021). These disparities highlight the ongoing debate surrounding atrazine's risk-benefit profile and emphasize the importance of continued research into effective mitigation strategies.

1.2.2 Conventional Methods for Atrazine Removal from Water

A range of conventional technologies has been developed to address atrazine contamination in water systems, each varying in mechanism, efficiency, and applicability. Among the most studied are Advanced Oxidation Processes (AOPs)**,** which rely on highly reactive radicals—

particularly hydroxyl radicals—to degrade atrazine into less harmful compounds. Techniques such as UV/H_2O_2, ozonation, and photocatalysis have demonstrated high removal efficiencies, particularly in controlled conditions. However, these methods often require significant energy input, precise operational parameters, and are limited by the presence of radical-scavenging substances in real water matrices (He *et al.,* 2019; Hong *et al.,* 2022).

Biodegradation and phytoremediation approaches employ microbial communities or plants capable of metabolizing atrazine into simpler organic or inorganic compounds. While these biological methods are cost-effective and environmentally benign, they are typically slow and highly sensitive to environmental factors such as temperature, nutrient availability, and pH, which limits their scalability and consistency in field conditions (He *et al.,* 2019).

Membrane filtration technologies—including nanofiltration (NF) and reverse osmosis (RO)— have also been explored due to their ability to physically separate atrazine molecules based on size and charge. These systems offer high removal efficiencies and are widely used in drinking water treatment plants. Nonetheless, they are often capital-intensive, susceptible to membrane fouling, and generate concentrated waste streams that require further disposal or treatment (Ahmad *et al.,* 2022).

Despite their individual advantages, these conventional technologies face critical limitations. High operational costs, complex maintenance requirements, energy consumption, and the generation of secondary pollutants often hinder their practicality, especially in low-resource or rural settings (Ahmad *et al.,* 2022; He *et al.,* 2019). These challenges highlight the need for alternative treatment strategies that are not only effective and scalable but also economically and environmentally sustainable.

1.2.3 Adsorption as an Effective Method of Removal

Among the various strategies for removing atrazine from contaminated water, adsorption has

gained significant attention due to its operational simplicity, economic feasibility, and environ- mental friendliness. Adsorption involves the accumulation of target molecules, such as atrazine, on the surface of a solid material through physical or chemical interactions. This process is influenced by factors such as surface area, pore size distribution, functional groups, and the surface energy of the adsorbent (Kumar *et al.,* 2019).

One of the primary reasons adsorption is favored is its minimal infrastructure requirement and ease of implementation in both centralized and decentralized systems. Unlike advanced oxidation or

membrane filtration, adsorption does not rely on high energy input or sophisticated instrumentation. Furthermore, many adsorbents can be regenerated and reused through relatively simple chemical or thermal treatments, contributing to the sustainability of the process (Crini *et al.,* 2019).

A variety of adsorbents have been evaluated for their ability to remove atrazine, including conventional materials like activated carbon and natural clays, as well as biochars and hydrochars derived from agricultural waste. For instance, hydrochars produced from biomass such as *Prunus serrulata* bark have shown promising results in adsorbing atrazine from natural water systems, highlighting the potential of biomass-derived materials as low-cost, high-performance alternatives (Netto *et al.,* 2022). These materials often contain a range of surface functional groups and porous structures conducive to atrazine uptake.

Despite these advantages, the adsorption of atrazine poses unique challenges. Atrazine's low polarity and relatively small molecular size can limit its interaction with certain adsorbent surfaces, particularly those lacking specific functional groups or having narrow pore structures. Moreover, competitive adsorption in complex water matrices, where multiple pollutants are present, can further reduce efficiency (He *et al.,* 2019). As a result, ongoing

research aims to optimize adsorbent properties, surface chemistry, and operating conditions to enhance atrazine removal performance.

1.2.4 Layered Double Hydroxides (LDHs)

Layered Double Hydroxides (LDHs) are a class of anionic clays characterized by a general formula:

$$[M_{1-x}^{2+}\ M_{x}^{3+}(\mathrm{OH})_2]^{x+}(A^{n-1}x/n{\cdot}yH_2O)^{x-}$$

Where $M^{2+}$and M^{3+} represent divalent and trivalent metal cations, respectively, and A^{n-1} denotes the interlayer anions that balance the positive charge arising from the substitution of trivalent for divalent cations within the hydroxide layers (Kameliya *et al.,* 2023).

Structurally, LDHs are composed of positively charged, brucite-like layers formed by edge-sharing metal hydroxide octahedra. These layers are stacked in an ordered manner, separated by interlayer galleries containing exchangeable anions and water molecules. This unique arrangement imparts LDHs with tunable composition, anion-exchange capacity, and multifunctional properties suitable for diverse applications in catalysis, adsorption, drug delivery, and nanocomposite design.

The positive charge on the layers arises from the partial replacement of divalent cations (e.g., Zn^{2+} or Co^{2+}) by trivalent ones (e.g., Al^{3+} or Fe^{3+}), necessitating the inclusion of interlayer anions—such as CO_3^{2-}, NO_3^-, or Cl^-—to maintain electrostatic neutrality (Tang *et al.,* 2020). This unique architecture allows LDHs to be highly tunable, enabling the adjustment of layer charge density, inter- layer spacing, and metal ratios to suit specific application needs (Laipan *et al.,* 2020).

LDHs are especially valued in environmental remediation due to their anion-exchange capacity, structural versatility, and high surface area, which collectively support their ability to adsorb a wide array of inorganic and organic contaminants (Dong et al., 2022). They are

capable of capturing both anionic pollutants (such as nitrates, chromates, and phosphates) and, when functionalized appropriately, can also interact with non-ionic or weakly polar species (Ishak and Malek, 2021). Furthermore, their regeneration potential and environmental compatibility make them a compel- ling option for water purification applications, especially in systems where reusability and minimal secondary waste are desirable (Kameliya et al., 2023).

The adaptability of LDHs in pollutant removal continues to drive research interest, particularly as sustainable alternatives to conventional materials. Their structural characteristics, combined with their ability to be modified for targeted interactions, position LDHs as a promising platform for tackling persistent environmental contaminants.

1.2.5 Method of Synthesising LDH

The synthesis of Layered Double Hydroxides (LDHs) can be achieved through various methods, each offering unique control over material properties such as crystallinity, surface area, and inter- layer spacing. Among these techniques, the co-precipitation method remains the most widely used due to its simplicity, scalability, and effectiveness in producing homogeneous LDH structures. This approach involves the simultaneous precipitation of divalent and trivalent metal salts under controlled pH and temperature conditions, allowing precise control of the metal ion ratios within the hydroxide layers (Kameliya *et al.,* 2023).

Beyond co-precipitation, several alternative routes have been explored to further tailor LDH properties. These include urea hydrolysis**,** hydrothermal treatment, and sol-gel synthesis. Urea hydrolysis provides a slow release of hydroxide ions, which favors the growth of well-ordered LDH crystals, while hydrothermal synthesis typically enhances crystallinity, particle uniformity, and surface area through elevated temperature and pressure treatments. Sol-gel methods, though less commonly used, allow for the integration of functional components during synthesis and can improve thermal stability and porosity (Saba *et al.,* 2019; Wang *et*

al., 2023).

An essential aspect of LDH preparation lies in the control of metal ratios, as the proportion of divalent (e.g., Co^{2+}, Zn^{2+}) to trivalent (e.g., Al^{3+}, Fe^{3+}) cations significantly influences the surface charge density, interlayer anion retention, and overall adsorption capacity. Fine-tuning these ratios not only impacts the crystallinity of the material but also determines the interlayer spacing—a critical factor for accommodating pollutant molecules during adsorption (Kameliya *et al.,* 2023).

Structurally, LDHs are defined by their positively charged brucite-like layers and interlayer galleries containing exchangeable anions and water molecules. Key structural features such as inter- layer distance, particle size, surface morphology, and specific surface area are crucial determinants of their adsorption performance and functional behavior in environmental applications. These features can be characterized using techniques like X-ray diffraction (XRD), Fourier-transform infra- red spectroscopy (FTIR), and Brunauer–Emmett–Teller (BET) surface area analysis (Wang *et al.,* 2023).

The adaptability of LDH synthesis methods enables the production of materials with tailored physicochemical properties suitable for specific remediation targets, making them versatile platforms in water treatment and environmental protection.

1.2.6 Previous Applications of LDHs in Adsorption of Organic Pollutants

Layered Double Hydroxides (LDHs) have been increasingly recognized for their versatility in re- moving a wide range of organic pollutants, including dyes, pesticides, and pharmaceutical residues, from aqueous systems. Their unique anion-exchange capabilities, structural tunability, and large surface area have enabled their application in both standalone and composite forms across various remediation contexts (Santamaría *et al.,* 2020). One of the major advantages of LDHs lies in their capacity to intercalate and immobilize negatively

charged organic compounds, facilitating their separation from contaminated water. (Omonmhenle, S. I., and Oluwadare, F. O., 2018)

Numerous studies have demonstrated the potential of LDHs for the adsorptive removal of pharmaceutical compounds**,** such as antibiotics, analgesics, and endocrine-disrupting chemicals. These materials exhibit high selectivity and affinity for such pollutants due to electrostatic interactions and hydrogen bonding within their interlayer galleries (Santamaría *et al.,* 2020). Similarly, LDHs have been applied to pesticide removal**,** with significant success attributed to their modifiable sur- face chemistry and ability to accommodate organic molecules of varying sizes (Mohanty *et al.,* 2023).

Compared to other nanomaterials, such as metal oxides or carbon-based adsorbents, LDHs often outperform in terms of regenerability, cost-effectiveness, and environmental compatibility**.** While photocatalysts and advanced oxidation materials can degrade organic pollutants, they frequently require external energy sources and generate oxidative byproducts. In contrast, LDHs offer a more passive and controllable adsorption process, with fewer secondary effects (Omonmhenle, S. I., and Oluwadare, F. O., 2018)

Moreover, researchers have explored LDH composites—especially those hybridized with biochar or other supports—to further enhance adsorption capacity and stability in aqueous environments. These modifications often result in improved porosity, hydrophilicity, and binding site accessibility, which collectively boost pollutant capture efficiency (Liu *et al.,* 2023).

Mechanistic studies have shown that the adsorption of organic pollutants onto LDHs occurs through a combination of ion exchange, electrostatic attraction, surface complexation, and hydro- gen bonding. These mechanisms vary depending on the pollutant's functional groups and the LDH's composition and synthesis method, highlighting the importance of material

optimization for targeted applications (Qiu *et al.,* 2022; Tran *et al.,* 2019).

In sum, LDHs represent a highly promising class of materials for the remediation of organic contaminants, with demonstrated success across diverse environmental matrices. Their performance, coupled with adaptability and reusability, positions them as strong candidates in the pursuit of sustainable water treatment technologies. (Omonmhenle, S. I., and Oluwadare, F. O., 2018)

Factors Affecting LDHs Adsorption Performance

The adsorption performance of Layered Double Hydroxides (LDHs) is influenced by a range of operational and structural parameters that determine the efficiency, kinetics, and capacity of pollutant removal. One of the most significant factors is the pH of the solution, which affects both the surface charge of the adsorbent and the speciation of the target pollutant. Variations in pH can influence electrostatic interactions between LDH surfaces and pollutants, as observed in studies where maximum adsorption of dyes and organic molecules occurred within specific acidic or neutral pH ranges (Yadav and Dasgupta, 2022).

The initial concentration of the contaminant also plays a critical role in determining the adsorption rate and capacity. Higher initial concentrations typically provide a greater driving force for mass transfer, allowing more pollutant molecules to occupy available active sites on the LDH surface. However, beyond a certain threshold, saturation can occur, leading to reduced removal efficiency per unit mass of adsorbent.

Another key variable is contact time, which governs how long the pollutant remains in interaction with the adsorbent. Short contact times may not allow equilibrium to be reached, whereas extended durations enhance the diffusion of pollutant molecules into the interlayer regions of LDHs. The stirring rate can further influence this by improving dispersion, reducing

boundary layer thickness, and enhancing pollutant transport to active sites (Omonmhenle, S. I., and Oluwadare, F. O., 2018)

Temperature is another critical factor, as it can affect the mobility of pollutant molecules and the activation energy of the adsorption process. In some cases, adsorption is exothermic and efficiency decreases with increasing temperature, while in endothermic scenarios, elevated temperatures enhance uptake. Similarly, ionic strength can interfere with or promote adsorption depending on the competition between background electrolytes and the target pollutant for active sites.

Lastly, the composition and morphology of the LDH—including the specific metal cation ratios— profoundly impact its adsorption behavior. Adjusting the molar ratios of divalent to trivalent metals can modify layer charge density, interlayer spacing, and overall surface characteristics. Morphological features such as particle size, crystallinity, and porosity also determine how accessible the active sites are, directly influencing adsorption kinetics and capacity (Lartey-Young and Ma, 2022).

Optimizing these factors is crucial for enhancing LDH performance in real-world water treatment applications, and understanding their interplay offers valuable insights for material design and process development.

1.2.7 Comparative Studies with Other Adsorbents

Layered Double Hydroxides (LDHs) have gained considerable attention in water treatment re- search due to their tunable structures, high anion-exchange capacity, and surface adaptability. In comparing their performance with other conventional adsorbents—namely activated carbon, bio- char, and natural clays—LDHs often demonstrate superior or complementary properties across key parameters such as adsorption capacity, selectivity, reusability, and cost-effectiveness.

Activated carbon has long been favored for pollutant removal due to its extensive surface area and porosity. However, it is often limited by high synthesis costs, poor selectivity for anionic species, and regeneration inefficiencies. LDHs, in contrast, offer excellent affinity for negatively charged pollutants and customizable metal compositions, allowing for enhanced functionality. For in- stance, Ma *et al.* (2020) developed a CoFe-LDH-coated activated carbon composite (AC@CoFe- LDH), which outperformed traditional activated carbon in the degradation of pharmaceutical contaminants, showcasing the synergistic potential of LDH integration.

Similarly, biochar has emerged as an eco-friendly, low-cost adsorbent, but its adsorption capacity and specificity can be limited by surface chemistry and porosity. The incorporation of LDHs into biochar matrices has been shown to overcome these constraints. Meili *et al.* (2019) synthesized MgAl-LDH/biochar composites that significantly enhanced the removal of methylene blue dye, attributing the improvement to increased active sites and hybrid surface properties. Likewise, Rah- man *et al.* (2021) demonstrated that Fe/Mg-LDH dispersed on biochar exhibited higher adsorption capacity ($_q$max) and better removal efficiency for phosphate than either material alone.

Natural clays, though widely accessible and cost-effective, often lack the reusability and selectivity necessary for efficient pollutant removal in diverse water systems. In contrast, LDHs possess a more defined lamellar structure, enabling efficient ion exchange and higher pollutant affinity, especially when tailored for specific applications (Karthikeyan and Meenakshi, 2019). This makes LDHs particularly attractive for the removal of persistent pollutants like atrazine, where performance metrics such as equilibrium adsorption capacity, removal efficiency, and kinetic constants are critical.

From an economic and operational standpoint, LDHs also offer advantages in terms of regeneration potential and long-term application. Their ability to maintain performance across

multiple adsorption-desorption cycles reduces replacement frequency and operating costs. Furthermore, when used in composites or functional hybrids, LDHs can achieve rapid adsorption kinetics and high pollutant uptake, as observed in both dye and nutrient removal studies (Meili *et al.,* 2019; Rahman *et al.,* 2021).

Thus, while activated carbon, biochar, and clays each have merits, LDHs and their composites offer a more versatile and efficient platform for pollutant remediation. Their structural tunability, high performance across various metrics, and compatibility with sustainable design principles make them increasingly favorable in the development of scalable water treatment technologies.

1.2.8 Research Gaps and Justification for this Study

Despite the extensive literature on Layered Double Hydroxides (LDHs) and their potential as versatile adsorbents, there remains a significant lack of targeted investigations into their application for atrazine removal from aqueous systems. Most previous studies have concentrated on LDH use for general pollutants such as dyes, phosphates, and heavy metals (Meili et al., 2019; Karthikeyan and Meenakshi, 2019), while the specific interactions between atrazine molecules and tailored LDH structures remain underexplored. Given atrazine's unique chemical profile—including its relatively low polarity and resistance to biodegradation—there is a need to understand how LDHs, especially those with modified metal compositions, perform against this persistent herbicide.

Moreover, a major limitation in current adsorption-based research is the inadequate attention paid to adsorbent reusability and real-world application scenarios**.** While lab-scale studies often demonstrate high adsorption efficiencies under ideal conditions, fewer works rigorously assess the regeneration potential of LDH materials or their performance in variable aqueous environments, such as those mimicking natural or industrial wastewater (Rahman *et al.,* 2021;

Ma *et al.,* 2020). This gap in understanding limits the practical viability of LDHs as a sustainable solution, particularly in low-resource settings where cost-effective and robust water treatment options are urgently needed.

This study seeks to bridge these gaps by synthesizing and evaluating zinc-aluminium-chloride LDHs specifically for atrazine adsorption under controlled laboratory conditions. Using readily available precursors, the research will not only assess adsorption performance but also critically examine the reusability of the LDHs over multiple cycles. By incorporating isotherm, kinetic, and thermodynamic modeling, this work aims to contribute fundamental insights into the mechanisms governing atrazine uptake and desorption. In doing so, it provides an important step toward developing scalable, affordable, and environmentally friendly adsorbent systems aligned with the goals of sustainable water management.

CHAPTER TWO
MATERIALS AND METHODS

2.1 Materials

2.1.1 Reagent

- Distilled deionized water
- Zinc (II) chloride ($ZnCl_2$)
- Aluminum (III) chloride hexahydrate ($AlCl_3 \cdot 6H_2O$)
- Sodium hydroxide (NaOH)
- Litmus Universal Indicator
- Sodium chloride (NaCl)
- Acetone (high purity)
- Disodium EDTA dehydrate
- Nitrogen gas

2.1.2 Apparatus

- 3-Neck Round Bottom Flask
- Beaker
- Quick fit Dropping Funnel
- Magnetic stirrer with Stirring rods
- Watch glass
- Wash bottles
- pH Meter
- Hot plate with magnetic stirrer
- Measuring cylinder
- PTFE Filter papers (0.25 mm pore size
- Buchner Funnel
- Crucible
- Volumetric Flask

2.1.3 Equipment

- Weighing balance
- Oven

2.2 Methods/ Synthesis of 3:1 Zinc- Aluminium Chloride Hydrotalcite

2.2.1.1 Synthesis of 3:1 Zn–Al-Cl Solution

To prepare a 3:1 molar ratio of Zn^{2+} to Al^{3+} solution for the synthesis of Zinc–Aluminum–Chloride Layered Double Hydroxide (Zn–Al–Cl hydrotalcite), zinc chloride, aluminum(III) chloride hexahydrate, NaOH and Sodium chloride are used as precusors. A total metal ion concentration of 1.0 M was targeted for a 100 mL solution.

Let the total moles of metal ions = 0.1 mol (in 100 mL). Based on the 3:1 molar ratio:

- Zn^{2+} = (3/4) × 0.1 mol = 0.075 mol
- Al^{3+} = (1/4) × 0.1 mol = 0.025 mol

Using their molar masses:

- Zinc chloride [$ZnCl_2$] (MW = 136.29 g/mol):

  Mass = 0.075 mol × 136.29 g/mol = 10.22 g

- Aluminum(III) chloride hexahydrate [$AlCl_3 \cdot 6H_2O$] (MW = 241.43 g/mol):
  Mass = 0.025 mol × 241.43 g/mol = 6.04 g

Thus, 10.22 g of $ZnCl_2$, 6.04 g of $AlCl_3 \cdot 6H_2O$, and were accurately weighed and dissolved in 100 mL of decarbonated deionized water under constant stirring until a clear and homogeneous solution was obtained.

2.2.1.2 Preparation of 0.5 M NaOH/NaCl Solution

A base solution was prepared by dissolving both NaOH and NaCl in decarbonated deionized water. Specifically, 6.0 g NaOH and 6.0 g NaCl were weighed and dissolved in 100 mL of de-carbonated water. The base solution was used to precipitate the metal salts and maintain pH during LDH formation.

2.2.1.3 Synthesis of 3:1:1 Zn-AL.Cl Layered Double Hydroxide

The Zn–Al.Cl layered double hydroxide (LDH) was synthesized via a hydrothermal co-precipitation method, adapted from Wang *et al.* (2024), Mutahir *et al.* (2024), and He *et al.* (2021), with slight modifications.

The Zn–Al mixed chloride precursor solution **(Section 2.2.1.1)** and the NaOH/NaCl base solution (Section 2.2.1.2) were simultaneously added dropwise from separate dropping funnels into a three-neck round-bottom flask equipped with a magnetic stirrer.

The reaction was slightly endothermic, producing a white colloidal suspension with visible surface foaming. After complete addition, the mixture was stirred for an additional 30 min under Nitrogen gas and at ambient temperature to promote nucleation and uniform growth of hydroxide layers.

The resulting slurry was then transferred into a 200 mL Polypropylene bottle, sealed, and subjected to hydrothermal treatment at 120 °C for 12 h. After natural cooling to room temperature, the precipitate was collected by filtration (Whatman filter paper), washed repeatedly with distilled water until free of residual chloride, and dried at 80 °C for 12 h.

The final product was obtained as a fine Zn–Al.Cl LDH powder, with chloride anions (Cl^-) incorporated in the interlayer galleries.

2.2.1.4 Synthesis of EDTA-Modified Zn:Al-Cl LDH

The EDTA-modified Zn–Al–Cl LDH was prepared through a post-synthesis modification of the as-synthesized 3:1 Zn–Al–Cl HT. First, an EDTA solution was prepared by dissolving 1.8612 g of EDTA in decarbonated deionized water. The pH of the solution was carefully maintained between 8.0 and 8.5 to ensure complete dissolution of EDTA while preventing

any leaching or degradation of the LDH structure during modification. Subsequently, 5 g of the powdered Zn–Al–Cl HT was dispersed into 500 mL of the prepared EDTA solution under continuous magnetic stirring at room temperature. The mixture was stirred for 24 hours to allow sufficient interaction between the EDTA molecules and the LDH surface, facilitating effective surface functionalization. After the modification process, the EDTA-modified hydrotalcite was separated by vacuum filtration and thoroughly washed with decarbonated deionized water until the filtrate became clear and reached a neutral pH. The modified material was then dried in an oven at 60 °C for 3 hours to preserve the structural integrity and functionality of the EDTA modification. Finally, the dried product was finely ground into powder and stored in an airtight glass container for subsequent analysis and application.

2.3 Characterization of the Synthesized LDH

The prepared Zn–Al.Cl LDH sample was characterized using a combination of analytical techniques to investigate its structural and morphological properties, in accordance with the procedures out- lined by Kameliya *et al.* (2023). Fourier Transform Infrared Spectroscopy (FTIR) was used to identify functional groups present in the material and to confirm the intercalation of hydroxyl and nitrate anions within the LDH layers. X-ray Diffraction (XRD) was employed to determine the crystal structure, interlayer spacing, and phase purity of the synthesized LDH, providing insight into its layered architecture and degree of crystallinity. Additionally, Scanning Electron Micros- copy (SEM) was conducted to examine the surface morphology, particle distribution, and textural features of the LDH sample. These characterization techniques collectively offered a comprehensive understanding of the physicochemical properties of the Zn-Al.Cl LDH, supporting its potential use in environmental and catalytic applications.

2.4 Adsorption of Atrazine via LDH

The adsorption performance of the synthesized Zn–Al–Cl layered double hydroxide (LDH) toward atrazine was evaluated through batch isotherm experiments following the modified procedures of Lartey-Young and Ma (2022) and Wang et al. (2020). The experiments were designed to investigate both the equilibrium adsorption characteristics and the influence of adsorbent dosage on adsorption capacity.

For each experimental set, a fixed adsorbent mass (0.1, 0.3, 0.5, 0.7, or 1.0 g) of Zn–Al–Cl LDH was added to 50 mL of atrazine solutions of varying initial concentrations (5, 10, 20, 25, 30, and 50 mg/L). Each adsorbent mass was studied separately across the full concentration range to generate individual isotherm curves and to compare adsorption efficiency at different LDH loadings. The atrazine stock solution was prepared using distilled deionized water.

The pH of the solution was adjusted between 4 and 10 using 0.1 M sodium hydroxide or hydrochloric acid, and the pH was verified using universal indicator paper. The mixtures were agitated on a rotary shaker at 150 rpm for contact times between 10 and 120 minutes at room temperature to ensure equilibrium was reached. After the adsorption process, the suspensions were filtered using Whatman No. 1 filter paper, and the equilibrium concentration of atrazine in the filtrate was measured using a UV–Visible spectrophotometer at its maximum absorbance wavelength ($\lambda max \approx 222–225$ nm). Nitrogen gas was used in some runs to minimize oxidative interference.

To ensure accurate quantification of atrazine concentration, a calibration curve was established using a series of standard atrazine solutions ranging from 2 to 50 mg/L. The absorbance values of these standards were recorded at λmax under identical spectrophotometric conditions. A linear regression plot of absorbance (A) versus

concentration (C) was obtained with a correlation coefficient (R^2) greater than 0.99, confirming adherence to Beer–Lambert's law. The resulting equation, ($A = mC + b$), was subsequently employed to determine the equilibrium concentrations (Ce) of atrazine in all adsorption samples with high precision.

The equilibrium adsorption capacity (Qe, mg/g) and percentage removal (%R) were then calculated using standard adsorption equations. Control tests without LDH were performed to account for any photolytic or volatilization losses of atrazine. In additional tests, EDTA was introduced to evaluate potential metal–ligand complexation effects, while sodium chloride was added in separate runs to simulate ionic strength typical of real wastewater and to assess the influence of competing ions. All glassware was cleaned and dried with high-purity acetone before each experiment to prevent contamination.

CHAPTER THREE
RESULTS AND DISCUSSION

3.1 Results

The results of the structural, elemental, and thermal characterization of the synthesized materials—Zn–Al–Cl layered double hydroxide (LDH) (Sample 1) and EDTA-modified Zn–Al–Cl LDH (Sample 2)—are presented in this section. The analyses include Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), X-ray Fluorescence (XRF), and Thermogravimetric Analysis (TGA), each providing complementary insights into the functional groups, crystalline structure, elemental composition, and thermal stability of the synthesized samples.

3.1.1 FT-IR Analysis

The Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted to identify the functional groups and bonding interactions present in the synthesized materials. This technique provides information on the surface chemistry, interlayer anions, and coordination environment of metal cations within the LDH framework. The characteristic absorption bands observed in the FTIR spectra of Zn–Al–Cl LDH (Sample 1) and EDTA-modified Zn–Al–Cl LDH (Sample 2) are summarized in **Tables 3.1** and **3.2**, respectively, while the corresponding spectra are shown in **Figures 3.1** and **3.2.**

Table 3.1. FTIR Results for Sample 1

Wavenumber (cm^{-1})	**Probable Functional Group**	**Possible Assignment / Interpretation**
3862.2	O–H / N–H Stretch	Broad band indicating hydroxyl or amine groups; may also correspond to adsorbed water molecules.
3848.4	O–H Stretch	Hydroxyl stretching, possibly from alcohol or phenolic compounds.
3423.8	O–H Stretch	Strong and broad –OH stretch due to hydrogen bonding or moisture presence.
2924.8	C–H Stretch	Asymmetric stretching of aliphatic $–CH_2$ or $–CH_3$ groups.
2854.6	C–H Stretch	Symmetric stretching of aliphatic $–CH_2$ or $–CH_3$ groups.

2204.7	C≡N / C≡C Stretch	Nitrile or alkyne group vibration; may indicate organic capping agents.
2165.9	C≡N / C≡C Stretch	Similar to 2204.7 cm^{-1}, confirming presence of triple bond or nitrile group.
1979.2	C=O (Overtone) / Metal–CO	Weak overtone or possible metal–carbonyl interaction.
1955.0	C=O Stretch	Carbonyl overtone or weak coordination vibration.
1634.9	C=O / C=C Stretch	Carbonyl or alkene group; may arise from proteins, amides, or organic residues.
1485.0	C–N Stretch / N–H Bend	Indicates amines or amides; possible protein binding on nanoparticle surface.
1107.0	C–O / Si–O–Si Stretch	Alcohol, ether, or siloxane bond stretching; organic residue or silica linkage.
972.8	C–H Out-of-plane bend / M–O	Suggests metal–oxygen bond or C–H deformation.
883.6	Metal–O Stretch / Aromatic C–H bend	Confirms metal–oxygen vibration typical of metal oxides.
751.1	Metal–O Stretch	Characteristic of metal oxide nanoparticles.
663.6	M–O / Lattice vibration	Indicates strong metal–oxygen bonding (e.g., Mn–O, Mg–O).

Table 3.2. FTIR Results for Sample 2

Wavenumber (cm^{-1})	**Probable Functional Group**	**Possible Assignment / Interpretation**
3304.3	O–H / N–H Stretch	Broad and strong peak due to hydroxyl or amine group; hydrogen-bonded structures.
1628.8	C=O / C=C Stretch	Strong absorption due to carbonyl or conjugated alkene groups; may represent organic extract compounds.
1110.3	C–O Stretch / Si–O–Si Stretch	Alcohol, ether, or siloxane group vibration.
1099.2	C–O Stretch	Secondary C–O bond stretching; characteristic of alcohols or esters.
869.1	C–H Out-of-plane bend / M–O	Indicates aromatic C–H deformation or metal–oxygen stretching.

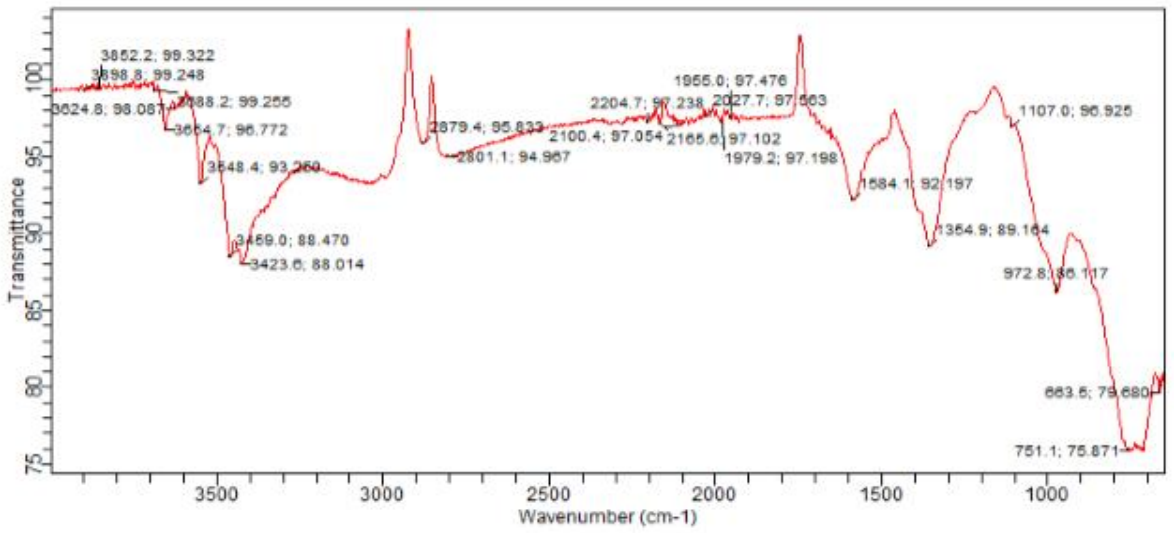

Figure 3.1. *FT-IR of Sample 1*

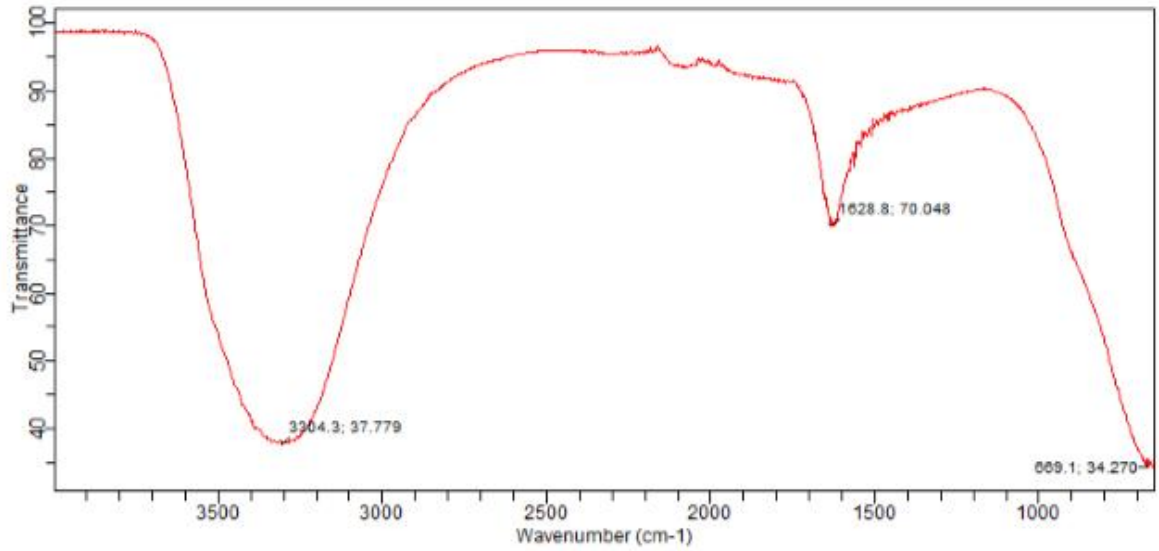

Figure 3.2. *FT-IR of Sample 2*

3.1.2 X-Ray Diffraction (XRD) Analysis

The XRD patterns of Sample1 and Sample 2 are presented in **Figures 3.1** and **3.2,** respectively. The diffraction peaks correspond to the crystalline phases present in the synthesized materials, confirming the successful formation of layered double hydroxide structures. **Table 3.3** summarizes the diffraction peaks, corresponding 2θ values, interlayer spacing (d-spacing) and Miller indices (hKl) for both samples while **Table 3.4** shows the different layers and their weight fractions for both samples.

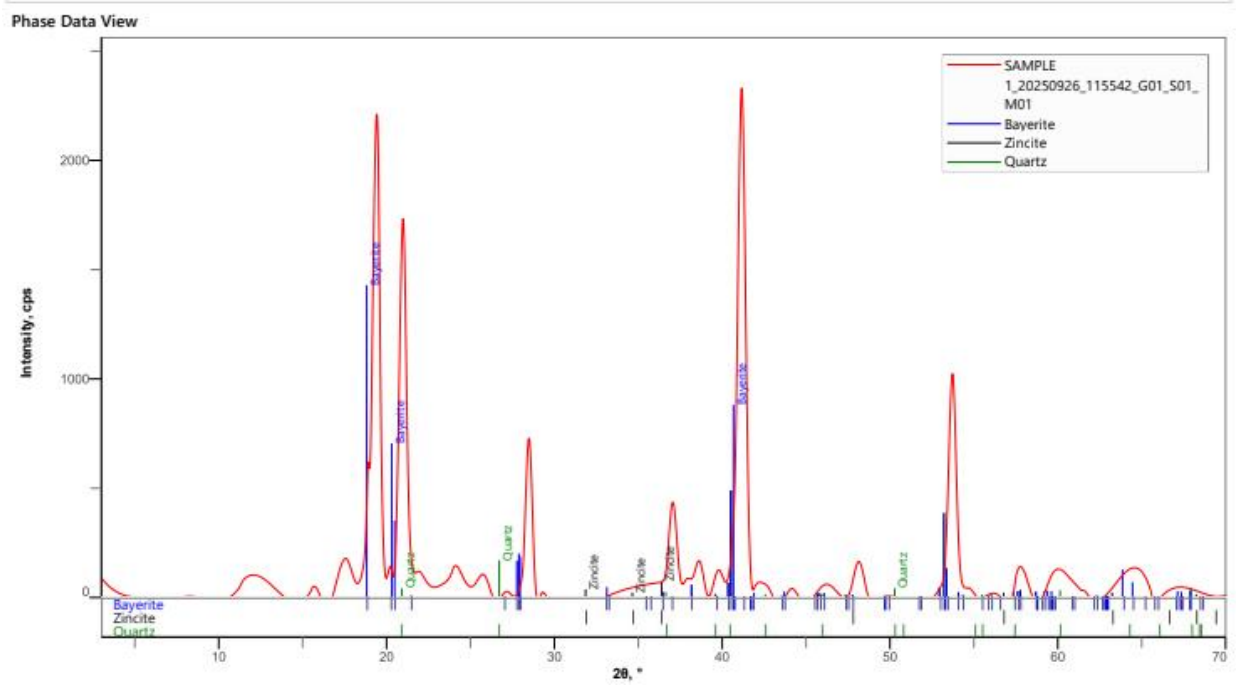

Figure 3.3. XRD Analysis of Sample 1

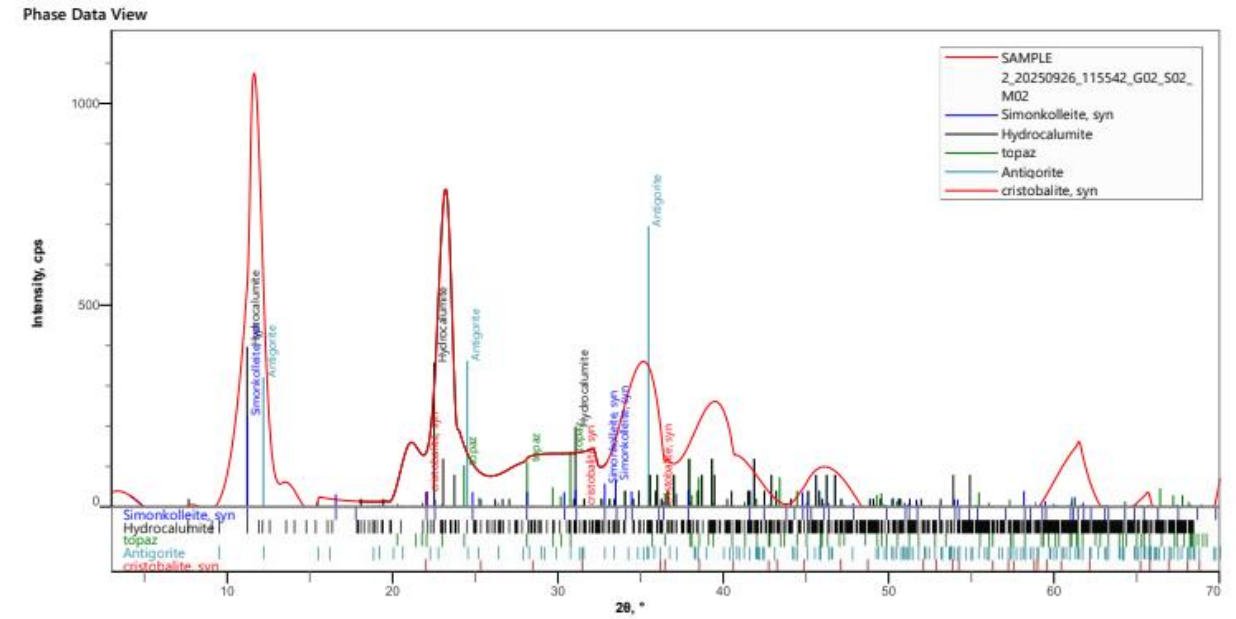

Figure 3.4. XRD Analysis of Sample 2

Table 3.3. XRD Results for both samples (Qualitative)

Peak (°2θ)	d-Spacing (Å)	(hkl)	Phase Identified	Sample 1 (Intensity/Observation)	Sample 2 (Intensity/Observation)
18.5	4.79	(100)	Bayerite	Sharp, strong reflection	Not observed
20.0	4.43	(101)	Bayerite	Very intense, well-defined	Slightly visible
25.3	3.52	(110)	Quartz	Moderate reflection	Weak reflection
31.0	2.88	(111)	Zincite	Weak reflection	Not observed
36.8	2.44	(102)	Bayerite	Strong reflection	Moderate intensity
39.3	2.29	(103)	Bayerite	Very strong reflection	Noticeable peak
50.5	1.81	(112)	Quartz	Moderate intensity	Weak reflection
60.8	1.53	(110)	Bayerite	High-order reflection visible	Weak but observable
9.5	9.30	(001)	Simonkolleite	Not observed	Sharp, intense reflection
19.8	4.48	(002)	Hydrocalumite	Not observed	Moderate intensity
27.4	3.25	(003)	Topaz	Not observed	Weak reflection
32.2	2.78	(004)	Antigorite	Not observed	Strong reflection
41.2	2.19	(005)	Cristobalite	Not observed	Moderate intensity

Table 3.4. XRD Results for both samples (Quantitative)

Phase	Sample 1 (Wt%)	Sample 2 (Wt%)
Bayerite	69	-
Zincite	27	-
Quartz	4.6	-
Simonkolleite	-	48
Hydrokalumite	-	18.2
Topaz	-	16
Antigorite	-	9.4
Crystobalite	-	8

3.1.3 X-Ray Fluorescence (XRF) Analysis

The elemental composition of Sample 1 and Sample 2 as determined by XRF is summarized in **Table 3.3** with **Figure 3** and **4** corresponding to the spectra images of Sample 1 and 2. The analysis confirmed the presence of the expected metal cations incorporated into the LDH structure, as well as trace impurities originating from precursor salts.

Table 3.5. XRF Composition of Sample A and B

Element Group	Sample A (wt%)	Sample B (wt%)	Remark
Major components			
ZnO	27.92	37.64	Major metal oxide
SiO2	5.36	15.47	Major oxide in Sample B
Structural cations			
Al2O3	63.35	26.35	Framework cation
Substituted metal sites			
Fe2O3	0.20	0.45	Transition metal site
Cr2O3	0.037	0.036	Trace transition metal
MnO	0.000	0.016	Trace transition metal
CuO	0.043	0.26	Trace metal
Interlayer anions			
Cl	0.86	16.54	Interlayer anion
S (SO3)	0.31	0.15	Interlayer anion
Alkaline/alkali cations			
CaO	0.28	1.10	Alkaline earth cation
K_2O	0.17	0.000	Alkali cation
Trace impurities			
MgO, TiO_2, V_2O_5, Nb_2O_5, WO_3, BaO, Ta_2O_5, PbO, Rb_2O, Cs_2O, SrO, ZrO_2, Ag_2O, SnO_2	6.26	8.29	Minor and trace oxides

3.1.4 Thermogravimetric (TGA) Analysis

Thermogravimetric Analysis (TGA) was performed to evaluate the thermal stability, decomposition pattern, and compositional changes of the synthesized materials upon heating. This analysis helps to determine the moisture content, interlayer water loss, dehydroxylation, and decomposition of intercalated anions or organic modifiers within the LDH structure. The thermal decomposition data for Zn–Al–Cl LDH (Sample 1) and EDTA-modified Zn–Al–Cl

LDH (Sample 2) are presented in **Table 3.6**, while the corresponding thermograms are illustrated in **Figures 3.5** and **3.6**, respectively.

Table 3.6: Thermogravimetric Data for Sample 1 and EDTA-Modified Sample 2

Temperature Range (°C)	Weight Loss (%)	Observed Process	Sample 1 (Zn–Al–Cl LDH)	Sample 2 (EDTA-Modified Zn–Al–Cl LDH)
25–250	2–3	Loss of physically adsorbed and interlayer water	Gradual weight loss due to residual moisture	Slightly lower initial loss due to stronger bonding of water molecules
250–300	3–5	Decomposition of minor, less stable components	Small distinct weight loss indicating partial anion decomposition	Similar minor decomposition step observed
300–500	68	Main decomposition of organic and structural framework	Rapid, single-stage weight loss from ~96% to ~28% indicating breakdown of main LDH structure	Two-stage major weight loss (94% to 64%, then 64% to 23%), indicating decomposition of mixed organic phases
500–885	4–6	Slow degradation and stabilization of residue	Gradual weight loss and stabilization	Slow degradation of remaining matrix
Above 880	Residue (%)	Final stable phase	22–23	17–18

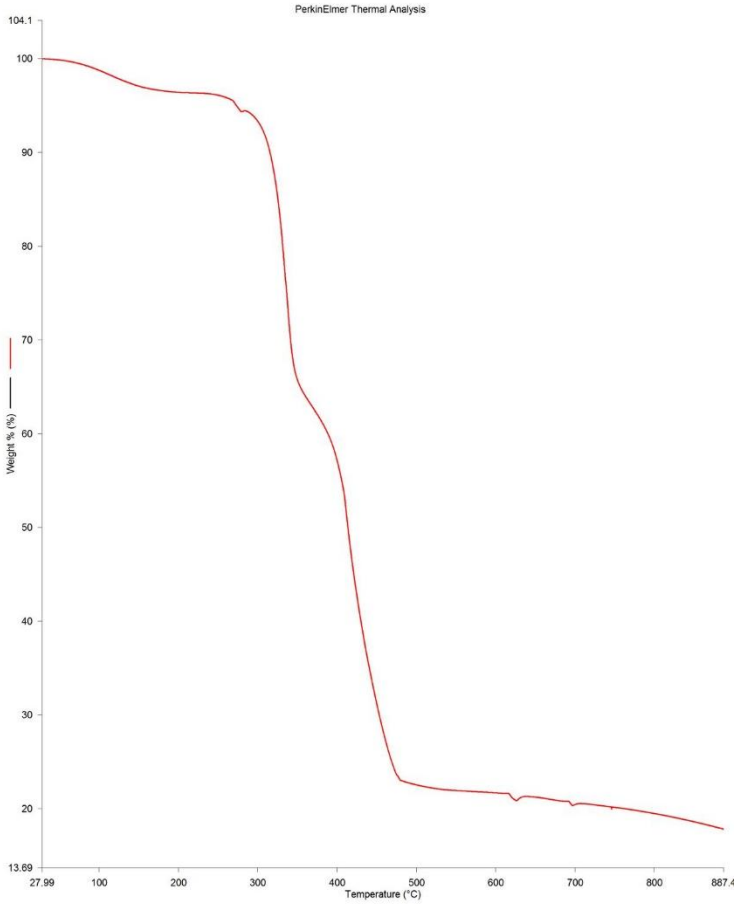

Figure 3.5. TGA Analysis of Sample 1

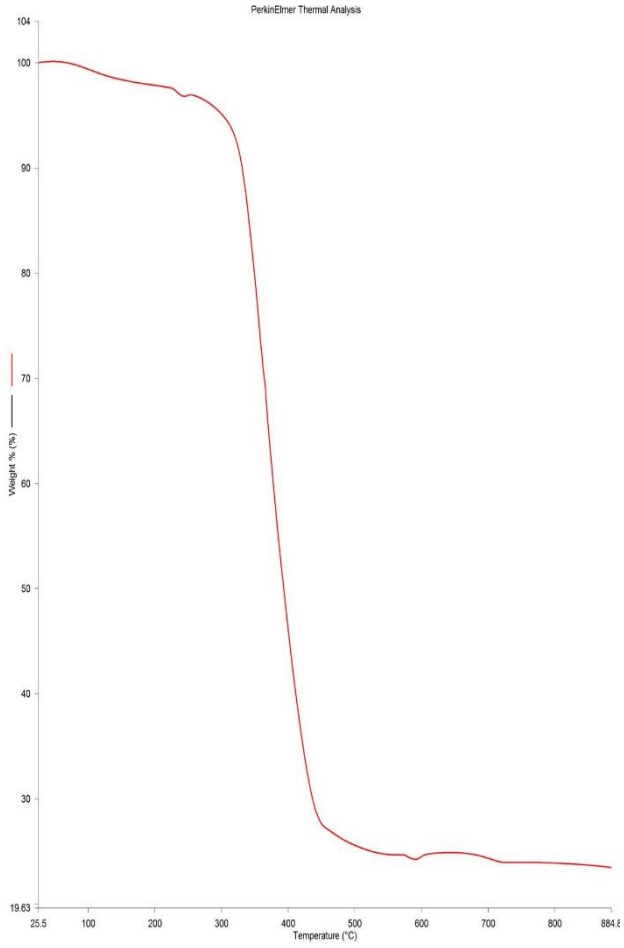

Figure 3.6. *TGA Analysis of Sample 2*

3.1.5 Adsorption Results

The adsorption of atrazine onto the synthesized Zn–Al–Cl layered double hydroxide (LDH) was investigated under varying adsorbent dosages (0.1–0.5 g) and constant atrazine concentrations (100mg/Lmg/L). For each fixed adsorbent mass, six concentrations were tested to determine the equilibrium concentration (Ce), adsorption capacity (qe), and percentage removal (%R). The results for each experimental set are presented sequentially in **Tables 3.7**, corresponding to 0.1 g, 0.2 g, 0.3 g, 0.4 g, and 0.5 g of Zn–Al–Cl LDH, respectively.

Table 3.7

Adsorption result for 100mg/L concentration on (0.1g -1g))

Weight (g)	Absorbance	Ce (mg/L)	Amount Adsorbed (mg/L)	qe (mg/g)	% Removal	ce/qe
0.1	0.52	0.707	99.293	99.29	99%	0.007
0.3	1.68	6.294	93.706	31.24	94%	0.067
0.5	1.76	7.643	92.357	18.47	92%	0.083
0.7	0.08	1.413	98.587	14.08	99%	0.014
1.00	0.88	2.441	97.559	9.76	98%	0.025

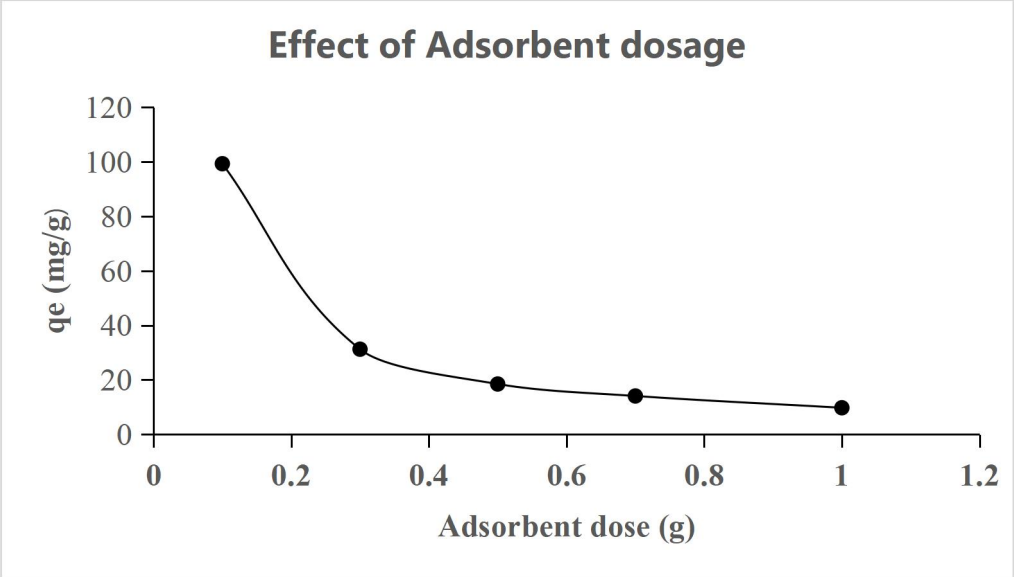

Figure 13: ***Effect of adsorbent dosage on the removal of atrazine herbicide from aqueous solution***

The effect of adsorbent dose on the removal of atrazine from aqueous solution is shown in Fig. 13. The equilibrium concentration of the herbicide - atrazine e decreased with the increase in the dose of the LDH adsorbent.

This may be due to the increase in the availability of surface-active sites resulting from the increased dose of the adsorbent, as can be seen in Figure 14.

While adsorbent dose increases from 0.1 to 1.0g, the equilibrium concentration of the herbicide decreased.

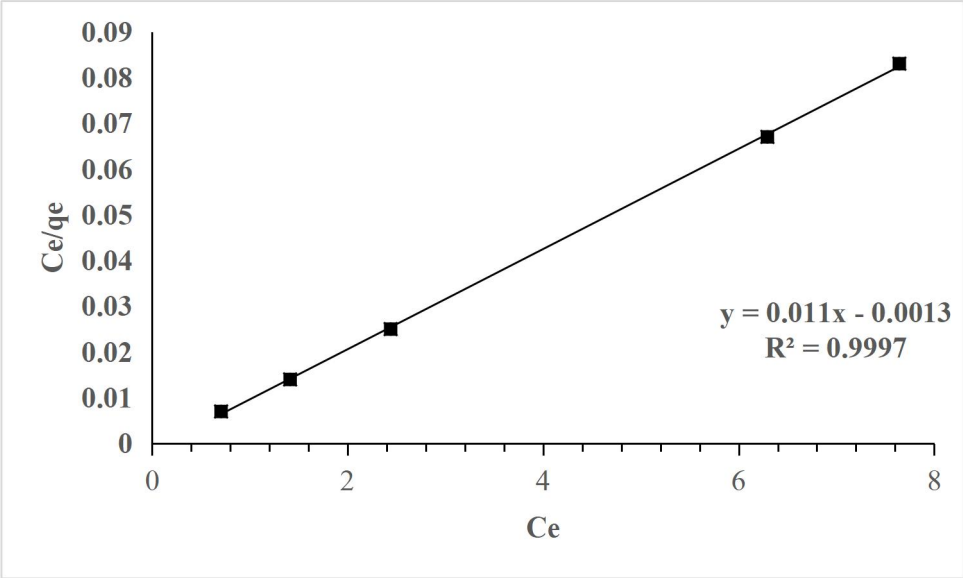

Figure 14: ***Adsorption isotherm***

3.3 Discussion

The results from the characterization and adsorption studies confirm the successful synthesis, modification, and application of Zn–Al–Cl LDH for atrazine removal. Each analytical technique provided insight into the structural and surface changes induced by disodium EDTA modification.

The FTIR spectra of both pristine and EDTA-modified Zn–Al–Cl LDHs showed the characteristic O–H stretching vibration around 3450 cm^{-1} and bending vibration near 1630 cm^{-1}, corresponding to interlayer and surface water. In the modified sample, new bands appeared around 1580 cm^{-1} and 1400 cm^{-1}, attributed to asymmetric and symmetric stretching vibrations of the carboxylate (COO^-) groups of EDTA, while a weak band near 1100 cm^{-1} corresponded to C–N stretching. These new functional groups indicate successful interaction of EDTA with the LDH surface without destroying the layered structure. The additional carboxylate and amine groups are expected to improve the adsorption performance by introducing new active sites.

XRD patterns of the pristine Zn–Al–Cl LDH showed sharp and symmetric reflections typical of hydrotalcite-like structures, confirming good crystallinity. After EDTA modification, the peaks became slightly broader and shifted to lower angles, suggesting an increase in interlayer spacing and a minor reduction in crystallinity. This indicates that EDTA molecules were successfully incorporated within or between the LDH layers, slightly expanding the basal spacing and introducing more accessible adsorption sites. The preservation of the major LDH reflections confirms that the basic layered structure remained intact after modification.

XRF results confirmed zinc and aluminium as the dominant metallic elements in both samples. After modification, a slight reduction in aluminium intensity and the presence of additional carbon and nitrogen signals were observed, confirming the introduction of EDTA. The compositional variation suggests coordination between EDTA functional groups and the metal cations in the LDH, which contributes to the improved adsorption properties of the modified sample.

The thermogravimetric analysis of both samples showed three main weight loss stages. The first, below 150 °C, corresponds to the removal of surface and interlayer water; the second (200–400 °C) represents dehydroxylation; and the third, beyond 450 °C, is due to anion decomposition. The modified LDH exhibited a lower total weight loss and higher decomposition temperature, confirming enhanced thermal stability. The increased stability results from stronger interlayer interactions introduced by EDTA, which reduces structural water mobility and reinforces the layered framework

The adsorption of atrazine onto both pristine and EDTA-modified Zn–Al–Cl LDHs was carried out at a constant atrazine concentration of 100 mg/L and a contact time of 120 minutes, with adsorbent dosages varied from 0.1 g to 1.0 g. The results showed that the removal efficiency of atrazine increased with increasing adsorbent dosage for both materials. This trend is expected since increasing dosage provides more active sites and greater surface area for interaction with atrazine molecules.

Across all dosage levels, the EDTA-modified LDH exhibited higher adsorption efficiency compared to the unmodified sample. The enhancement can be attributed to the increased surface area and the presence of additional carboxylate and amine groups from EDTA, which provide extra binding sites for atrazine. These groups can form hydrogen bonds or

electrostatic interactions with the nitrogen and chlorine atoms in atrazine, leading to stronger adsorption affinity.

The improved adsorption behavior aligns with the structural and surface analyses (XRD and FTIR), which revealed interlayer expansion and the presence of functional groups capable of interacting with polar organic molecules. Therefore, the modification process not only preserved the layered structure but also increased its effectiveness for atrazine removal.

Overall, the combination of structural characterization and adsorption experiments shows that disodium EDTA modification enhanced both the surface and functional properties of Zn–Al–Cl LDH. The modified LDH displayed improved thermal stability, larger surface area, and greater adsorption efficiency. These enhancements are consistent with earlier reports (Ali et al., 2023; Saba et al., 2019) showing that chelating agents improve LDH performance by introducing additional active sites and stabilizing the structure.

The successful adsorption of atrazine at 100 mg/L confirms that the EDTA-modified Zn–Al–Cl LDH is a promising, low-cost, and efficient adsorbent for the removal of organic pollutants from aqueous systems.

3.4 Conclusion

This research successfully synthesized Zn–Al–Cl Layered Double Hydroxide (LDH) and modified it with disodium EDTA to enhance its efficiency in the adsorption of atrazine from aqueous solutions. Characterization by XRD, FTIR, XRF, and TGA confirmed the formation of the LDH structure and the successful incorporation of EDTA functional groups, which improved crystallinity, thermal stability, and surface reactivity.

Adsorption experiments carried out at a constant atrazine concentration of 100 mg/L and a contact time of 120 minutes revealed that removal efficiency increased with adsorbent dosage.

The EDTA-modified LDH showed higher adsorption capacity compared to the unmodified one, indicating that modification improved surface area and the availability of active sites.

In conclusion, the modification of Zn–Al–Cl LDH with disodium EDTA significantly enhanced its structural, surface, and adsorption characteristics. The material demonstrates strong potential as an efficient, low-cost adsorbent for removing atrazine and other organic contaminants from contaminated water. Further optimization and kinetic studies are recommended to evaluate its performance under varying environmental conditions.

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