ADSORPTION OF MANGANESE IONS (Mn^{2+}) USING ASENI CLAY OBTAINED FROM KOTON KARIFI REGION IN KOGI STATE

BY

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UNIVERSITY OF BENIN.

OCTOBER, 2025.

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A PROJECT SUBMITTED TO THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BENIN, BENIN CITY, IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF BACHELOR OF SCIENCE DEGREE (B.Sc. HONOURS) IN CHEMISTRY.

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CERTIFICATION

This is to certify that this project work was carried out and completed by ODUNIYI DORCAS OLUWAFUNMILAYO with matriculation number PSC2105273, Department of Chemistry, Faculty of Physical Science, University of Benin.

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DEDICATION

This project work is dedicated to God Almighty, through whom the success of this work became a reality, my mum (Mrs. M.M Oduniyi), and siblings (Deborah, David, Joshua, and Jeremiah) for their immense support, and every other person who made this achievable

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LIST OF ABBREVIATIONS

MMT-	METHYLCYCLOPENTADIENYLMANGANESETRICARBONYL
ATSDR-	AGENCY FOR TOXIC SUBSTANCES AND DISEASES REGISTRY
MEEPRC-	MINISTRY OF ECOLOGY AND ENVIRONMENT OF THE PEOPLE'S REPUBLIC OF CHINA
DCCEEW-	DEPARTMENT OF CLIMATE CHANGE, ENERGY, THE ENVIRONMENT, AND WATER
AAS-	ATOMIC ABSORPTION SPECTROSCOPY
FTIR-	FOURIER TRANSFORM INFRARED SPECTROSCOPY
USGS-	UNITED STATES GEOLOGICAL SURVEY

ABSTRACT

This research focused on the adsorption of manganese ions (Mn^{2+}) from $MnSO_4$ salt solution using kaolinite clay obtained from Aseni, Kogi State, Nigeria. This study aimed to evaluate the adsorption efficiency of kaolinite clay and to investigate the influence of process parameters, including contact time, pH, adsorbent dosage, and initial manganese concentration, on the removal efficiency. Batch adsorption experiments were conducted under controlled conditions, and residual manganese concentrations were determined using an atomic absorption spectrophotometer (AAS). The results revealed that adsorption efficiency increased with pH, contact time, and adsorbent dosage but decreased slightly with higher initial concentrations. Maximum removal was recorded at 78% at an initial concentration of 10Mn/l, 55.00% (1.0 g dosage), 22.0g (120 minutes), and 63.13% (pH 9). Equilibrium data fitted better to the Freundlich isotherm model, indicating multilayer adsorption on a heterogeneous surface, while the pseudo-second-order kinetic model provided the best correlation, suggesting a chemisorption-controlled mechanism.

The study concludes that kaolinite clay is an effective, locally available, and eco-friendly adsorbent for manganese removal from aqueous solutions, highlighting its potential for use in wastewater treatment and environmental remediation.

CHAPTER ONE

1.1 INTRODUCTION

Access to clean and safe water is essential for human health, environmental sustainability, and economic development. However, increasing industrialization, mining activities, and agricultural practices have contributed to the contamination of water sources with various pollutants, including heavy metals. Unlike organic pollutants, heavy metals are non-biodegradable and can persist in the environment for decades, accumulating in living organisms and causing long-term health effects. Among these metals, manganese (Mn) holds a unique position it is both an essential nutrient for biological functions and a potential toxin when present in excess. The balance between its beneficial and harmful effects depends largely on its concentration in water and the form in which it occurs. Understanding and addressing manganese contamination is therefore crucial to ensuring water safety, especially in regions where mining and industrial activities are prevalent.

Water contamination by heavy metals has become a major global concern due to their persistence, ability to bioaccumulate, and toxicity. Over the years, various treatment methods such as chemical precipitation, ion exchange, oxidation, membrane filtration, and biological processes have been developed to reduce heavy metal pollution. However, many of these methods are expensive, energy-consuming, and less effective at low metal concentrations. As a result, adsorption has become a popular, cost-effective, and environmentally friendly water treatment option.

This literature review examines adsorption as a water purification method, focusing on its use in removing heavy metals from aqueous solutions. It starts with an overview of adsorption technology, then discusses the general characteristics and effects of heavy metals, before specifically highlighting manganese, its sources, occurrence, and health effects. The review also looks at existing manganese removal techniques, the role of clay minerals as adsorbents, and the specific potential of Aseni clay. By synthesizing current research, this chapter identifies knowledge gaps that this study intends to fill

1.1.1 BACKGROUND OF STUDY

Heavy metals are a specific group of elements, including both metals and metalloids, characterized by their relatively high density, typically greater than 5 g/cm^3. They are also referred to as trace metals because they can be toxic even at very low concentrations. These elements occur naturally in the Earth's crust and are non-biodegradable, which makes it easier to monitor their concentrations in the environment.

Some heavy metals serve as essential micronutrients in small amounts, playing vital roles in various biochemical and physiological processes. Humans are exposed to them primarily through air, drinking water, and food. However, when their levels exceed safe limits, they become toxic and can pose a serious health risk. (Maria Bibi *et al* ., 2023). Heavy metals are particularly harmful because they tend to bioaccumulate in the human body, a process in which their concentration within an organism increases over time compared to the surrounding environment. In bioaccumulation, the rate at which these substances are stored in the body exceeds the rate at which they are metabolized or excreted.

Environmental contamination and human exposure to heavy metals occur largely due to anthropogenic (human) activities. These include the use of fertilizers, various industrial processes, application of waste materials to fertilize soil, municipal waste disposal, dumping sites, poor waste management, transportation, and agricultural activities. Industrial sources include coal combustion in power plants, pharmaceutical manufacturing, metal refining, textile production, petroleum combustion, high-voltage transmission lines, power stations, microelectronics, plastics, paper processing plants, and wood preservation. (Maria Bibi *et al* ., 2023).

In addition to human activities, heavy metals enter the environment through natural processes such as vaporization of oceans, volcanic eruptions, rock degradation, metal corrosion, soil erosion of metal ions, sediment re-suspension, heavy metal leaching, forest fires, and soil formation. These metals are also found in plants and various products—such as drinking water, food, cosmetics, and commercial goods—used by humans.

Among heavy metals, some are essential for plants and humans (e.g., Cr^{3+}, Cu^{2+}, Co^{3+}, Fe^{3+}, Ni^{3+}, Mn^{2+}, Zn^{2+}), while others are non-essential (e.g., As^{3+}, Cd^{2+}, Hg^{2+}, Pb^{2+}) and exhibit toxic effects. Essential heavy metals play important roles in oxidation–reduction reactions and are constituents of various enzymes. The toxicity of heavy metals affects biological systems, including cellular organelles and their components. When metal ions interact with cellular components such as deoxyribonucleic acid (DNA) and proteins, they can damage DNA and cause conformational changes, leading to carcinogenesis and modulation of the apoptosis cycle.

Because of their high toxicity, arsenic, cadmium, chromium, lead, and mercury rank among the priority metals of public health concern. These elements are considered systemic toxicants capable of inducing multiple organ damage even at low exposure levels. According to reports by the United States Environmental Protection Agency (U.S. EPA) and the International

Agency for Research on Cancer (IARC), these heavy metals are classified as carcinogenic. Each metal has unique physicochemical properties that define its toxicological mechanisms of action.

Manganese is the fifth most common metal in the Earth's crust. Its sources include food (meat, tea leaves, nuts, cereals, green vegetables, and grapes), ceramics, batteries, air, pigments, and methylcyclopentadienyl manganese tricarbonyl (MMT) used in gasoline. Trace amounts of manganese are vital for humans, serving as a cofactor in physiological processes and enzyme reactions. It is necessary for urea synthesis, glycoprotein and proteoglycan metabolism, and pyruvate metabolism. Manganese deficiency in humans is rare, whereas manganese toxicity has become a global concern due to the use of MMT in gasoline. (Maria Bibi *et al* ., 2023).

MMT exposure is linked to postural instability, tremor syndromes, gait disturbances, and cognitive impairment. High manganese levels cause accumulation in the central nervous system (CNS), resulting in neurotoxicity. In plants, manganese is essential for oxidation–reduction processes, with its concentration influenced by plant species, soil manganese content, and plant metabolism. Manganese deficiency in plants is uncommon, but toxicity can occur in highly alkaline soils ($pH \approx 8$) (Maria Bibi *et al* ., 2023).

Beyond its toxicity to humans, manganese pollution disrupts ecosystems and reduces biodiversity. In aquatic systems, excessive manganese can lower dissolved oxygen levels, hinder reproduction, feeding, and growth of aquatic organisms, and cause declines in fish and other species. On land, manganese accumulation in soil disturbs microbial balance, reduces nutrient availability, and limits plant growth. These environmental effects lead to reduced soil fertility, lower agricultural productivity, and threats to food security and rural economies. Crops grown in contaminated soils may absorb manganese, introducing it into the food chain and contributing to bioaccumulation and biomagnification, thereby endangering both animals and humans.

The economic consequences are also significant. Contamination reduces crop quality and yield, limits export potential, and increases reliance on costly remediation and healthcare measures. Manganese-polluted areas often lose economic value—especially in agriculture and water-dependent industries and failure to meet environmental standards can result in legal penalties for industries and governments.

Given the persistence, toxicity, and harmful effects of heavy metals like manganese on health, agriculture, and ecosystems, there is an urgent need to control their presence in the environment. If left unaddressed, manganese pollution could cause long-term degradation of natural resources such as soil and water, rendering them unsuitable for cultivation, consumption, or recreation, and threatening sustainability for future generations. (Maria Bibi *et al* ., 2023).

Wastewater containing heavy metal ions can be treated using various methods, including chemical precipitation, coagulation, flocculation, phytoremediation, membrane-based processes, ion exchange, and adsorption. While chemical precipitation, coagulation, and flocculation are highly effective, they require significant chemical and energy inputs and generate large amounts of sludge, making them less practical for routine use. Phytoremediation is environmentally friendly and selective but has moderate efficiency and depends heavily on environmental conditions, limiting its large-scale application. Membrane-based processes are effective but costly and energy-intensive, thus mainly reserved for specialized cases.

In comparison, adsorption is a cost-effective and promising approach. It works under varying conditions, removes a wide range of metal ions, allows recovery of the removed metals, and enables reuse of the adsorbent. These advantages make adsorption one of the most preferred methods for toxic metal removal from water (Bianca-Elena Azanfire *et al* ., 2025). The adsorption process depends on both the physical and chemical properties of the adsorbent and the heavy metal, as well as operational factors such as temperature, adsorbent dosage, pH, contact time, and initial metal ion concentration. In general, heavy metal ions bind to the adsorbent surface (Qasem *et al* ., 2021).

Clay minerals have been widely applied in removing toxic pollutants from water, particularly in developing countries. Examples include kaolinite, montmorillonite, illite, and bentonite, valued for their high surface area, stability, natural abundance, and structural properties. These *non-toxic minerals remove contaminants through adsorption, ion exchange, or both. In ion* exchange, naturally occurring cations such as sodium, potassium, calcium, or magnesium on the clay surface are replaced by heavy metal ions from solution. This happens because negatively charged sites on the clay structure have a stronger affinity for certain heavy metals, allowing effective capture and immobilization. Adsorption at the solid–liquid interface involves counter ions binding to the surface, altering its charge relative to the crystal lattice.

Kaolinite, a 1:1 layer silicate, consists of a tetrahedral silica (SiO_2) sheet linked via an oxygen atom to an octahedral alumina (Al_2O_3) sheet. It has high chemical stability, low swelling capacity, and relatively low cation exchange capacity, and is classified structurally into dioctahedral and trioctahedral types (Uddin, 2016, as cited in Mustapha *et al* ., 2019). In this study, Aseni clay, naturally rich in kaolinite, will be used as the adsorbent. Its abundance, stability, and ability to exchange surface cations with manganese ions make it a suitable and eco-friendly option for reducing manganese contamination in water.

1.1.2 STATEMENT OF PROBLEM

Manganese (Mn) is an essential trace element vital for numerous biological functions, as several enzymes rely on its redox activity for optimal performance (Mou *et al* ., 2011, as cited in Yongchao Li *et al* ., 2019). It contributes to healthy cartilage and bone formation, participates in the urea cycle, supports mitochondrial maintenance, aids glucose production, and lays an important role in wound healing (ATSDR, 2012).

However, at elevated concentrations, Mn becomes toxic. Once absorbed, Mn can accumulate in bones, with an estimated half-life of 8–9 years (O'Neal *et al* ., 2014, as cited in Yongchao Li *et al* ., 2019). Chronic exposure to high Mn levels in drinking water can result in aesthetic problems such as staining porcelain surfaces and imparting unpleasant taste to beverages (Gerke *et al* ., as cited in Liu *et al* ., 2019). More critically, prolonged ingestion has been linked to cognitive decline and hyperactivity in school-aged children (Bouchard *et al* ., 2011, as cited in Yongchao Li *et al* ., 2019), as well as neurotoxicity manifesting as anxiety, dementia, ataxia, and "mask-like" facial expression (Yongchao Li *et al* ., 2019).bou

In mining regions such as South Africa, a neurological disorder called manganism has been reported as endemic, with symptoms including impotence, loss of libido, and impaired fertility (ATSDR, 2012). Experimental studies in animals also indicate that high Mn exposure can negatively affect sperm quality, reduce testicular weight, and disrupt male reproductive tract development.

Respiratory effects from inhalation exposure include inflammatory lung responses, bronchitis, tissue injury, and increased susceptibility to infections such as pneumonitis and pneumonia (ATSDR, 2012). Children are particularly vulnerable, as prolonged exposure can cause cognitive deficits, reduced memory, motor impairments, aggression, and hyperactivity, although the direct causality remains uncertain (ATSDR, 2012).

Due to these health risks, Mn release into freshwater from human activities has become a major environmental concern. The World Health Organization (WHO, 2011) recommends a limit of 0.2 mg/L for Mn in drinking water. The Pennsylvania Department of Health notes that while the U.S. Environmental Protection Agency (EPA) does not enforce a mandatory drinking water standard for manganese, it recommends a secondary maximum contaminant level (SMCL) of 0.05 mg/L (Pennsylvania Department of Health, 2025). This recommendation aims to address aesthetic concerns such as taste and staining, rather than direct health risks.

In China, the maximum allowable concentration is 0.1 mg/L for surface water and 5.0 mg/L for wastewater (MEEPRC, 2002, as cited in Yongchao Li *et al* ., 2019).

Industrially, Mn is widely used in non-ferrous metallurgy, steel production, battery manufacturing, and catalysis (Rongrong Wu *et al* ., 2022). It enters waterways through rock and soil erosion, mining, industrial discharge, and leaching from discarded materials such as dry-cell batteries (ATSDR, 2012). The mining industry remains the primary contributor, with drainage waters often containing high Mn concentrations and solid waste residues steadily releasing Mn into surrounding environments (Silva *et al* ., 2012; Outram *et al* ., 2018; Biswas *et al* ., 2016).

Several methods exist for Mn removal, including pH adjustment, sorption, oxidation, precipitation, and various physical, chemical, and biological approaches. Chemical precipitation using hydroxide, carbonate, or sulfide is effective at pH > 9 but is costly, consumes large amounts of reagents, and produces hard-to-dewater sludge (Patil *et al.*, 2016).

Adsorption is considered a more efficient, low-cost, and environmentally friendly option (Ali *et al*, 2016). It offers operational flexibility, regenerability, no sludge generation, and the ability to remove pollutants at low concentrations with minimal energy demand (Goher *et al.*, 2015; Mthombeni *et al.*, 2016; Al-Jubouri & Holmes, 2017). Adsorption occurs when molecules from a liquid (adsorbate) adhere to a solid (adsorbent) through physical or chemical forces such as van der Waals interactions or covalent bonding (Lakherwal, 2014; Kale *et al*, 2017; Rashid & Yaqub, 2017; Nurul Nadia Rudi *et al,* 2020).

While various adsorbents—such as activated carbon, zeolites, synthetic resins, and chemically modified clays—have been studied for Mn removal, research has largely focused on commercial kaolinite or modified clays from outside the study region. There is limited literature on the adsorption performance of locally sourced Aseni clay, a naturally occurring kaolinite clay. Its mineralogical composition, surface properties, ion exchange potential, and adsorption kinetics for Mn removal have not been thoroughly investigated.

Furthermore, manganese adsorption studies often emphasize other metals such as lead, cadmium, and copper, leaving a knowledge gap in the removal of manganese, especially from $MnSO_4$ salt solutions, using local kaolinite sources. This uncertainty extends to adsorption efficiency, isotherm behavior, and operational optimization for Aseni clay.

Therefore, this study aims to fill the identified gap by evaluating the adsorption capacity of Aseni clay for Mn removal from $MnSO_4$ solutions. The findings will provide scientific evidence for its potential as a sustainable, low-cost, and environmentally friendly treatment option for manganese-contaminated water.

1.1.3 JUSTIFICATION OF STUDY

Although considerable research has been conducted on removing heavy metals from water, very little has focused on the use of Aseni clay for manganese removal. Most available studies emphasize commercial materials such as activated carbon or zeolites, which are effective but often too expensive or not easily accessible in rural communities. This creates a gap, particularly for areas that require affordable and practical solutions.

At the same time, manganese contamination in drinking water is a growing concern due to its harmful health effects. Since limited research exists on the performance of Aseni clay for this purpose, there is a clear need to test its efficiency and potential as a low-cost adsorbent.

This study is therefore justified because it provides new knowledge by being among the first to evaluate Aseni clay for manganese removal. It adds to the scientific literature and offers a practical option that could guide the design of affordable and locally available water treatment systems. In the long run, this could make safe water more accessible to vulnerable communities while also contributing to sustainable environmental practices.

1.1.4 SCOPE OF STUDY

This study focuses on evaluating the adsorption potential of locally sourced Aseni clay, a kaolinite-based clay, for the removal of manganese from $MnSO_4$ salt solutions. The work will involve the preparation and characterization of the clay to determine its physicochemical properties, including mineral composition, surface area, and ion exchange capacity.

Batch adsorption experiments will be conducted under varying operational parameters such as contact time, initial manganese concentration, pH, and adsorbent dosage, to assess removal efficiency. The adsorption process will also be modeled using isotherm and kinetic equations to better understand the interaction between manganese ions and the Aseni clay surface.

The scope of this study does not extend to large-scale treatment or pilot plant operations; rather, it is limited to laboratory-scale investigations. The findings will provide baseline data that may guide the development of low-cost, locally available adsorbents for manganese removal in water treatment applications.

1.1.5 LIMITATIONS

This research is limited to laboratory-scale experiments and does not extend to pilot-scale or full-scale water treatment applications. As a result, the findings may not fully capture the challenges of applying Aseni clay in real environmental conditions.

The study focuses only on manganese removal from $MnSO_4$ salt solutions, which represents a simplified system compared to actual wastewater that may contain multiple contaminants and competing ions. This could influence the adsorption efficiency in real-world applications.

Additionally, only batch adsorption experiments were conducted. While these provide valuable insight into adsorption capacity, isotherm behavior, and kinetics, they do not reflect the continuous flow conditions commonly used in practical water treatment systems.

The characterization of Aseni clay in this study is limited to selected physicochemical properties. More advanced surface and structural analyses could provide deeper insights into the adsorption mechanisms.

Laboratory challenges also posed limitations. For instance, fluctuations in pH control, difficulties in maintaining constant temperature, and potential human error during sample preparation or measurement could affect the accuracy and reproducibility of results.

Finally, the study does not consider the regeneration and reuse potential of the clay, nor the long-term environmental impacts of using Aseni clay as an adsorbent.

1.1.6 AIM AND OBJECTIVES

This study aims to investigate the adsorption potential of locally sourced Aseni clay, a kaolinite-based clay, for the removal of manganese from $MnSO_4$ salt solutions under laboratory conditions.

OBJECTIVES

To achieve the aim of the study, the following objectives will be pursued:

1. To prepare and characterize Aseni clay in terms of its physicochemical properties, including mineral composition, surface area, and ion exchange capacity.
2. To determine the effect of operational parameters such as pH, contact time, initial manganese concentration, and adsorbent dosage on the adsorption efficiency.
3. To model the adsorption process using adsorption isotherm models (Langmuir and Freundlich) to understand the adsorption mechanism.
4. To analyze adsorption kinetics to determine the rate and controlling steps of the process.

5. To evaluate the potential of Aseni clay as a low-cost, locally available adsorbent for manganese removal in water treatment applications.

1.2 LITERATURE REVIEW

1.2.1 ADSORPTION

Adsorption refers to the process in which atoms, ions, or molecules from a gas, liquid, or dissolved solid adhere to the surface of another material (Guruge, 2021). During this interaction, a thin film of the adsorbate is formed on the surface of the adsorbent. This mechanism differs from absorption, in which the absorbate penetrates the bulk of a solid or liquid (Glossary, 2008). While adsorption may occur before absorption, the two are distinct phenomena: adsorption is confined to the surface without entering the internal structure of the material (Memidex Dictionary, 2018). The broader term *sorption* encompasses both adsorption and absorption, whereas *desorption* refers to the reverse process (Atkins *et al*, 2018). Adsorption is the process by which atoms, ions, or molecules from a gas, liquid, or dissolved solid stick to the surface of another material (Guruge, 2021). During this process, a thin layer of the adsorbate forms on the surface of the adsorbent. This differs from absorption, where the absorbate penetrates the entire bulk of a solid or liquid (Glossary, 2008). The broader term sorption includes both adsorption and absorption, while desorption is the reverse process (Atkins *et al*, 2018).

Based on the type of interaction between the adsorbate and adsorbent, adsorption is generally divided into two categories, which are:

- **Physical adsorption (Physisorption)**
- **Chemical adsorption (Chemisorption)**.

Although both involve the accumulation of substances on surfaces, they differ in bonding strength, energy requirements, and reversibility.

- **Physisorption:** This occurs when adsorbate molecules are retained on the adsorbent surface through weak Vander Waals forces, similar to those responsible for gas condensation. No chemical bonds are formed; instead, the attraction is purely physical. This process is characterized by a low enthalpy of adsorption (typically less than 40 kJ/mol) and is favored at low temperatures. Because the forces are weak, physisorption is usually reversible, and adsorbed molecules can be released by increasing temperature or lowering pressure. In addition, it allows the formation of multiple layers (multilayer adsorption), since there is no restriction on how many layers of adsorbate can build up. A common example is the adsorption of nitrogen or oxygen onto activated charcoal

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- **Chemisorption:** This, by contrast, involves the formation of strong covalent or ionic bonds between the adsorbate and the surface of the adsorbent. This process generally requires activation energy and has a much higher enthalpy of adsorption, typically ranging from 40 to 400 kJ/mol. Unlike physisorption, chemisorption is restricted to a monolayer, since each adsorption site can form a chemical bond with only one adsorbate molecule. Due to the strong bonding, chemisorption is usually irreversible and occurs more readily at moderately high temperatures. A classic example is the adsorption of hydrogen molecules onto a nickel catalyst during hydrogenation reactions.

1.2.2 DIFFERENCES BETWEEN PHYSICAL AND CHEMICAL ADSORPTION

Feature	**Physical Adsorption**	**Chemical Adsorption**
Activation energy	Negligible	Requires activation energy
Speed	Rapid at low temp	Slower initially (due to bond formation)
Example	Adsorption of N_2 on charcoal	Adsorption of H_2 on Ni
Temperature effect	Favored at low temperatures	Favored at moderate to high temperatures
Type of forces	Weak Vander Waals forces	Strong chemical bonds (covalent or ionic)
Energy of adsorption	Low (< 40 kJ/mol)	High (40–400 kJ/mol)
Layer formation	Multilayer possible	Monolayer only
Reversibility	Reversible	Irreversible

1.2.3 ADVANTAGES OF ADSORPTION IN WASTE WATER TREATMENT

Adsorption has emerged as a leading method for removing heavy metals from polluted water because of its high efficiency, affordability, and ease of operation. A major advantage is its effectiveness at low contaminant concentrations, a point at which conventional methods, such as chemical precipitation or membrane filtration, often fail (Babel &

Kurniawan, 2003). Unlike precipitation, adsorption requires fewer chemical inputs and produces minimal sludge, making it more environmentally sustainable.

Another strength of adsorption lies in its versatility. A wide variety of adsorbents can be used, ranging from activated carbon to low-cost materials such as clays and agricultural byproducts (Gupta *et al*, 2019). This adaptability allows communities to rely on locally available resources, which is particularly valuable in regions with limited infrastructure. Moreover, adsorption units are simple to design and operate, consuming less energy compared to advanced systems like oxidation or membrane technologies (Ali *et al*, 2020).

For heavy metal removal, adsorption is especially effective due to the large surface area, functional groups, and ion-exchange properties of many adsorbents. These features enable strong and selective binding of toxic metals such as lead, cadmium, chromium, and manganese. Importantly, many adsorption processes are reversible, allowing the regeneration and reuse of adsorbents, which further reduces treatment costs (Nguyen *et al*, 2018).

Because of these combined advantages, high removal efficiency, low operational cost, adaptability, minimal waste generation, and regeneration potential, adsorption remains one of the most widely applied techniques for treating heavy metal–contaminated water.

1.2.4 TYPES OF ADSORBENTS

Adsorbents can be broadly grouped according to their origin. They are:

- **Natural adsorbents**: clays, minerals, zeolites, ores, and charcoal.
- **Synthetic adsorbents**: materials derived from industrial synthesis, agricultural residues, or waste sludge. They include: sewage sludge biochar, coconut shell, rice husk, sawdust, corncob, MCM-41, SBA-15, Graphene oxide, CNTs, etc.

1.2.5 FACTORS INFLUENCING ADSORPTION EFFCIENCY

The effectiveness of adsorption for removing contaminants such as heavy metals is largely determined by several operational and material-related factors.

1. pH of the solution:

pH level plays a critical role in controlling both the surface charge of the adsorbent and the chemical form (speciation) of the adsorbate. Under optimal pH conditions, electrostatic attraction and ion exchange processes are enhanced, whereas highly acidic or alkaline environments can significantly reduce adsorption efficiency (Foo & Hameed, 2010).

2. Initial metal ion concentration

At lower initial concentrations, the available adsorption sites on the adsorbent are sufficient to capture most ions, resulting in higher removal efficiency. However, as the concentration increases, these sites become saturated, leading to a decrease in efficiency (Gupta *et al* ., 2019).

3. **Adsorbent dosage**

A higher dosage of adsorbent generally provides more active sites, improving metal ion removal. Nevertheless, when the dosage is excessive, particle aggregation may occur, reducing the available surface area and limiting adsorption capacity (Babel & Kurniawan, 2003).

4. Contact time

Adsorption efficiency typically increases with prolonged contact time until equilibrium is achieved. Beyond this point, further increases in time have little to no impact on removal efficiency. The time required to reach equilibrium depends on the type of adsorbent, the contaminant, and operating conditions (Ali *et al*, 2020).

5. Temperature

Temperature influences adsorption capacity by affecting molecular motion and the activity of the adsorbent's surface. In physical adsorption, higher temperatures often reduce efficiency due to weaker binding forces, while in chemical adsorption, elevated temperatures can enhance the process by increasing reaction rates (Nguyen *et al*, 2018).

6. **Particle size of adsorbent**

Smaller particles provide a greater surface area for adsorption, which generally improves removal rates. However, extremely fine particles may cause operational challenges, such as difficulties in separating the adsorbent from treated water (Gupta *et al*, 2019).

In adsorption systems, equilibrium is established when the rate at which adsorbate molecules adhere to the surface (adsorption) equals the rate at which they detach (desorption). Initially, adsorption dominates due to the abundance of available surface sites. However, as these sites become occupied, desorption increases until equilibrium is reached. This dynamic balance forms the conceptual foundation for adsorption isotherms such as the Langmuir and the Freundlich.

Mathematically, at equilibrium:

$$R_{adsorption} = R_{desorption}$$

Recent studies have strengthened the theoretical foundation of adsorption–desorption equilibria by emphasizing their dynamic nature. For example, Knopf and Ammann (2021) introduced a statistical thermodynamics framework that explains adsorption and desorption kinetics. Using transition state theory, they derived equilibrium constants and rate coefficients, demonstrating that adsorption and desorption occur simultaneously and are influenced by both thermodynamic and kinetic parameters. Their work highlights that surface coverage and desorption lifetimes are not static but are part of a continuous dynamic balance.

From a water treatment perspective, this understanding explains why extending contact time alone does not always enhance removal efficiency, since equilibrium constraints ultimately govern the process. Optimizing adsorption, therefore, requires not only the right operating conditions but also the careful selection of adsorbents with adequate capacity and stability.

Fundamentally, adsorption represents a surface equilibrium in which adsorbate molecules adhere to adsorbent surfaces. This relationship is typically described using adsorption isotherms, which link the concentration of solutes in solution with the amount adsorbed at equilibrium under constant temperature (Foo & Hameed, 2010).

One of the most widely used models is the **Langmuir isotherm**, developed by Irving Langmuir in 1918. This model assumes adsorption occurs on a uniform surface with a finite number of identical active sites, resulting in only a monolayer of adsorbate. Once a site is filled, no further adsorption can occur there, and interactions among adsorbed molecules are neglected. The Langmuir equation is expressed as:

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

Where:

q_e = equilibrium adsorption capacity (mg/g)

q_m = maximum monolayer adsorption capacity (mg/g)

K_L = Langmuir constant related to affinity (L/mg)

C_e= equilibrium concentration of adsorbate in solution (mg/L)

For linearized fitting, one common form is:

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

In contrast, the **Freundlich isotherm** is an empirical model suited to heterogeneous surfaces. Unlike Langmuir's single-layer approach, Freundlich accounts for variations in adsorption energies and the possibility of multilayer adsorption. Its equation is:

$$q_e = K_F C_e^{1/n}$$

Where:

$\mathrm{K_F}$ = Freundich adsorption constant(indicator of adsorption capacity)

$1/\mathrm{n}$ =adsorption intensity, where n>1 indicates favorable adsorption

In linearized form, it is expressed as

$$\mathrm{Inq_e = InK_F + \frac{1}{n} InC_e}$$

This model is particularly relevant for natural adsorbents such as clays and soils, where surface heterogeneity significantly influences performance. Both Langmuir and Freundlich models serve not only as theoretical constructs but also as practical tools to interpret experimental data, optimize treatment conditions, and compare the adsorption efficiencies of different materials and contaminants (Foo & Hameed, 2010; Ayawei *et al* ., 2017).

1.3 HEAVY METALS

DEFINITION

Heavy metals are a group of elements characterized by distinctive physical and chemical properties. Although definitions vary across disciplines, they generally share certain traits. These include relatively high atomic masses (typically above 40), elevated atomic numbers (often greater than 20), and significant densities, with specific gravity commonly exceeding 5.0 g/cm^3 (Food Safety Institute, 2023). In addition, many possess metallic or metalloid properties such as luster, electrical conductivity, malleability, and ductility (Darwesh & Matter, 2021). It is important to note that not all heavy metals pose the same level of risk to human health or the environment. Their toxicity depends on chemical form, biological interactions, and exposure pathways.

1.3.1 GENERAL CHARACTERISTICS

1. **High Density and Atomic Weight**

   Heavy metals are distinguished from lighter metals by their density (greater than 5 g/cm^3) and relatively high atomic weight or atomic number (Hazrat Ali *et al* ., 2019).

2. **Persistence and non-biodegradability**

These elements do not degrade or decompose easily, allowing them to persist in soils, sediments, and aquatic environments for decades or even centuries (Food Safety and Quality Institute, 2023).

3. **Bioaccumulation and Biomagnification**

   Heavy metals tend to accumulate in the tissues of living organisms and magnify along food chains, leading to elevated concentrations at higher trophic levels. This process poses significant ecological and health concerns (Food Safety and Quality Institute, 2023).

4. **High Toxicity a Trace Levels**

   Metals such as lead, cadmium, mercury, and arsenic are highly toxic even at low concentrations and can cause severe health problems in humans and animals (Paul, B.T. *et al*, 2014).

5. **Diverse Oxidation States and Reactivity**

   Many heavy metals exist in multiple oxidation states, enabling them to form different chemical species. These variations influence their mobility, reactivity, and toxicity (Kilaru H.V. *et al*, 2019).

6. **Essential vs. Non-Essential Roles**

   Some heavy metals, including manganese, iron, copper, and zinc, serve as essential micronutrients in trace amounts. Others, such as cadmium, lead, and mercury, have no biological function and are purely toxic (Hazrat Ali *et al*, 2019)

1.3.2 SOURCES OF HEAVY METAL CONTAMINATION

Heavy metals enter the environment through both natural processes and human activities. Understanding these pathways is vital for designing preventive and remedial strategies.

Natural Sources

- Geological processes: Rock weathering and soil erosion release metals naturally present in the Earth's crust into the surrounding soil and water (Piwowarska, 2024).
- Volcanic activity: Eruptions discharge elements such as arsenic, mercury, and lead into the atmosphere, facilitating their global spread.
- Forest fires: Combustion of biomass reintroduces heavy metals previously absorbed by vegetation back into the environment.

Anthropogenic (Human-Caused) Sources

- Industrial operations: Mining, smelting, fertilizer production, and battery manufacturing release large quantities of toxic metals into the environment (Mohammad *et al*, 2025).
- Waste mismanagement: Improper disposal of e-waste, waste incineration, and untreated sewage discharge significantly contribute to heavy metal pollution.
- Agricultural practices: Fertilizers and pesticides, especially phosphate-based types, often contain cadmium and other heavy metal residues that gradually accumulate in soil (Mohammad *et al*, 2025).
- Combustion of fossil fuels: Burning coal and petroleum products releases heavy metals such as mercury and arsenic into the air.

- Traffic-related emissions: Even after the phase-out of leaded gasoline, wear from brakes, tires, and road surfaces continues to emit trace metals into the environment

1.3.3 CLASSIFICATION OF HEAVY METALS BASED ON TOXICITY AND BIOLOGICAL ROLE

1. TOXIC HEAVY METALS

Element	**Atomic Number**	**Specific Gravity (g/cm³)**	**Health Effects**	**Key properties**
Lead (Pb)	82	11.34	Neurotoxic; damages the nervous system, kidneys, blood-forming tissues, and reproductive organs. Children are at risk of intellectual impairment.	Soft and malleable, it is a poor conductor of electricity that accumulates in bones and tissues and persists in the environment. Its melting point is 327 °C, with oxidation states of +2 and +4.
Mercury (Hg)	80	13.6	Methylmercury accumulates in fish, resulting in neurological and developmental harm.	Only liquid metal at room temperature, with high vapor pressure, it forms organic compounds like methylmercury, and has oxidation states of +1 and +2
Cadmium (Cd)	48	8..65	Builds up in the kidneys and liver; it leads to kidney dysfunction, bone demineralization, and increased cancer risk.	A soft, bluish-white metal that resists corrosion with a long biological half-life (~10–30 years in humans). It melts at 321 °C and has an oxidation state of +2.
Arsenic (As)	33	5.73	It causes skin lesions, cardiovascular disease, and cancers, often due	Metalloid; present in both inorganic and organic forms; soluble compounds are extremely toxic. It exhibits oxidation states

			to contaminated water or food.	of −3, +3, and +5 and is brittle.

2. CONDITIONALLY TOXIC HEAVY METALS

Element	**Atomic Number**	**Specific Gravity (g/cm³)**	**Health Effects**	**Key properties**
Chromium (Cr)	24	7.19	Cr(III) is essential for glucose metabolism; Cr(VI) is highly toxic and carcinogenic.	Hard and corrosion-resistant; oxidation states +3 (essential) and +6 (toxic); melting point 1907 °C.
Copper (Cu)	29	8.96	Essential for enzymatic processes; too much intake can lead to liver damage and gastrointestinal issues.	Excellent electrical and thermal conductor; oxidation states +1 and +2; melting point 1085 °C. Redox-active.
Zinc (Zn)	30	7.13	Supports immune function, protein synthesis, and wound healing; but high doses can impair copper absorption and weaken immunity.	Reactive metal; oxidation state +2; melting point 420°C does not accumulate long-term.
Manganese (Mn)	25	7.43	Essential for bone growth and enzyme activity; excessive exposure leads to neurological damage (*manganism*).	Hard, brittle; oxidation states +2, +4, +7; melting point 1246 °C not easily oxidized

3. NON-TOXIC HEAVY METALS

Element	Atomic Number	Specific Gravity (g/cm³)	Health Effects	Key properties
Gold (Au)	79	19.32	Biologically inert with minimal toxicity to humans.	Highly malleable, an excellent conductor, and resistant to corrosion.
Silver (Ag)	47	10.49	Low toxicity to humans; prolonged exposure may lead to argyria; harmful to aquatic life.	Ductile, Antimicrobial properties; ductile; good conductor

1.4 MANGANESE

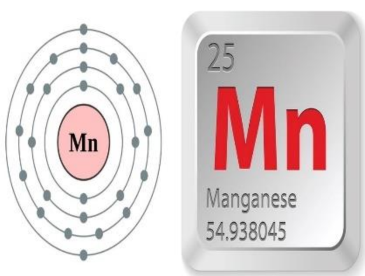

Fig. 1.1: Electronic configuration of manganese (Rachel Ross, 2017)

Fig. 1.2: Pyrolusite(Rachel Ross., 2017)

HISTORY OF MANGANESE

Manganese has been utilized by humans for thousands of years, although it was not scientifically identified as a distinct element until the 18th century. Archaeological findings show that as far back as the Upper Paleolithic period, around 17,000–30,000 years ago, people used manganese dioxide as a pigment in cave paintings, giving them their characteristic dark hues (Chalmin *et al* ., 2006).

In the classical period, manganese contributed to materials and artifacts, even if its role was not always recognized. For instance, the durability of Spartan weapons may have been linked to the manganese content in the iron ores they used. Ancient Egyptians and Romans also discovered manganese's effect on glass, removing unwanted colors or imparting purple, pink, and black shades. This application continued for centuries in traditional glassmaking (International Manganese Institute, 2024).

The scientific study of manganese advanced during the 17th and 18th centuries. German chemist Johann Glauber first produced permanganate, a manganese salt, and manganese oxide later became essential in chlorine production. The element itself was identified in 1771 by Swedish chemist Carl Wilhelm Scheele and isolated in 1774 by Johan Gottlieb Gahn. Shortly thereafter, researchers recognized that manganese improved the hardness of iron without reducing toughness, paving the way for its role in steel production. By the early 19th century, scientists in Europe, such as Prieger in Germany, were producing ferromanganese alloys

containing high manganese levels, innovations that revolutionized metallurgy (International Manganese Institute, 2024).

Since then, manganese has continued to drive innovation, finding uses in pigments, glass, agriculture, batteries, and electronics. Today, it is mined in more than 30 countries, with South Africa, Australia, Brazil, Gabon, and Ghana as leading producers. Most manganese ore is processed into alloys, with China currently dominating global production. From prehistoric cave art to modern steelmaking and energy technologies, manganese has played an indispensable role in human culture and industrial development.

1.4.1 OCCURRENCE OF MANGANESE

Manganese is relatively abundant in the Earth's crust, making up about 0.1% (1,000 ppm) and ranking as the 12th most abundant element (Emsley, 2001). In soils, manganese levels range from 7 to 9,000 ppm, with an average concentration of about 440 ppm, while atmospheric levels are much lower at approximately 0.01 $\mu g/m^3$ (Emsley, 2001).

The most important manganese ore is pyrolusite (MnO_2), although other minerals such as braunite ($Mn^{2+}Mn_6^{3+}SiO_{12}$), psilomelane [(Ba, H_2O)$_2$ Mn_5O_{10}], and rhodochrosite ($MnCO_3$) also occur . About 80% of the world's manganese resources are located in South Africa, particularly in the Kalahari Manganese Field, which contained an estimated 15 billion tons as of 2011. Additional reserves are found in Ukraine, Australia, India, China, Gabon, and Brazil (USGS, 2009; Manganese Mining in South Africa, 2016). Commercial production is concentrated in South Africa, Australia, China, Gabon, Brazil, India, Kazakhstan, Ghana, Ukraine, and Malaysia (Elliott *et al* ., 2018). In 2011, South Africa was the leading producer, supplying about 3.4 million tons (Manganese Mining in South Africa, 2016).

Manganese is also abundant in marine environments, particularly in the form of deep-sea manganese nodules that contain around 29% manganese (International Seabed Authority, 2021). Global estimates once suggested nearly 500 billion tons of nodules, especially concentrated in the Clarion–Clipperton Zone of the Pacific Ocean (Hein, James R., 2016). In seawater, manganese occurs primarily as dissolved manganese (dMn), about 90% of which is derived from hydrothermal vents (Hernroth *et al.*, 2020).

In soils, manganese exists in three main oxidation states: Mn^{2+}, Mn (III), and Mn (IV). The dominant form depends on pH and redox conditions—acidic or anaerobic conditions favor Mn^{2+}, while alkaline and aerobic conditions stabilize Mn (III, IV) oxides. Microbial processes further mediate manganese cycling by driving both oxidation and reduction reactions (Bartlett & Ross, 2005).

In Nigeria, manganese mineralization is associated with Precambrian basement rocks. A notable deposit occurs in the Oban Massif of Cross River State, where manganese is found within quartzite, schist, and banded iron formations. Recent geological and geophysical investigations confirm the presence of economically viable deposits, signaling strong potential for future development (Okon *et al.*, 2022). Other reported occurrences include Benue, Kebbi, and Nasarawa States, where manganese is hosted in both sedimentary and basement complex formations. However, large-scale mining remains underdeveloped, primarily due to limited geological exploration, poor infrastructure, and insufficient investment in Nigeria's mineral sector (Akintola, 2019).

Despite these challenges, Nigeria's manganese reserves hold strategic importance, particularly given the rising global demand in steelmaking, battery production, and renewable energy technologies. Further exploration and exploitation of these resources could significantly contribute to Nigeria's economic diversification and industrial advancement.

Fig.1.3. Rhodochrosite, from the Sweet Home Mine, Colorado, private collection (Eric hunt, 2006)

Fig.1.4. Psilomelan (Wikipedia,2025)

Fig.1.6 Braunite (Ra'ike, 2009)

1.4.2 PHYSICAL PROPERTIES OF MANGANESE

- **Appearance**

  Manganese is a silvery-gray transition metal with a bright metallic luster. Despite its attractive appearance, it is very hard and brittle, which makes it unsuitable for machining in its pure metallic state. This brittleness is why manganese is often used in alloyed forms rather than as a pure metal (Encyclopedia.com, 2024; DCCEEW, 2022).

- **Atomic Structure**

  The element has an atomic number of 25, meaning it contains 25 protons in its nucleus. Its standard atomic mass is 54.94 u, which is a weighted average of its naturally occurring isotopes. This atomic configuration places manganese in the first-row transition metals, giving it unique chemical versatility (Helmenstine, 2021).

- **Density**

  Manganese has a density that ranges between 7.2 and 7.47 g/cm^3. This positions it among the moderately dense transition metals. Its density contributes to its strength and stability, making it suitable for alloy production and heavy-duty industrial applications (DCCEEW, 2022; Helmenstine, 2021).

- **Melting and Boiling Points**

The melting point of manganese is between 1244 and 1247 °C, while its boiling point is about 2061 °C. These high thermal values indicate that manganese is very stable at

elevated temperatures, which is why it is widely used in industries such as steelmaking that require heat-resistant materials (Encyclopedia.com, 2024; DCCEEW, 2022).

- **Allotropic Forms**

Manganese exists in several allotropes, with the α-manganese phase being the most stable at room temperature. Other allotropic forms appear at higher temperatures and can alter manganese's structural and mechanical properties. This polymorphism adds to its versatility in industrial processes (Wikipedia Contributors, 2025c).

- **Mohs Hardness**

On the Mohs scale, manganese has a hardness rating of about 6. This indicates that the metal is relatively hard compared to common materials like glass, but is still brittle, limiting its direct applications in structural engineering without alloying

- **Magnetic Properties**

Pure manganese and many of its ionic states are paramagnetic. This means that they are weakly attracted to external magnetic fields due to the presence of unpaired d-electrons. However, manganese can also exhibit antiferromagnetic properties in some of its compounds, further showing its complex magnetic behavior (Wikipedia Contributors, 2025c).

1.4.3 CHEMICAL PROPERTIES OF MANGANESE

- **Electronic Configuration**

The electronic configuration of manganese is:

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$$

or in shorthand notation:

$$[Ar]\ 3d^5\ 4s^2.$$

The half-filled $3d^5$ subshell gives manganese additional stability and explains why it can exist in multiple oxidation states (Encyclopedia Britannica, 2023).

- **Oxidation States**

Manganese can exhibit oxidation states ranging from –3 to +7. The most common states are +2, +3, +4, +6, and +7, with +2 (Mn^{2+}) being the most stable in aqueous systems. For example:

$$Mn \rightarrow Mn^{2+} + 2e^-$$

This versatility in oxidation states is what makes manganese a vital element in redox chemistry and catalysis (Encyclopedia Britannica, 2023).

- **Reactivity with Oxygen**

Manganese reacts readily with oxygen to form oxides, such as manganese (II) oxide:

$$2Mn+O_2 \rightarrow 2MnO$$

These oxides are important industrially, especially in the production of batteries and pigments (DCCEEW, 2022).

- **Reaction with Acids**

Pure manganese dissolves in dilute non-oxidizing acids, liberating hydrogen gas. For instance:

$$Mn + 2HCl \rightarrow MnCl_2 + H_2$$

This reactivity demonstrates its strong metallic character and its role in forming soluble salts like $MnCl_2$ (DCCEEW, 2022).

- **Reaction with Halogens and Non-Metals**

At elevated temperatures, manganese reacts with halogens to form halides. For example, with chlorine:

$$Mn + Cl_2 \rightarrow MnCl_2$$

This shows its ability to form a wide range of compounds, many of which are industrially valuable (sciencemadness.org, 2020).

- **Solubility of Compounds**

The solubility of manganese compounds varies. Compounds such as $MnO_2, MnCO_3$ are sparingly soluble, while $MnSO_4, MnCl_2 and\ KMnO_4$. They are highly soluble in water. This variation influences how manganese behaves in environmental and industrial systems (DCCEEW, 2022).

- **Strong Oxidizing Behavior**

Compounds of manganese in the +7oxidation state, such as potassium permanganate($KMnO_4$), are strong oxidizers. They are widely applied in analytical and industrial chemistry. In acidic solutions, $KMnO_4$ oxidizes Fe^{2+} to Fe^{3+} as follows:

$$2MnO_4 + 5Fe^{2+} + 16H^+ \rightarrow 2Mn^{2+} + 5Fe^{3+} + 8H_2O$$

This strong oxidizing ability makes $KMnO_4$ one of the most important compounds of manganese (Encyclopedia Britannica, 2023).

1.4.4 ISOTOPES OF MANAGANESE

Manganese (Mn) has only one stable isotope, ^{55}Mn, which accounts for 100% of naturally occurring manganese. This makes it both monoisotopic and mononuclidic, since only one stable nuclide of the element exists in nature (Wikipedia Contributors, 2025c).

Beyond this stable isotope, scientists have identified more than 25 radioactive isotopes of manganese, with mass numbers ranging from ^{46}Mn to ^{73}Mn (Wikipedia Contributors, 2025c). Among these, ^{53}Mn is cosmogenic and long-lived, with a half-life of approximately 3.7 million years. It is especially important in cosmochemistry and planetary science, where it serves as a chronometer for early solar system processes. Advances in resonance ionization mass spectrometry have refined its half-life determination, further enhancing its relevance in geochronology (Kneip *et al.*, 2022).

Some isotopes also hold practical and medical significance. For example, ^{52}Mn (half-life ~5.6 days) is gaining attention in PET/MRI imaging because of its favorable decay properties and the potential for cyclotron-based production (Brandt, 2019; Porto *et al.*, 2024). Likewise, ^{54}Mn (half-life ~312.08 days) is widely employed as a tracer in biological and environmental studies (Wikipedia Contributors, 2025c).

In the field of nuclear astrophysics, neutron-rich manganese isotopes with mass numbers between 53 and 63 play an important role. Their beta-decay and electron-capture rates significantly affect stellar nucleosynthesis and core-collapse supernova modeling. Recent advances in nuclear modeling have provided more precise decay data, shedding light on manganese's contribution to astrophysical processes (Shehzadi *et al.*, 2023).

Below are the key isotopes of manganese:

Isotope	abundance	half-life (t1/2)	Decay Mode	Decay Product
^{52}Mn	Synth	5.591 days	β^+	^{52}Cr
^{53}Mn	Trace	3.7×10^6 years	ε	^{53}Cr
^{54}Mn	Synth	312.08 d	ε β^- β^+	^{54}Cr ^{54}Fe ^{54}Cr
^{55}Mn	100%	Stable	--	-

Table 1.4.4 Isotopes of manganese

1.4.5 EXPOSURE ROUTES, HEALTH EFFECTS, AND ENVIRONMENTAL IMPACTS OF MANGANESE

Manganese (Mn) is an essential micronutrient; however, excessive intake through environmental, dietary, or occupational exposure can be harmful to human health. The primary pathways of exposure are inhalation, ingestion, and dermal contact.

Exposure Routes:

- **Inhalation:** This is the most significant route of manganese exposure, especially in workplaces such as welding, alloy manufacturing, and mining. Fine airborne particles (≤5 µm) can bypass normal lung defenses and even reach the brain directly via the olfactory nerve (Williams *et al.*, 2012).

- **Ingestion:** Occurs mainly through contaminated water and food. Children are particularly vulnerable because their detoxification systems are underdeveloped, making them more susceptible to neurological effects (Williams *et al.*, 2012; O'Neal *et al.*, 2015).
- **Dermal contact:** This route is usually minimal. However, certain compounds such as methylcyclopentadienyl manganese tricarbonyl (MMT) can penetrate the skin under specific conditions (Williams *et al.*, 2012).

Health Effects

Chronic overexposure to manganese is strongly associated with neurotoxicity. Prolonged inhalation can lead to *manganism*, a neurological disorder similar to Parkinson's disease but less responsive to L-DOPA therapy. Symptoms include movement disorders, mood changes, and reduced cognitive ability (O'Neal *et al.*, 2015). Even at lower exposure levels, subtle neurological effects such as poor memory, reduced attention, and impaired coordination have been reported (Williams *et al.*, 2012).

Children face higher risks, with studies linking elevated manganese in drinking water to reduced IQ, behavioral issues, and in severe cases, increased infant mortality (Williams *et al.*, 2012). On a biological level, excess manganese disrupts neurotransmitter regulation, impairs mitochondrial function, and increases oxidative stress (O'Neal *et al.*, 2015). Neuroimaging studies confirm manganese accumulation in the basal ganglia of exposed workers, providing direct evidence of its neurotoxic impact (Williams *et al.*, 2012).

Environmental Effects

Environmental contamination arises mostly from industrial emissions, mining, and the use of fuel additives like MMT. Once released into the air, manganese settles onto soils and water surfaces, contaminating farmland and water supplies (O'Neal *et al.*, 2015). Elevated levels in groundwater degrade drinking water quality, often leaving metallic taste and stains, while simultaneously posing chronic health risks to nearby populations (Williams *et al.*, 2012).

In ecosystems, manganese pollution can disrupt soil microbial functions and aquatic systems, threatening food security and ecological balance. This makes manganese contamination a serious environmental concern.

1.4.6 APPLICATIONS OF MANGANESE

1. Fundamental Role in Steelmaking

Manganese is indispensable in steel production, which accounts for about 85–97% of global manganese demand. It is used in making ferromanganese and silicomanganese alloys that enhance strength, hardness, and ductility in steel (International Manganese Institute, n.d.). Additionally, manganese serves as a deoxidizer and sulfur fixer, preventing impurities and cracking during processing (Wikipedia, 2025).

2. **High-Manganese ("Mangalloy") Applications**

Mangalloy, also known as manganese steel or Hadfield steel, contains about 13% manganese. It is renowned for its high impact strength and resistance to abrasion once work-hardened. This makes it suitable for mining equipment, railway tracks, and other high-stress applications (Wikipedia Contributors, 2025b).

3. **Alloying in Non-Ferrous Metals**

Manganese improves the properties of non-ferrous alloys. In AlMn alloys, it enhances corrosion resistance and strength, making them widely used in beverage cans and industrial cladding (Wikipedia Contributors, 2025a). It also strengthens copper and other alloys by improving deoxidation and mechanical stability (International Manganese Institute, n.d.)

4. **Energy Storage and Batteries**

Manganese is a vital component in lithium-ion battery cathodes, particularly in NMC (nickel-manganese-cobalt) and LMO (lithium-manganese-oxide) formulations. These compounds improve energy density, thermal stability, and lifespan, making manganese crucial in electric vehicles (EVs) and electronic devices (Investing News Networks, 2023).

5. **Catalysts and Chemical Uses**

Manganese dioxide (MnO_2) plays a key role in dry-cell battery cathodes and serves as a decolorizing agent in glass manufacturing. It is also widely used as an oxidizing agent in organic synthesis, such as the conversion of alcohols to aldehydes or ketones (Wikipedia Contributors, 2025d).

6. **Agricultural and Environmental Uses**

Manganese compounds such as sulfates and oxides are used in fertilizers and animal feed, supporting plant and livestock nutrition (International Manganese Institute, n.d.). Potassium permanganate is extensively applied in water purification, odor control, and industrial sanitation.

7. **Industrial Casting and Abrasion Resistance**

Manganese castings are highly valued in industries that require durability under abrasive and high-impact conditions, such as the cement industry. Their toughness and resilience make them indispensable for heavy-duty applications (Akjay Industrial, 2025).

1.5 CLAY

The clay used in this research was obtained from **Aseni in Kogi State, Nigeria**, specifically from the second layer of the deposit. This layer was chosen because it is richer in mineral content and less affected by surface impurities. Previous studies have shown that deeper clay horizons often exhibit more stable physicochemical properties and reduced organic contamination, making them more suitable for adsorption applications (Irabor & Emudiobagware, 2023).

Mineralogical and chemical analyses of Aseni clay reveal that it is predominantly **kaolinite**, with a framework mainly composed of silica (SiO_2) and alumina (Al_2O_3). It also contains accessory minerals such as feldspar, quartz, and trace amounts of iron, magnesium, calcium, and potassium oxides (Irabor & Emudiobagware, 2023). This mineralogical composition classifies it as a kaolinitic clay, a group widely recognized in adsorption studies for their structural stability and tunable surface activity (Abu *et al.*, 2024).

1.5.1 PHYSIOCHEMICAL PROPERTIES OF CLAY

The physicochemical features of Aseni clay further support its potential as an effective adsorbent. Similar to other kaolinitic clays, it exhibits the following properties:

- **Moderate cation exchange capacity (CEC):** This enables effective interaction with positively charged ions, such as Mn^{2+}.
- **Plasticity:** The clay can be molded and activated without breaking apart, enhancing its usability in treatment processes.
- **Surface charge and functional groups:** Hydroxyl and silicate groups, as confirmed by FTIR, provide reactive sites for adsorption.

- **Porosity and surface area:** While moderate in the natural state, these properties increase significantly after acid or thermal activation, resulting in improved adsorption efficiency (Mbouga *et al.*, 2018; Abu *et al.*, 2024).
- **Morphology:** SEM micrographs typically show a flaky, layered structure, which becomes more open and porous following activation.

1.5.2 ENVIRONMENTAL AND HEALTH SAFETY

One of the key advantages of clay minerals such as kaolinite is their environmental safety. Unlike some synthetic adsorbents or chemical coagulants that may leave harmful residues, clay-based adsorbents are non-toxic, biodegradable, and naturally abundant (Qi *et al.*, 2024). Their application in water purification not only avoids the introduction of harmful by-products but also improves overall water safety. Additionally, research has demonstrated that clay minerals effectively reduce heavy metal concentrations to below guideline limits, thereby lowering the risk of chronic exposure. This is particularly important for contaminants such as manganese, which at elevated levels is associated with neurological and developmental health problems (Fan Zhao *et al.*, 2023).

1.5.3 SUSTAINABILITY AND LOCAL RELEVANCE

From a sustainability perspective, the use of locally available Aseni clay offers an affordable, accessible, and renewable material for water treatment in Nigeria. Activation treatments further enhance its performance by increasing surface area and generating more active binding sites, which directly improves manganese uptake. Thus, the use of Aseni clay in this study not only addresses environmental challenges but also supports the development of safe, low-cost, and eco-friendly water treatment technologies, contributing to both environmental protection and improved public health.

1.5.4 ADSORPTION ISOTHERM

An **adsorption isotherm** describes the quantitative relationship between the amount of adsorbate adsorbed onto the surface of an adsorbent and its equilibrium concentration (or pressure) in the surrounding phase at a constant temperature. It is a crucial curve that illustrates the mechanisms controlling the retention, release, or mobility of a substance from aqueous solutions or porous media onto a solid surface under constant temperature and pH conditions (Foo & Hameed, 2010; Ayawei *et al.*, 2017). Adsorption equilibrium is attained when the quantity of adsorbate bound to the adsorbent surface becomes balanced with the concentration remaining in solution after sufficient contact time. This equilibrium relationship provides fundamental insights into surface characteristics, adsorption capacity, and the interaction strength between adsorbent and adsorbate, making isotherms essential for understanding pollutant removal in environmental systems. (Foo & Hameed, 2010; Ayawei *et al.*, 2017).

1.5.5 SIGNIFICANCE OF ADSORPTION ISOTHERM

Adsorption isotherms play a crucial role in elucidating how adsorbates interact with adsorbent surfaces. Their importance can be summarized as follows:

- They help in identifying whether adsorption occurs as a single molecular layer on a uniform surface (Langmuir type) or as multilayer adsorption on irregular surfaces (Freundlich type) (Ayawei *et al*, 2017).

- Isotherms provide data on the maximum amount of a substance that an adsorbent can capture, which is vital for designing effective water and wastewater treatment systems (Foo & Hameed, 2010).
- They give insights into the heterogeneity of the adsorbent's surface, the distribution of binding energies, and the strength of adsorbent–adsorbate interactions (Dada *et al.*, 2012).
- Adsorption isotherms help in assessing the movement, availability, and persistence of pollutants such as heavy metals and organic compounds in soils and aquatic environments (Ayawei *et al.*, 2017).
- By describing adsorption equilibria, isotherms guide the choice of suitable adsorbents, required dosage, and operating conditions for efficient and cost-effective remediation technologies (Foo & Hameed, 2010).

1.6 TYPES OF ADSORPTION ISOTHERMS

1. Langmuir Isotherm (*most relevant)*
2. Freundlich Isotherm *(most relevant)*
3. Temkin Isotherm
4. Dubinin–Radushkevich (D–R) Isotherm
5. BET (Brunauer–Emmett–Teller) Isotherm
6. Redlich–Peterson Isotherm
7. Sips Isotherm
8. Elovich Isotherm

1.6.1 LANGMUIR ISOTHERM

The Langmuir adsorption isotherm, originally developed to describe gas–solid phase adsorption, has also been widely applied to evaluate and compare the adsorption capacities of different adsorbents. The model is based on the principle of dynamic equilibrium, where adsorption is proportional to the fraction of free surface sites available, while desorption depends on the fraction of occupied sites. It assumes that adsorption occurs in a monolayer, with a fixed number of identical sites, constant adsorption energy, and no lateral migration of adsorbed molecules across the surface. Additionally, all adsorption sites are considered to be energetically equivalent, and the strength of intermolecular interactions decreases with increasing distance from the surface. The Langmuir equation can be written in the following linear form

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

Where

Ce = concentration of adsorbate at equilibrium (mg/g).

KL = Langmuir constant related to adsorption capacity (mg/g)

which can be correlated with the variation of the suitable area and porosity of the adsorbent which implies that large surface area and pore volume will result in higher adsorption capacity. The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the separation factor

$$R_L = \frac{1}{1+K_L C_0}$$

where K_L = Langmuir constant (mg/g)

Co = initial concentration of adsorbate (mg/g).

NB: R_L values indicate the adsorption to be unfavourable when R_L >1,

linear when R_L=1

favorable when 0<$R_L < 1$

irreversible when R_L =0.

1.6.2 FREUNDLICH ISOTHERM

The Freundlich adsorption isotherm accounts for the heterogeneity of the adsorbent surface, assuming an exponential distribution of active sites with varying adsorption energies. It is represented by the equation

Where

$$q_e = K_F C_e^{1/n}$$

K_F(mg/g) = the Freundlich constant indicating adsorption capacity,

n = a dimensionless exponent that reflects adsorption intensity.

The model can be linearized into the form:

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

From this linear plot, the slope ($1/n$) and intercept ($Log K_F$) are used to determine the constants. The value of ($1/n$) generally lies between 0 and 1, reflecting the degree of nonlinearity between solute concentration and adsorption.

A value of $1/n$=1 indicates linear adsorption. Higher n values suggest a relatively uniform adsorbent surface, while lower values imply stronger adsorption at low concentrations and the presence of a higher proportion of energetically active sites.

1.6.3 TEMKIN ISOTHERM

The Temkin isotherm model considers the influence of indirect adsorbate–adsorbent interactions on adsorption behavior. Unlike other models that assume constant adsorption energy, Temkin postulates that the heat of adsorption (ΔH) decreases linearly with increasing surface coverage. This makes the model most applicable within an intermediate concentration range of adsorbates.

Mathematically, the model is expressed as:

$$q_e = Bln(K_T C_e)$$

or in its linearized form:

$$q_e = BlnC_e + BlnK_T$$

where:

- B = $\frac{RT}{b}$ with being the Temkin constant related to the heat of adsorption (J/mol),
- K_T is the Temkin equilibrium binding constant (L/g)
- R and T represent the universal gas constant and absolute temperature, respectively.

The constants B and K_T can be determined from the slope and intercept of a plot of $q_e$versuslnC_e . Overall, the Temkin isotherm provides valuable insight into adsorption systems where interactions among adsorbed species cannot be neglected.

1.6.4 DUBININ-RADUSHKEVICH

The Dubinin–Radushkevich (D–R) isotherm is an empirical model often applied to describe adsorption mechanisms involving heterogeneous surfaces with a Gaussian energy distribution. Unlike Langmuir and Freundlich, it does not assume a uniform surface or constant adsorption potential. Instead, it is based on a pore-filling mechanism and is typically used for physical adsorption processes governed by Van der Waals forces.

The model is represented by the equation:

where:

$$q_e = q_s e^{-K_{DR\varepsilon^2}}$$

- q_s= theoretical adsorption capacity (mg/g),
- K_{DR} = Dubinin–Radushkevich constant (mol²/kJ²),
- ε=RT ln $(1 + \frac{1}{C_e})$=Polanyi potential,
- R= universal gas constant (8.314 × 10⁻³ kJ/mol K),
- T = absolute temperature (K), and
- C_e= equilibrium concentration of adsorbate (mol/L).

In linear form, it can be written as:

ln$q_e = lnq_s - K_{DR\varepsilon^2}$

From the slope and intercept of this plot, the constants q_s and K_{DR} can be determined. Furthermore, the mean free energy of adsorption (E), which provides insight into the adsorption mechanism, is calculated as:

E= $\frac{1}{\sqrt{2K_{DR}}}$

The magnitude of **E** helps distinguish the adsorption type:

- $E<8$ kJ/mol → physical adsorption,
- $8<E<16$ kJ/mol → ion exchange,
- $E>16$ kJ/mol → chemical adsorption.

The D–R model is mainly applicable to intermediate concentrations because it does not obey Henry's law at very low concentrations and shows unrealistic behavior at very high pressures. Despite this limitation, it is particularly useful for differentiating between physical and chemical adsorption and for analyzing adsorption data at different temperatures, since the model is temperature-dependent.

Adsorption isotherms matter because they allow you to quantify manganese uptake, understand the mechanism (physical vs. chemical), evaluate the energy of interaction, and design practical treatment systems using clay as a low-cost adsorbent.

1.6.5 APPLICATION OF ADSORPTION ISOTHERM

Adsorption isotherms are widely applied in both environmental and industrial research to explain how contaminants interact with adsorbents. They provide essential information for designing adsorption systems used in wastewater treatment, purification, and recovery processes. For instance, in heavy metal remediation, adsorption isotherms help predict the efficiency of adsorbents in removing ions such as lead, cadmium, and manganese from aqueous solutions. In material science, these models are also employed to characterize the surface properties and adsorption capacity of clays, activated carbon, and other adsorbents.

In this study, adsorption isotherm models are crucial for evaluating the ability of kaolinite clay to remove manganese ions from $MnSO_4$ solutions.

1.6.6 LIMITATIONS OF ADSORPTION ISOTHERM MODELS

Although adsorption isotherm models provide valuable insights, they have certain limitations. Many models rely on simplified assumptions that may not accurately represent real adsorption systems.

- **Langmuir isotherm** assumes monolayer adsorption on a homogeneous surface, which does not fully describe natural adsorbents such as clay that often possess heterogeneous surfaces and multiple binding sites.
- **The Freundlich isotherm** can describe multilayer adsorption but does not predict adsorption capacity at high concentrations.

These limitations imply that no single model can universally describe adsorption under all conditions, making it necessary to compare different models to identify the best fit for experimental data.

1.7 ADSORPTION KINETICS

Adsorption kinetics refers to the study of the rate at which adsorbate molecules are taken up by an adsorbent and the factors that influence this process over time. In simpler terms, it explains how quickly adsorption occurs and reveals the mechanisms that govern the interaction between the adsorbate and the adsorbent (Patel *et al*., 2020).

The adsorption process generally occurs in stages:

1. **External mass transfer** across the boundary layer between the bulk solution and the adsorbent surface.
2. **Intraparticle diffusion**, where solute molecules move into the pores of the adsorbent.
3. **Surface interaction**, where physical or chemical interactions occur at the active sites within the pores (Kristic, 2021).

To describe these steps, kinetic models are employed. Among them, Lagergren's pseudo-first-order and Ho's pseudo-second-order models are the most widely used, while diffusion-based models such as film diffusion and intraparticle diffusion provide further insights into underlying mechanisms (Kristic, 2021).

Beyond explaining mechanisms, adsorption kinetics also help in understanding time-dependent interactions of adsorbates with adsorbent surfaces. This knowledge is critical not only for fundamental chemical processes such as biosorption, enzyme immobilization, and controlled drug delivery but also for optimizing applications in wastewater treatment, pharmaceutical manufacturing, and biotechnology (Patel *et al*, 2020).

1.7.1 IMPORTANCE OF ADSORPTION KINETICS

Studying adsorption kinetics is important because it provides insights into how adsorption occurs and how processes can be optimized. Key points include:

1. **Understanding the adsorption mechanism** – Kinetics help determine whether adsorption is controlled by film diffusion, intraparticle diffusion, or chemical interactions.

This distinction also indicates whether adsorption follows physisorption or chemisorption pathways (Kristic, 2021).

2. **Determining adsorption rate and equilibrium time** – Kinetic studies reveal how quickly adsorption occurs and the time required to reach equilibrium, which is essential for designing efficient processes (Patel, Sharma, & Singh, 2020).

3. **Optimization of adsorbent performance** – By fitting data to kinetic models, researchers can calculate rate constants, adsorption capacity, and other parameters needed to evaluate the effectiveness of adsorbents (Patel *et al*, 2020).

4. **Design and scale-up of treatment systems** – Kinetic parameters provide the data needed for scaling up adsorption systems in industrial and environmental applications, including wastewater treatment and pharmaceutical purification (Kristic, 2021).

5. **Applications across disciplines –** Adsorption kinetics are widely relevant in environmental engineering, biotechnology, and material science, where understanding adsorption rates enhances processes such as biosorption, enzyme immobilization, and drug delivery (Patel *et al*, 2020).

1.7.2 TYPES OF ADSORPTION KINETICS

The most common kinetic models include:

- Pseudo-first-order model (Lagergren model)
- Pseudo-second-order model (Ho and McKay model)
- Elovich model
- Intraparticle diffusion model (Weber–Morris model)

- Film diffusion model
- Boyd kinetic model
- Bangham’s model
- Avrami kinetic model

Among these, the first four are most frequently applied in heavy metal adsorption studies

1.7.3 PSEUDO-FIRST ORDER MODEL

The pseudo-first-order kinetic model is one of the earliest and most widely applied models to describe adsorption processes. It assumes that the rate of adsorption is directly proportional to the number of unoccupied active sites on the adsorbent surface. This makes it especially suitable for systems with low adsorbate concentrations and adsorption dominated by physisorption, which involves weak van der Waals interactions (Abidemi, 2025).

The model further assumes adsorption occurs on a homogeneous surface, where all sites have equal energy and there are no interactions between adsorbed molecules. It emphasizes external mass transfer as the rate-limiting step, describing the diffusion of adsorbate molecules across the boundary layer surrounding the adsorbent (Abidemi, 2025).

This model is based on the idea that adsorption occurs on a homogeneous surface, where all sites possess equal energy and no interactions occur between adsorbed molecules. It further emphasizes external mass transfer as the rate-limiting step, describing diffusion across the boundary layer around adsorbent. Abidemi Anthony, 2025).

Applications of the pseudo-first-order model include water and wastewater treatment, where it has been used to study the adsorption of organic pollutants, dyes, and light metal ions onto activated carbon and other adsorbents. It is also applied in environmental remediation processes and in adsorption studies involving gases on uniform solid surfaces under controlled conditions (Abidemi Anthony, 2025).

Despite its usefulness, the model has limitations. It does not adequately describe systems where **chemisorption** dominates, since it does not account for electron sharing or exchange between adsorbent and adsorbate. Its reliability also decreases for heterogeneous surfaces with varied adsorption site energies, and linearization of the equation often introduces errors in estimating kinetic parameters, especially at low equilibrium capacities (Abidemi Anthony, 2025).

The pseudo-first-order kinetic model is expressed mathematically as:

$$\frac{dqt}{dt} = k_1(q_e - q_t)$$

The integrated form is:

$$q_t = q_e(1 - e^{-k_1 t})$$

and the linear form:

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

Where q_e (mg/g) is the amount of adsorbate at equilibrium,q_t (mg/g) is the adsorption amount at time t and k_1(min−1^{-1}−1) is the rate constant. A plot of $log(q_e - q_t)$ versus t provides the slope$\frac{k_1}{2.303}$ and intercept $logq_e$. (Abidemi Anthony, 2025).

1.7.4 PSEUDO-SECOND-ORDER KINETIC MODEL

The pseudo-second-order kinetic model assumes that the rate of adsorption is proportional to the square of the number of unoccupied sites. This model is particularly useful when adsorption is dominated by **chemisorption**, where strong interactions occur due to electron sharing or exchange between adsorbent and adsorbate molecules (Mohamed Nasser, Abbas, & Trari, 2024).

Compared to physisorption, chemisorption results in stronger binding, making this model highly applicable in explaining the uptake of metal ions and organic compounds onto biomaterials (Abidemi Anthony, 2025).

The model also assumes that adsorption occurs uniformly across the adsorbent surface, which simplifies the mathematical interpretation of adsorption kinetics (Abidemi Anthony, 2025).

The applicability of the pseudo-second-order model spans several disciplines. In environmental remediation, it has been successfully used to describe the removal of heavy metals such as lead (Pb) and cadmium (Cd) from contaminated waters, as well as the adsorption of dyes, phenols, and other pollutants during wastewater treatment (Abidemi Anthony, 2025).

Beyond aqueous systems, it has also been employed in gas adsorption studies, such as CO_2 storage and separation, and in catalysis, where it helps explain the adsorption behavior of reactants on catalyst surfaces (Abidemi Anthony, 2025).

Despite its wide use, the model has some limitations. It is most appropriate when chemisorption is the rate-limiting step, and is less reliable for systems dominated by physical adsorption, multilayer adsorption, or heterogeneous surfaces. Its accuracy also depends strongly on the quality of experimental data used for model fitting and validation (Abidemi Anthony, 2025).

The pseudo-second-order model can be expressed in both nonlinear and linear forms:

$$\frac{dqt}{dt} = k_2(q_e - q_t)^2$$

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

The linear form is:

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

Where q_t (mg/g) is the adsorption amount at time q_e (mg/g) is the equilibrium adsorption capacity, and k_2(g mg−1^{-1}−1 min−1^{-1}−1) is the rate constant. A plot of $\frac{t}{q_t}$ against t gives a slope $\frac{1}{q_e}$and an intercept of $\frac{1}{k_2 q_e^2}$.

1.7.5 FACTORS AFFECTING ADSORPTION KINETICS

The rate and mechanism of adsorption are influenced by several physicochemical and operational factors. Key factors include:

- **Particle and pore size of the adsorbent**

Smaller particle sizes increase surface area and shorten diffusion paths, leading to faster adsorption. Larger pore diameters (>10 nm) reduce resistance and enhance diffusion efficiency (Suresh Kumar *et al*, 2019).

- **Agitation or mixing rate**

  Stirring reduces the boundary layer thickness around adsorbent particles, which accelerates mass transfer. Higher agitation generally increases the adsorption rate up to an optimum point (Fouad *et al*, 2024).

- **Initial adsorbate concentration**

  Elevated solute concentrations provide a stronger driving force for mass transfer, resulting in faster adsorption. However, once adsorbent sites are saturated, further increases do not improve uptake (Wasilewska *et al*, 2024).

- **Solution pH**

  The pH controls both the ionization state of the adsorbate and the surface charge of the adsorbent. For example, adsorption of Mn^{2+} ions are usually enhanced at neutral to slightly alkaline pH, while acidic conditions reduce efficiency due to competition with H^+ ions (Wasilewska *et al.*, 2024).

- **Temperature**

  In endothermic systems, higher temperatures improve adsorption by enhancing diffusion and molecular interaction with the adsorbent. In exothermic systems, however, increased temperature can lower adsorption efficiency (Wasilewska *et al.*, 2024).

1.7.6 COMPARISON OF ASORPTION KINETICS MODELS

- The **pseudo-second-order model** continues to be widely validated for heavy metal adsorption, including manganese, because it aligns well with chemisorption-based processes. A 2023 study on Mn (II) adsorption onto kaolin confirmed this by showing a strong fit to pseudo-second-order kinetics (Chouchane *et al.*, 2023).

- The **intraparticle diffusion model** still serves as a critical tool for understanding diffusion limitations, particularly with porous materials. A 2025 review introduced a diffusion-chemisorption model and classification system, highlighting how intraparticle diffusion influences adsorption kinetics across multiple adsorbent types (Mohamed Naser, S., *et al,* 2025).

- When it comes to **complex, non-linear adsorption behaviors**, models like **Avrami** are increasingly applied. For instance, a 2024 investigation using coconut-shell activated carbon for dye adsorption applied the Avrami model and found it effectively captured multi-mechanism kinetics better than simple pseudo-order models (Yusuf *et al.*, 2024).

Although the **pseudo-second-order model** remains a robust option for describing chemisorption-driven processes such as manganese adsorption onto kaolinite (Chouchane *et al*, 2023), the **intraparticle diffusion model** continues to be essential for assessing pore-related transport resistance in porous adsorbents (Mohamed Naser, S., *et al*, 2025). For systems exhibiting non-linear or multi-stage kinetics, the **Avrami model** has gained traction, particularly in scenarios where sigmoidal uptake curves are observed (Yusuf, A.A. 2024).

Relevance of Adsorption Kinetics to This Study

Studying adsorption kinetics helps explain how quickly and by what pathway manganese ions are taken up by kaolinite clay. The models show whether the process is controlled mainly by **chemical bonding (chemisorption)**, **movement through the liquid film**

around the particles (film diffusion), or **movement into the pores of the clay (pore diffusion)**. Knowing this is important because it points to the dominant mechanism and guides how conditions like particle size, pH, and contact time can be adjusted to improve manganese removal from solution.

1.8 ATOMIC ABSORPTION SPECTROSCOPY (AAS)

Atomic Absorption Spectroscopy (AAS) is a highly sensitive analytical technique widely used for detecting and quantifying trace and heavy metals in solution. The principle of AAS is based on the fact that free atoms, when vaporized in a flame or graphite furnace, selectively absorb light at element-specific wavelengths. The degree of absorption is directly proportional to the concentration of the target element, in accordance with the Beer–Lambert law (Ravindra *et al*, 2022).

In this study, AAS was employed to measure the residual concentration of manganese ions (Mn^{2+}) in solution after adsorption by Aseni clay. The data obtained were used to calculate adsorption efficiency and uptake capacity under varying experimental conditions. AAS was particularly chosen because of its high sensitivity, precision, and selectivity for transition metals like manganese, while remaining more cost-effective than advanced techniques such as ICP-OES (**Trevor J.,2025;** Wang *et al*, 2024).

Applications of AAS

It extends beyond water treatment research. It is commonly applied in:

- **Environmental monitoring** – detecting heavy metal pollutants in water, soil, and air.

- **Clinical diagnostics** – measuring essential and toxic elements in biological samples such as blood, urine, and tissues.
- **Pharmaceutical and food industries** – ensuring safety and compliance by detecting trace metals in drugs and consumables.
- **Mining and metallurgy** – analyzing ore composition and monitoring metal recovery efficiency.

1.8.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Fourier Transform Infrared (FTIR) Spectroscopy is a versatile technique widely used in material characterization to identify functional groups and bonding structures. The method relies on the absorption of infrared radiation, which excites molecular vibrations at specific frequencies. Since each bond absorbs at characteristic wavenumbers, FTIR produces a spectrum that provides a chemical fingerprint of the material under study (El-Maghrabi *et al*, 2023).

For adsorption studies, FTIR plays a critical role in comparing spectra before and after interaction with metal ions. In kaolinitic clays, characteristic absorption bands typically include Si–O stretching around 1000–1100 cm^{-1}, Al–O bending near 910 cm^{-1}, and OH stretching between 3620–3690 cm^{-1}. After exposure to manganese, shifts or intensity changes in these bands reveal the involvement of hydroxyl, silanol, and alumina groups in the adsorption process (Abbas *et al*, 2023). This provides direct evidence of the functional groups responsible for binding Mn^{2+} ions to the clay surface.

1.8.2 APPLICATIONS OF FTIR

It extends across various scientific disciplines, including:

- **Environmental studies** – identifying functional groups responsible for the adsorption of pollutants.
- **Polymer and material science** – analyzing bonding structures and modifications after chemical treatments.
- **Pharmaceuticals** – detecting drug–excipient interactions and verifying compound purity.
- **Biotechnology** – monitoring biomolecule interactions and structural changes.

1.8.3 COMBINED USE OF AAS AND FTIR

The integration of AAS and FTIR in this study provided both quantitative and qualitative insights into the adsorption process. AAS offered accurate measurements of manganese removal efficiency, while FTIR confirmed the functional groups on Aseni clay involved in binding. Together, these techniques not only validated the adsorption capacity but also revealed the mechanism of interaction between manganese ions and the clay surface. This complementary approach strengthens the reliability of the study's findings and ensures a more comprehensive understanding of the adsorption process.

CHAPTER TWO

2.0 MATERIALS AND METHODS

This chapter presents the materials and methods employed in the study. It highlights the reagents, apparatus, and clay sample used, the procedures adopted for sample collection and preparation, as well as the experimental design for the adsorption of lead from aqueous solution. The characterization techniques and analytical procedures employed for data collection and analysis are also described.

2.1 MATERIALS

2.1.1 REAGENTS AND CHEMICALS USED

- $MnSO_4.H_2O$
- Clay Sample (Aseni clay)
- Sodium hydroxide
- Nitric acid
- Distilled Water
- Buffers
- Hydrochloric acid

2.1.2 INSTRUMENT AND APPARATUS USED

- Mortar& Pestle
- Sieve
- Beakers

- Conical flasks
- Measuring Cylinder
- Sample bottles
- Analytical balance
- Dropper
- Volumetric flask
- Separating Funnel
- Mechanical Shaker
- Filter paper
- Spatula
- pH meter
- Fume Cupboard
- Atomic Absorption spectroscopy
- Fourier transform infrared spectroscopy
- Thermometer

2.2 PREPARATION OF ADSORBENT (ASENI CLAY)

The Aseni second-layer clay used in this study was prepared in its untreated form but subjected to basic pre-treatment steps to ensure consistency and remove unwanted impurities. First, the raw sample was air-dried at room temperature until a stable mass was obtained, which eliminated free moisture without altering the structural hydroxyls of the clay. The dried material was then crushed with a mortar and pestle and sieved through a 2 mm mesh to exclude coarse debris such as stones and roots. To enhance surface area and achieve a more homogeneous particle size, finer sieving (<63 μm) was carried out, a procedure commonly recommended in adsorption studies (Sun *et al*, 2024).

The sieved clay was thoroughly washed with deionized water to remove soluble salts, dust, and organic residues that might interfere with adsorption performance. In practice, the clay was suspended in deionized water, stirred, allowed to settle, and the supernatant was decanted repeatedly until the wash water became clear. This washing and decantation method is a low-cost and widely accepted approach to reduce background contaminants in raw clays (Hammal *et al*, 2025; Urbancl *et al*, 2023). After washing, the sample was oven-dried at 60–80 °C to constant weight, lightly ground to break aggregates, and re-sieved to maintain uniformity (Abdelazeem *et al*, 2024).

Finally, the prepared clay was stored in clean, airtight containers to prevent moisture uptake or contamination before use.

2.2.1 PREPARATION OF ADSORBATE (HYDRATED MANGANESE SULPHATE SOLUTION)

Standard solutions of manganese ions were prepared from analytical grade hydrated manganese sulfate monohydrate ($MnSO_4{\cdot}H_2O$). A 1000 mg/L stock solution was obtained by dissolving 3.073 g of $MnSO_4{\cdot}H_2O$ in 1000 mL of distilled water, following stoichiometric calculation to yield 1 g of Mn^{2+} per liter. From this stock, working solutions ranging from 10 to 100 mg/L were prepared by serial dilution using distilled water. The pH of the prepared solutions was adjusted between 2 and 8 with standardized 0.1 M HCl or 0.1 M NaOH solutions, since pH is a critical parameter influencing adsorption efficiency, surface charge distribution, and ionic mobility in aqueous media (Sun *et al.*, 2024). All solutions were freshly prepared and stored in polyethylene containers to minimize contamination and avoid precipitation before adsorption experiments.

2.3 BATCH ADSORPTION TESTING

Batch adsorption experiments were carried out in 250 mL Erlenmeyer flasks containing 100 mL of Mn^{2+} solution at predetermined concentrations. Varying doses of Aseni clay (0.1–1.0 g) were added to the flasks, which were then placed on an orbital shaker set at 150 rpm for contact times ranging from 10 to 180 minutes. Experimental parameters such as adsorbent dosage, initial Mn^{2+} concentration, contact time, solution pH, and temperature (25–50 °C) were systematically studied following established adsorption protocols (Chouchane *et al*, 2023).

After equilibration, the suspensions were centrifuged and filtered to separate the solid phase. The residual Mn^{2+} concentration in the supernatant was quantified using Atomic Absorption Spectrophotometry (AAS). The adsorption performance of the clay was assessed in terms of equilibrium adsorption capacity (q_e, mg/g) and percentage removal (R, %) using Equations (1) and (2):

$$q_e = \frac{(C_0 - C_e) \times V}{m} (1)$$

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100(2)$$

Where $C_0$and $C_e$are the initial and equilibrium Mn^{2+} concentrations (mg/L), $V$is the solution volume (L), and $m$is the mass of adsorbent used (g).

2.3.1 EFFECT OF CONCENTRATION

Batch adsorption experiments were conducted using 100 mL aliquots of Mn^{2+} solutions at nominal concentrations of 10, 20, 30, 40, 50, and 100 $mg \cdot L^{-1}$. Before contacting the adsorbent, an aliquot of each prepared solution was measured by Atomic Absorption Spectrophotometry (AAS) to confirm the actual initial Mn^{2+} concentration. For each test, 1.0 g of untreated Aseni 2nd-layer clay was placed in a 250 mL Erlenmeyer flask, and 100 mL of the verified Mn^{2+} solution was added. The flasks were agitated on a mechanical shaker at room temperature for 30 minutes; following agitation, the suspensions were centrifuged and/or filtered, and the supernatants collected. AAS determined the residual Mn^{2+} concentration in each filtrate, and the adsorption capacity was calculated. This procedure follows standard batch adsorption practice: increasing the initial Mn^{2+} concentration increases the driving force for mass transfer to the adsorbent until the available surface sites become saturated (Chouchane *et al.*, 2023).

2.3.2 EFFECT OF CHANGE IN ADSORBENT DOSAGE

Five Erlenmeyer flasks were prepared, each containing 0.2 g, 0.4 g, 0.6 g, 0.8 g, and 1.0 g of untreated Aseni 2nd-layer clay, respectively. To each flask, 100 mL of Mn^{2+} solution at an initial concentration of 30 $mg \cdot L^{-1}$ was added. The suspensions were agitated on a mechanical shaker at room temperature for 30 minutes to promote effective interaction between the clay particles and manganese ions. After agitation, the mixtures were filtered, and the residual Mn^{2+} concentrations in the filtrates were determined using Atomic Absorption Spectrophotometry (AAS). The adsorption efficiency was then evaluated based on the reduction in Mn^{2+} concentration. Such systematic variation of adsorbent dosage is a standard approach in adsorption studies, as increasing the mass of adsorbent generally enhances metal removal efficiency due to the greater availability of active binding sites, until equilibrium or site overlap occurs (Chouchane *et al.*, 2023).

2.3.3 EFFECT OF CHANGE IN AGITATION TIME

A fixed mass of 1.0 g of untreated Aseniclay was added to 100 mL of 30 $mg \cdot L^{-1}$ $MnSO_4 \cdot H_2O$ solution in each of six conical flasks. The suspensions were placed on a mechanical shaker and agitated at a constant speed at room temperature for varied contact times of 10, 30, 45, 60, 90, and 120 minutes. At the end of each interval, the mixtures were immediately filtered, and the filtrates were analyzed via Atomic Absorption Spectroscopy (AAS) to determine the remaining Mn^{2+} concentration. Removal efficiency (%) and adsorption at time t (q_t, mg/g) were then computed from the changes in concentration before and after treatment. The selected time points follow findings from Chouchane *et al* (2023), who observed that adsorption of Mn(II) on kaolin and blast furnace slag increases rapidly in the first 30-60 minutes and reaches near-equilibrium by about 50-60 minutes under comparable conditions.

2.3.4 EFFECT OF CHANGE IN PH

Six Erlenmeyer flasks were prepared, each containing 100 mL of a 100 $mg \cdot L^{-1}$ $MnSO_4 \cdot H_2O$ solution adjusted to initial pH values of 4, 5, 6, 7, 8, and 9 using dilute HCl or NaOH. A fixed mass of 1.0 g of untreated Aseni 2nd-layer clay was added to each flask. The suspensions were agitated on a mechanical shaker at room temperature for 45 minutes to ensure sufficient contact between the adsorbent and solution. After agitation, the mixtures were filtered, and the residual Mn^{2+} concentrations in the supernatants were measured using Atomic Absorption Spectrophotometry (AAS).

The pH of the solution strongly influences adsorption because it alters both the surface charge of clay minerals and the speciation of Mn^{2+} in aqueous systems. At low pH values, competition between H^+ ions and Mn^{2+} reduces adsorption, while moderate to slightly alkaline conditions favor enhanced uptake due to reduced electrostatic repulsion and increased availability of adsorption sites. However, the pH range was limited to 4–9 in this study to avoid the formation of $Mn(OH)_2$ precipitates, which typically occur at pH values above 9 and would interfere with adsorption measurements (Chouchane *et al*, 2023).

CHAPTER THREE

3.0 RESULTS AND DISCUSSION

The tables below were generated from results obtained through Atomic Absorption Spectrophotometric analysis conducted on the various filtrates from the experiment using Aseni clay (Kaolinite clay) in a manganese aqueous solution.

NB: All the equilibrium concentrations were calculated from the triplicate value obtained from Atomic Adsorption Spectroscopy.

3.1 EFFECT OF CONCENTRATION

The effect of concentration was determined by varying the concentration of the manganese aqueous solution and taking a constant weight of 1g of Aseni clay at a constant agitation time of 30minutes.

TABLE 3.1 EFFECT OF CHANGE IN CONCENTRATION ON Mn^{2+} ADSORPTION

S/N	INITIAL CONC.(C_O) (mg/l)	EQUILIBRIUM CONC. (C_e) (mg/l)	AMOUNT ADSORBED(C_a) (mg/l)	% ADSORBED	ADSORPTION CAPACITY(q_e) (mg/g)	SD	($C_e \pm SD$)
1	10	2.20	7.80	78.00%	0.78	0.17	2.20±0.17
2	20	8.80	11.20	56.00%	1.12	0.10	8.80±0.10
3	30	13.70	16.30	54.33%	1.63	0.21	13.70±0.21
4	40	21.60	18.40	46.00%	1.84	0.21	21.60±0.21
5	50	27.10	22.90	45.80%	2.29	0.17	27.10±0.17

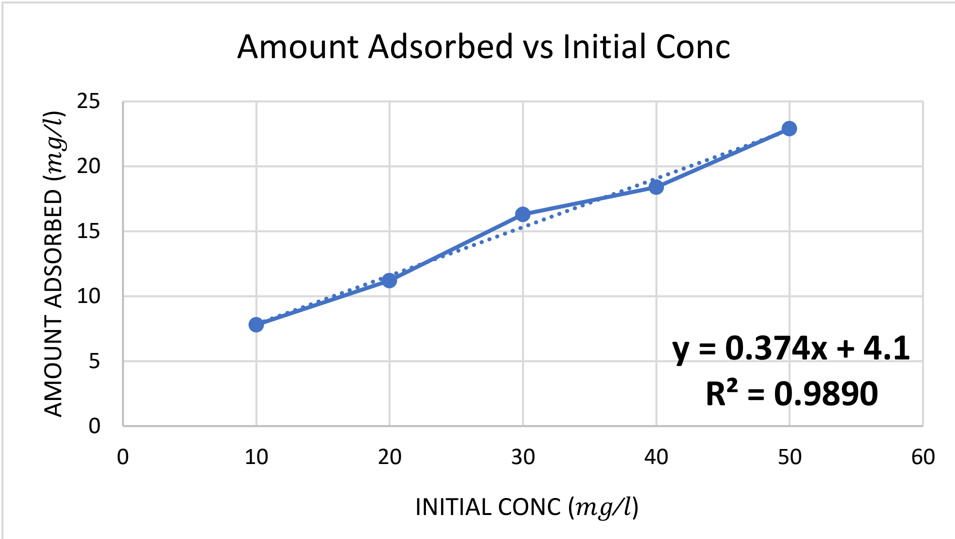

Fig 3.1. Graph of the amount of Mn^{2+} *ions adsorbed at different initial concentrations*

DISCUSSION: Table 3.1 shows the effect of initial manganese ion concentration on the adsorption capacity of Aseni clay.

From the table above, it was observed that the amount of Mn^{2+} adsorbed increased steadily with increasing initial concentration, from **7.8 mg/g at 10 mg/L** to **22.9 mg/g at 50 mg/L**. This trend suggests that higher initial concentrations provide a greater driving force for mass transfer between the solution and the adsorbent surface, leading to higher adsorption uptake.

The sharp increase at lower concentrations (10–30 mg/L) may be attributed to the presence of abundant vacant active sites on the kaolinite surface. However, at higher concentrations (40–50 mg/L), the adsorption capacity still increased but at a slower rate, indicating a gradual approach towards surface saturation.

This behavior is consistent with previous studies where adsorption capacity increased with concentration until equilibrium was approached (Chouchane *et al.*, 2023; Hasani *et al.*, 2022). It also reflects the typical adsorption process in which higher solute concentration enhances the diffusion rate of ions towards active sites on the adsorbent surface.

3.2. EFFECT OF ADSORBENT DOSAGE

TABLE 3.2: EFFECT OF CHANGE IN ADSORBENT DOSAGE ON Mn^{2+} ADSORPTION

S/N	CONC. (C_o) (mg/l)	ADSORBENT DOSAGE (g)	EQUILIBRIUM (C_e) (mg/l)	AMOUNT ADSORBED(C_a) (mg/l)	% ADSORBED	ADSORPTION CAPACITY	SD	(C_e $\pm SD$)
1	30	0.20	16.80	13.20	44.00%	6.60	0.15	16.80 ± 0.15
2	30	0.40	15.96	14.04	46.80%	3.51	0.21	15.96 ± 0.21
3	30	0.60	14.59	15.41	51.37%	2.57	0.20	14.59 ± 0.20
4	30	0.80	14.27	15.73	52.43%	1.97	0.23	14.27 ± 0.23
5	30	1.00	13.50	16.50	55.00%	1.65	0.23	13.50 ± 0.23

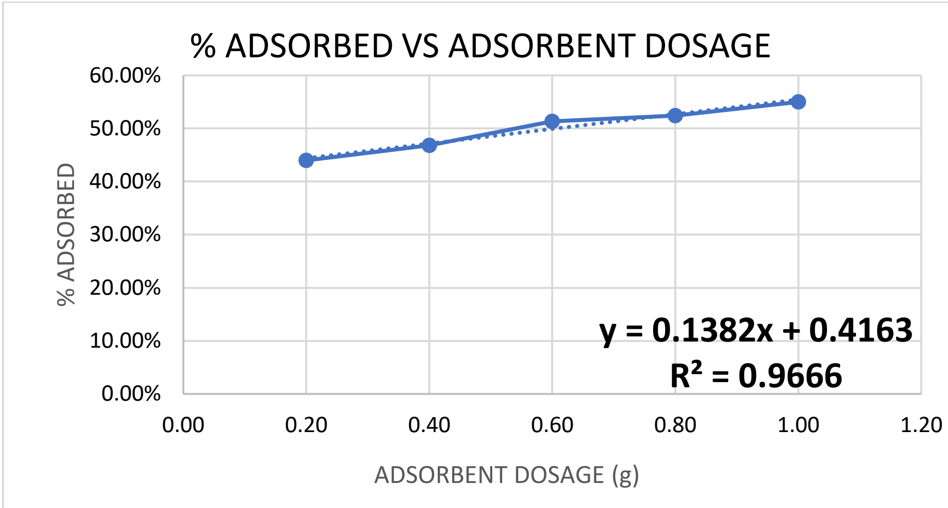

Fig 3.2. Graph of % of Mn^{2+} ions adsorbed at different adsorbent dosages

DISCUSSION: Table 3.2 shows the effect of adsorbent dosage on the percentage removal of Mn^{2+} ions using kaolinite *clay.*

The results indicate that the percentage removal of manganese increased steadily with dosage, from **44.00% at 0.20 g** to **55.00% at 1.00 g**. This trend shows that higher dosages of kaolinite clay provided more surface area and active sites for adsorption, which enhanced the uptake of manganese ions from solution.

However, the increase in removal efficiency became less pronounced at higher dosages (0.8–1.0 g). This is because the number of manganese ions in the solution was fixed, and most had already been adsorbed at lower dosages. Although more adsorption sites were introduced at higher dosages, there were not enough manganese ions left in the solution to occupy all of them. Furthermore, some of the sites within the clay structure may not have been easily accessible due to pore limitations, which explains why a small amount of manganese remained in solution even at the highest dosage.

This observation is consistent with findings from other adsorption studies, where removal efficiency improves with adsorbent dosage up to a certain point, after which equilibrium is reached and further increases in dosage do not result in a proportional increase in adsorption.

3.3 EFFECT OF TIME

TABLE 3.3: EFFECT OF CHANGE IN TIME ON Mn^{2+} ADSORPTION

S/N	TIME(MINS)	CONC. (C_o) (mg/l)	EQUILIBRIUM (C_e) (mg/l)	AMOUNT ADSORBED(C_a) (mg/l)	% ADSORBED	ADSORPTION CAPACITY	SD	$(C_e \pm SD)$
1	10	30	15.50	14.50	48.33%	1.45	0.29	15.50 ± 0.29
2	30	30	13.20	16.80	56.00%	1.68	0.27	13.20 ± 0.27
3	45	30	11.10	18.90	63.00%	1.89	0.28	11.10 ± 0.28
4	60	30	10.40	19.60	65.33%	1.96	0.29	10.40 ± 0.29
5	90	30	9.20	20.80	69.33%	2.08	0.26	9.20 ± 0.26
6	120	30	8.00	22.00	73.33%	2.20	0.29	8.00 ± 0.29

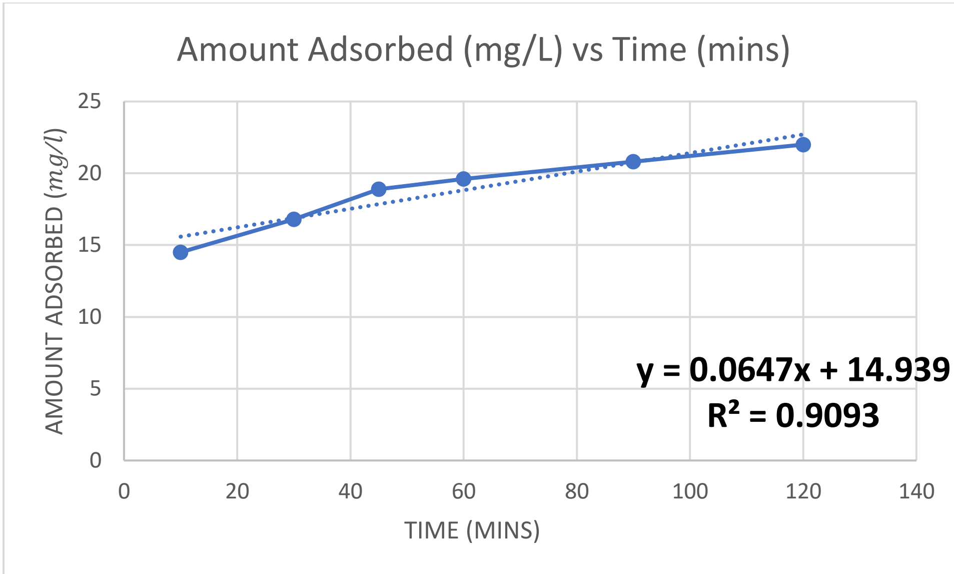

Fig3.3.. Graph of the amount of Mn^{2+} *ions adsorbed at different agitation times*

DISCUSSION: Table 3.3 shows the effect of contact time on the adsorption of Mn^{2+} **ions onto Aseni clay**.

It was observed that the adsorption capacity increased with time, from **14.5 mg/g at 10 minutes** to **22.0 mg/g at 120 minutes**. The increase was rapid during the first 45 minutes, after which the rate of adsorption became slower until it gradually reached equilibrium around 90–120 minutes.

The initial rapid adsorption could be due to the availability of a large number of free active sites on the surface of the kaolinite clay, which allowed manganese ions to be quickly taken up. As time progressed, fewer sites were left available, and repulsive forces between the adsorbed ions and those still in solution likely reduced the rate of uptake.

This behavior is typical of adsorption processes and has been reported in similar studies, where equilibrium was attained after a certain period, depending on the adsorbent-adsorbate system. It shows that sufficient contact time is essential to achieve maximum adsorption efficiency.

3.4 EFFECT OF pH

TABLE 3.4: EFFECT OF CHANGE IN pH ON Mn^{2+} ADSORPTION

S/N	CONC. (C_o) (mg/l)	pH	EQUILIBRUM CONC. (C_e) (mg/l)	AMOUNT ADSORBED (C_a) (mg/l)	% ADSORBED	ADSORPTION CAPACITY (q_e) (mg/g)	SD	$C_e \pm SD$
1	100	4.00	40.97	59.03	59.03%	5.90	6.88	40.97± 6.88
2	100	5.00	39.53	60.47	60.47%	6.05	6.50	39.53± 6.50
3	100	6.00	38.50	61.50	61.50%	6.15	6.30	38.50± 6.30
4	100	7.00	38.40	61.60	61.60%	6.16	6.64	38.40± 6.64
5	100	8.00	38.00	62.00	62.00%	6.20	7.17	38.00± 7.17
6	100	9.00	36.87	63.13	63.13%	6.31	5.24	36.87± 5.24

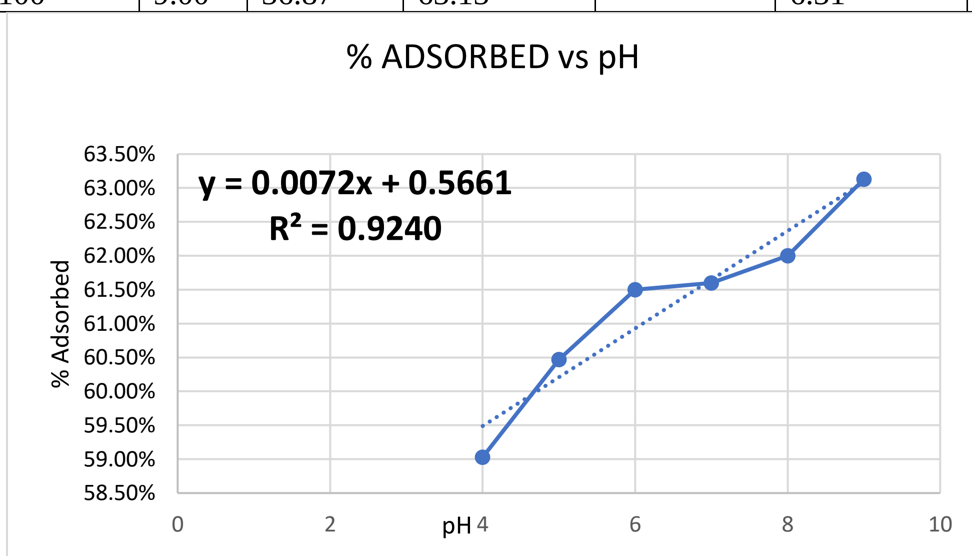

Fig 3.4. Graph of % of Mn^{2+} ions adsorbed under different pH conditions

DISCUSSION: Table 3.4 presents the effect of solution pH on the adsorption of Mn^{2+} ions by kaolinite clay.

The results show that manganese removal increased gradually as the pH of the solution increased from **59.03% at pH 4** to **63.13% at pH 9**. This trend indicates that higher pH values favored adsorption efficiency.

At lower pH (acidic medium), the kaolinite surface is more protonated, which causes electrostatic repulsion between H^+ ions and the positively charged Mn^{2+} ions. This competition reduces the number of available sites for manganese adsorption. As the pH increased, proton concentration decreased, thereby reducing competition and allowing more Mn^{2+} ions to bind to the adsorbent surface.

The slight but steady increase from pH 6 to pH 9 suggests that the adsorption sites were becoming more accessible to manganese ions under less acidic conditions. The highest removal (63.13%) was recorded at pH 9, which may represent the optimal condition within the tested range.

This observation aligns with reports in the literature that adsorption of divalent metal ions generally increases with pH up to an optimum level, after which further increase may cause precipitation of hydroxides (e.g., $Mn(OH)_2$), reducing adsorption efficiency. Since no sharp drop was observed in this study within the pH range tested, it can be inferred that precipitation did not significantly interfere under the conditions investigated.

3.5 RESULT FROM ISOTHERM STUDIES

Table 3.5 Langmuir isotherm model

S/N	(C_o) (mg/l)	(C_e) (mg/l)	(C_a) (mg/l)	V(L)	(q_e) (mg/g)	$\left({}^{C_e}/_{q_e}\right)$ (g/l)
1	10	2.2	7.80	0.10	0.78	2.82
2	20	8.8	11.20	0.10	1.12	7.86
3	30	13.7	16.30	0.10	1.63	8.40
4	40	21.6	18.40	0.10	1.84	11.74
5	50	27.1	22.90	0.10	2.29	11.83

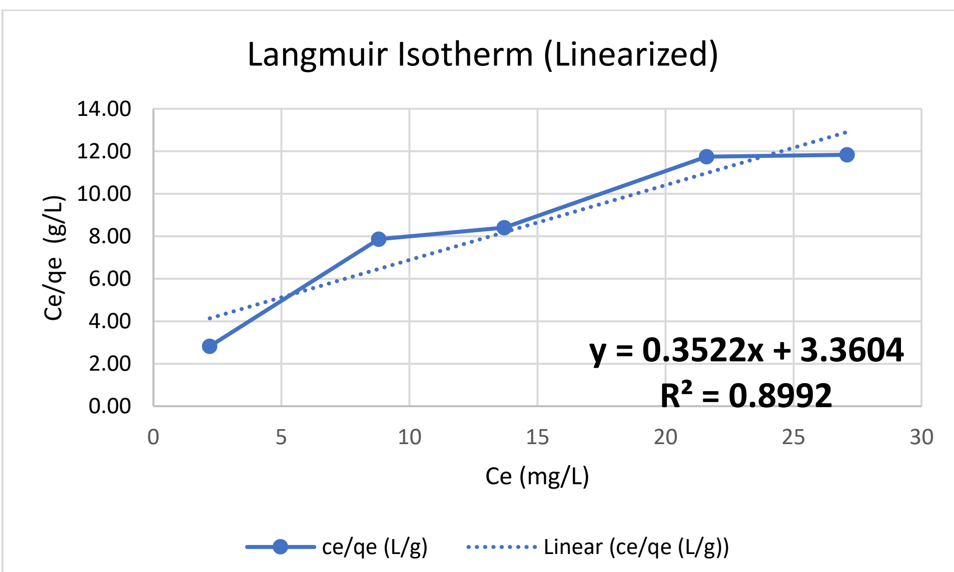

Fig3.5. Langmuir isotherm graph

DISCUSSION: The Langmuir equation (linear form) is:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{1}{q_{max}} C_e$$

Comparing with the value obtained from the graph

$$y = 0.3522x + 3.3604$$

- **Slope(1/qmax) = 0.3522**

→ $q_{max} = \frac{1}{0.3522} \approx 2.84$ mg/g

- **Intercept(1/qmaxb) = 3.3604**

→ $b = \frac{1}{q_{max} \times \text{intercept}} = \frac{1}{2.84 \times 3.3604} \approx 0.105$ L/mg

- **R^2 = 0.8992**

→ Shows a reasonably good fit (close to 1).

The Langmuir isotherm plot of $C_e$versus C_e/q_e(Figure …) gave a straight line with the regression equation $y = 0.3522x + 3.3604$and a correlation coefficient (R^2) of 0.8992. From the slope and intercept of the plot, the maximum adsorption capacity (q_{max}) was calculated to be **2.84 mg/g**, while the Langmuir constant (b), which reflects the affinity of the adsorbent for Mn^{2+} ions, was determined as **0.105 L/mg**. The relatively high R^2 value indicates that the Langmuir model provided a good description of the adsorption of manganese ions onto kaolinite clay.

Table 3.6 Freundlich isotherm model

S/N	(C_o) (mg/l)	(C_e) (mg/l)	$LogC_e$	q_e	$Log\ q_e$
1	10	2.20	0.34	0.78	-0.11
2	20	8.80	0.94	1.12	0.05
3	30	13.70	1.14	1.63	0.21
4	40	21.60	1.33	1.84	0.26
5	50	27.10	1.43	2.29	0.36

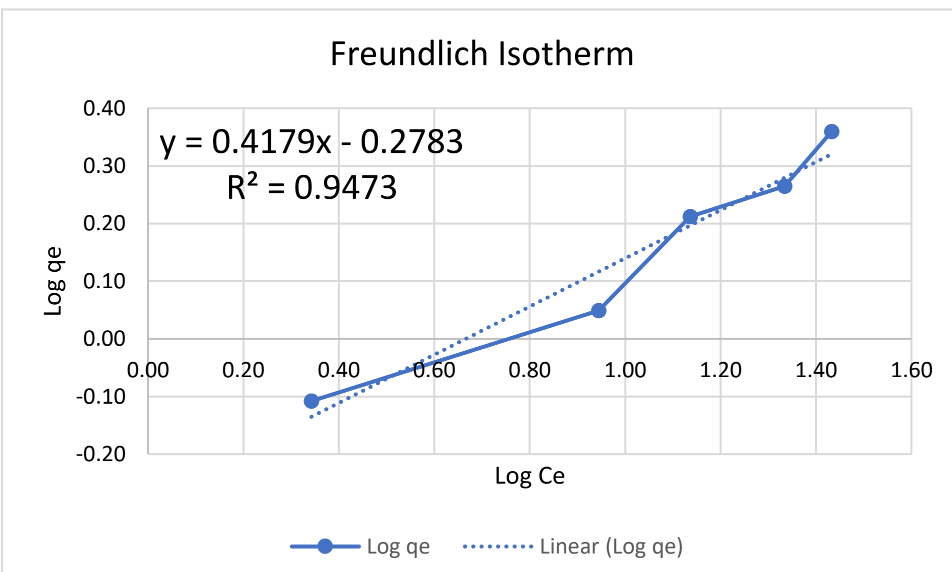

Fig 3.6. Freundlich isotherm graph

DISCUSSION: Freundlich linear form

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

So:

- Slope = $\frac{1}{n}$
- Intercept = $\log K_f$

Comparing with the value obtained from the graph

$$y = 0.4179x - 0.2783$$

$$R^2 = 0.9473$$

- $y = \log\ q_e$
- $x = \log\ C_e$

Identifying constants

- Slope = 0.4179 = 1/n

$\rightarrow n = \frac{1}{0.4179} \approx 2.39$

- Intercept = –0.2783
- $K_f = 10^{-0.2783} = 0.5269$

$$K_f \approx 0.53$$

From the slope, the heterogeneity factor (1/n) was determined as **0.418**, giving n = 2.39. Since n > 1, this confirms that the adsorption process was favorable and occurred on a heterogeneous surface. The intercept gave a Freundlich constant (Kf) of **0.53**, which represents the adsorption capacity of kaolinite clay. The high R^2 value (0.9473) indicates that the Freundlich model provided an excellent fit to the experimental data.

Both Langmuir and Freundlich isotherm models were applied to the adsorption data. The results showed that the Langmuir model gave a good fit, indicating the possibility of monolayer adsorption of Mn^{2+} ions on the kaolinite surface. However, the Freundlich model provided a higher correlation coefficient, which suggests a better overall fit to the data.

This implies that the adsorption process did not occur strictly on a uniform surface, but rather on a **heterogeneous surface with sites of varying energies**, as described by the Freundlich model. Therefore, the Freundlich isotherm better explains the adsorption behavior of Mn^{2+} onto kaolinite clay under the experimental conditions.

3.6. RESULTS FROM KINECTICS ISOTHERM

Table 3.7 Pseudo first-order and pseudo second-order model

S/N	**TIME(MINS)**	(C_o) (mg/l)	(C_e) (mg/l)	(q_t) (mg/g)	(q_e) (mg/g)	$ln(q_e - q_t)$	(t/q_t)
1	10	30	15.50	1.45	1.63	-1.72	6.90
2	30	30	13.20	1.68	1.63	-3.00	17.86
3	45	30	11.10	1.89	1.63	-1.35	23.81
4	60	30	10.40	1.96	1.63	-1.11	30.61
5	90	30	9.20	2.08	1.63	-0.80	43.27
6	120	30	8.00	2.20	1.63	-0.56	54.55

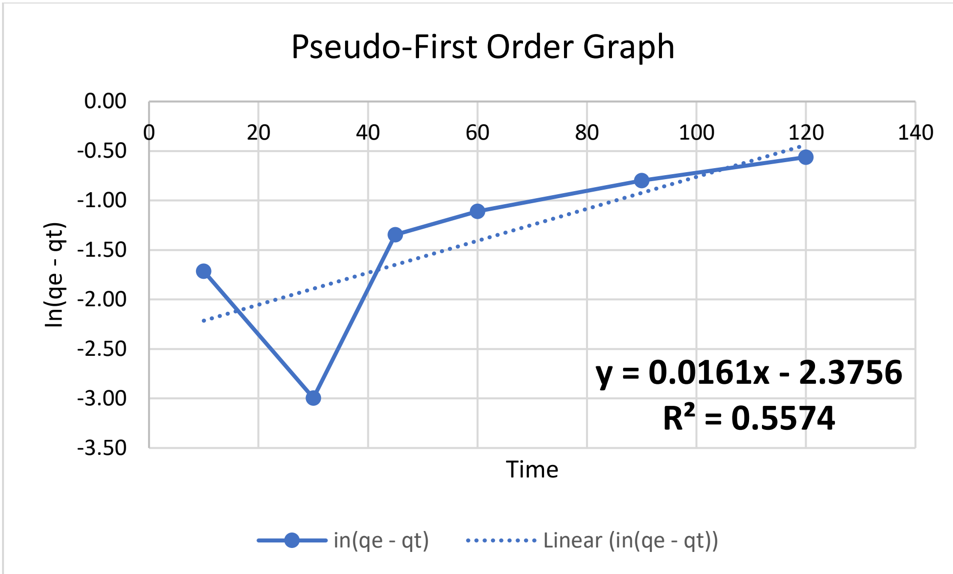

Fig3.6. Pseudo first-order graph

DISCUSSION:

The adsorption data were analyzed using the pseudo-first-order kinetic model by plotting **ln(q_e – q_t)** against **time (t)** for the adsorption of manganese ions onto kaolinite clay. The resulting linear plot produced the regression equation:

$$\ln{(q_e - q_t)} = 0.0161t - 2.3756(R^2 = 0.5574)$$

From the slope, the pseudo-first-order rate constant (**k_1**) was calculated as **0.0161 min^{-1}**, while the intercept gave a theoretical equilibrium adsorption capacity (**q_e**) of approximately **0.093 mg/g** (since $q_e = e^{-2.3756}$).

The calculated q_e value is **much lower** than the experimental equilibrium adsorption capacity of **1.63 mg/g**, and the correlation coefficient (**R^2 = 0.5574**) is relatively poor. These results indicate that the pseudo-first-order kinetic model does **not adequately**

describe the adsorption of manganese ions onto kaolinite clay. This suggests that the adsorption process may involve more complex mechanisms, possibly chemisorption or intraparticle diffusion, rather than being controlled solely by physical adsorption.

Table 3.8. Pseudo-second-order model

S/N	TIME(MINS)	(C_o) (mg/l)	(C_e) (mg/l)	(q_t) (mg/g)	(q_e) (mg/g)	$ln(q_e - q_t)$	(t/q_t)
1	10	30	15.50	1.45	1.63	-1.72	6.90
2	30	30	13.20	1.68	1.63	-3.00	17.86
3	45	30	11.10	1.89	1.63	-1.35	23.81
4	60	30	10.40	1.96	1.63	-1.11	30.61
5	90	30	9.20	2.08	1.63	-0.80	43.27
6	120	30	8.00	2.20	1.63	-0.56	54.55

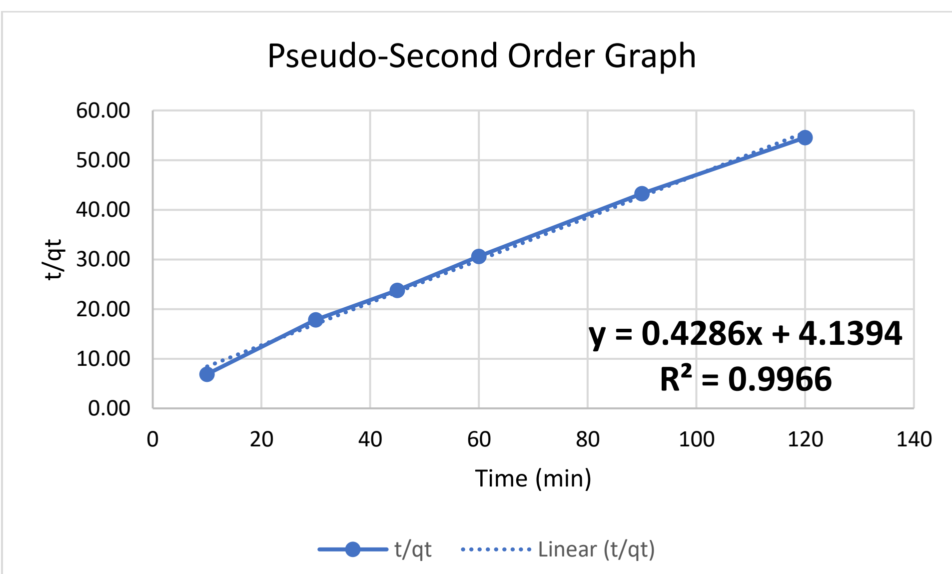

Fig3.7. Pseudo-second order graph

DISCUSSION: The adsorption data were further analyzed using the pseudo-second-order (PSO) kinetic model. The linear form of the PSO equation is expressed as:

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

where $q_t$is the amount adsorbed at time t(mg/g), $q_e$is the equilibrium adsorption capacity (mg/g), $k_2$is the pseudo-second-order rate constant (g/mg·min), and tis the contact time (min).

The plot of t/q_tagainst t(Fig.3.7) gave the regression equation:

$$\frac{t}{q_t} = 0.4286t + 4.1394 (R^2 = 0.9966)$$

From the slope (0.4286), the equilibrium adsorption capacity was calculated as:

$$q_e = \frac{1}{\text{slope}} = \frac{1}{0.4286} \approx 2.33 \text{ mg/g}$$

The intercept (4.1394) corresponds to $\frac{1}{k_2 q_e^2}$, from which the rate constant was derived as:

$$k_2 = \frac{1}{\text{intercept} \times q_e^2} = \frac{1}{4.1394 \times (2.33^2)} \approx 0.045 \text{ g/mg}$$

The high correlation coefficient (R^2 = 0.9966) indicates an excellent fit to the experimental data. These results confirm that the adsorption of Mn^{2+} onto kaolinite clay is best described by the pseudo-second-order model, which implies that the process is controlled by **chemisorption**, involving electron sharing or exchange between adsorbate and adsorbent.

3.7 COMPARISON WITH PREVIOUS STUDY

The results of this study show that manganese adsorption onto kaolinite clay follows the Freundlich isotherm model more closely than the Langmuir model, and that the adsorption kinetics are best described by the pseudo-second-order (PSO) model. These findings are in agreement with the work of **Chouchane *et al.* (2023)**, who reported that Mn (II) adsorption on kaolin also exhibited a better fit with the Freundlich isotherm, indicating heterogeneous surface adsorption sites. They further observed that the PSO kinetic model provided the best description of adsorption behavior, consistent with chemisorption mechanisms.

Additionally, the observed influence of pH on adsorption efficiency in this study is in line with widely reported adsorption behavior, where higher pH values enhance metal ion removal by reducing competition with protons for active sites on the adsorbent surface. For example, **Chouchane *et al.* (2023)** noted a similar trend in their study of Mn (II) adsorption onto kaolin, emphasizing that pH plays a crucial role in determining both surface charge and metal speciation in solution.

Overall, the consistency between the present study and previous findings strengthens the conclusion that kaolinite clay is an effective low-cost adsorbent for manganese removal from aqueous solutions.

3.8 SUMMARY OF RESULTS

This study examined how pH, adsorbent dosage, and contact time affect the adsorption of Mn^{2+} ions onto kaolinite clay. The results showed that adsorption increased with pH, dosage, and contact time, although the rate of increase reduced at higher values of dosage and longer contact times.

Equilibrium studies indicated that the Freundlich isotherm described the process better than the Langmuir model, suggesting adsorption on a heterogeneous surface. Kinetic analysis revealed that the pseudo-second-order model provided the best fit, indicating that chemisorption is the primary adsorption mechanism.

Overall, the results confirm that kaolinite clay can serve as an effective adsorbent for the removal of manganese from aqueous solutions.

3.9 CONCLUSION AND RECOMMENDATION

The study has demonstrated that kaolinite clay is a promising natural adsorbent for removing manganese from aqueous solutions. By applying both equilibrium and kinetic models, it was established that manganese uptake is controlled by surface heterogeneity and chemisorption processes. These findings suggest that kaolinite clay has the potential to serve as a cost-effective and environmentally friendly alternative to conventional treatment methods for manganese-contaminated water.

Based on the findings of this study, the following recommendations are made for future research and application:

1. **Adsorbent Improvement**: Further work can focus on modifying kaolinite clay (e.g., acid treatment, activation, or composite formation) to enhance its adsorption capacity.
2. **Practical Application**: Pilot-scale or field studies are needed to test the performance of kaolinite clay under real wastewater conditions.
3. **Regeneration Studies**: Investigating how kaolinite can be regenerated and reused will help determine its cost-effectiveness in long-term applications.
4. **Multi-Metal Systems**: Since industrial wastewater often contains different heavy metals, future studies should examine how kaolinite performs in multi-ion systems.
5. **Thermodynamic Analysis**: Carrying out temperature-based studies would provide more insight into the energy changes and the feasibility of the adsorption process.

REFERENCES

Abbas, A., *et al* (2023). FTIR characterization of clay-based adsorbents for heavy metal removal. *Applied Clay Science, 241,* 106977

Abdelazeem, R., Younes, H. A., Eldin, Z. E., Allam, A. A., Rudayni, H. A., Othman, S. I., Farghali, A. A., Mahmoud, H. M., & Mahmoud, R. (2024). A selective, efficient, facile, and reusable natural clay/metal organic framework as a promising adsorbent for the removal of drug residue and heavy metal ions. *Colloids and Interfaces, 8*(5), 50. https://doi.org/10.3390/colloids8050050

Abidemi Anthony Sangoremi. (2025, May 29). *Adsorption kinetic models and their applications: A critical review*. Department of Chemistry, Federal University Otuoke, Bayelsa State, Nigeria. https://doi.org/10.51244/IJRSI.2025.120500019

Abu, T. O., Adegoke, H. I., Odebunmi, E. O., & Shehzad, M. A. (2024). *Enhancing adsorption capacity of a kaolinite mineral through acid activation and manual blending with a 2:1 clay.* Nigerian Journal of Technological Development.DOI:10.4314/njtd.v21i1.2269

Agency for Toxic Substances and Disease Registry (2012) *Potential for human exposure, in Toxicological Profile for Manganese* Archived 5 December 2023 at the Wayback Machine, Atlanta, GA: U.S. Department of Health and Human Services.

Akintola Ojo Adeoye . 2019. "Distribution and Economic Potential of Manganese Deposits in Nigeria: A Review". *Asian Journal of Geographical Research* 2 (1):1–8. https://doi.org/10.9734/ajgr/2019/v2i130076.

Akjay Industrial. (2025). Top applications of manganese casting in modern industries. Retrieved from blog.akjayint.com

Ali, I., Asim, M., & Khan, T. A. (2020). Low-cost adsorbents for the removal of organic pollutants from wastewater. *Journal of Environmental Management, 113*, 170–183. https://doi.org/10.1016/j.jenvman.2020.111838

Al-Jubouri, S. M., & Holmes, S. M. (2017). Hierarchically porous zeolite X composites for manganese ion-exchange and solidification: Equilibrium isotherms, kinetic and thermodynamic studies. *Chemical Engineering Journal, 308*, 476–491. https://doi.org/10.1016/j.cej.2016.09.081

Atkins, P. W., De Paula, Julio, & Keeler, James. (2018). *Atkins' physical chemistry* (11th ed.). Oxford University Press. ISBN 978-0-19-876986-6.

Ayawei, N., Ebelegi, A. N., & Wankasi, D. (2017). Modelling and interpretation of adsorption isotherms. *Journal of Chemistry, 2017*, 3039817. https://doi.org/10.1155/2017/3039817

Azanfire, B.-E., Bulgariu, D., Cimpoesu, N., & Bulgariu, L. (2025, June 26). Efficient removal of toxic heavy metals on kaolinite clay: Adsorption characteristics, mechanism, and applicability perspectives. *Water, 17*(13), 1938. https://doi.org/10.3390/w17131938

Babel, S., & Kurniawan, T. A. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: A review. *Journal of Hazardous Materials, 97*(1–3), 219–243. https://doi.org/10.1016/S0304-3894(02)00263-7

Bartlett, Richmond; Ross, Donald (2005). "Chemistry of Redox Processes in Soils". In Tabatabai, M.A.; Sparks, D.L. (eds.). *Chemical Processes in Soils. SSSA Book Series, no. 8. Madison, Wisconsin: Soil Science Society of America. pp. 461–487. LCCN 2005924447*.

Bouchard. F Maryse , Sébastien Sauvé, Benoit Barbeau, Melissa Legrand, Marie-Ève Brodeur, Thérèse Bouffard, Elyse Limoges, David C. Bellinger, and Donna Mergler (2011). Intellectual Impairment in School-Age Children Exposed to Manganese from Drinking Water. *Publication: Environmental Health Perspectives*, Volume 119, Issue 1 Pages 138 – 143 https://doi.org/10.1289/ehp.1002321

Brandt Marie, Jens Cardinale, Ivo Rausch, Thomas L. Mindt. (May 2019) Manganese in PET imaging: Opportunities and challenges. DOI: 10.1002/jlcr.37

Chalmin, E.; Vignaud, C.; Salomon, H.; Farges, F.; Susini, J.; Menu, M. (2006). "Minerals discovered in paleolithic black pigments by transmission electron microscopy and micro-X-ray absorption near-edge structure" (PDF). *Applied Physics A*. **83** (12): 213–218. Bibcode:2006ApPhA..83..213C. doi:10.1007/s00339-006-3510-7. hdl:2268/67458. S2CID 9221234.

Chouchane, T., Boukari, A., Khireddine, O., Chibani, S., & Chouchane, S. (2023). Equilibrium, kinetics, and thermodynamics of batch adsorption of Mn(II) ions on blast furnace slag and kaolin. *Journal of Engineering and Applied Sciences, 70,* Article 58. https://doi.org/10.1186/s44147-023-00218-4

Dada, A. O., Olalekan, A. P., Olatunya, A. M., & Dada, O. (2012). Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} onto phosphoric acid modified rice husk. *IOSR Journal of Applied Chemistry, 3*(1), 38–45. https://doi.org/10.9790/5736-0313845

Darwesh, O. M., & Matter, I. A. (2021). Heavy metals. In *Nanomaterials for Soil Remediation* (Chapter 14.2.2). Elsevier. Retrieved from https://www.sciencedirect.com/science/article/pii/B9780128228913000141

Department of Climate Change, Energy, the Environment, and Water (DCCEEW). (2022). *National Inventory Report 2022: Australia's greenhouse gas emissions 1989–90 to 2021–22.* Vol. 1. Australian Government.

Elliott, R; Coley, K; Mostaghel, S; Barati, M (2018). "Review of Manganese Processing for Production of TRIP/TWIP Steels, Part 1: Current Practice and Processing Fundamentals". JOM. **70** (5): 680-690.

Bibcode:2018JOM....70e.680E. doi:10.1007/s11837-018-2769-4. S2CID 139950857.

El-Maghrabi, H. H., Selim, H., Sheha, E. R., Elshypany, R., Raynaud, P., & Nada, A. A. (2023). Superior Photocatalytic Activity of $BaO@Ag_3PO_4$ Nanocomposite for Efficient Organic Dye Degradation under Visible Light. Catalysts, 13(7), 1073. https://doi.org/10.3390/catal13071073

Emsley, John (2001). "Manganese". *Nature's Building Blocks: An A-Z Guide to the Elements*. Oxford, UK: Oxford University Press. pp. 249–253. ISBN 978-0-19-850340-8.

Encyclopaedia Britannica. (2023). *Manganese.* In *Encyclopaedia Britannica*. Retrieved from https://www.britannica.com

Encyclopedia.com. (2024). Manganese. In The Gale Encyclopedia of Science (7th ed.). Gale, a Cengage Company. Retrieved from https://www.encyclopedia.com/science-and-technology/chemistry/compounds-and-elements/manganese

Fan Zhao, Guangyao Zhang, Yong Jiang, Hui Wang, Chi Cao, Yongbo Qi, Qingyun Wang, & Huaiyan Zhao. (2023). The formation and transformation of manganese oxide minerals on the surface of kaolinite. *Clays and Clay Minerals.* https://doi.org/10.1007/s42860-023-00234-1

Foo, K. Y., & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal, 156*(1), 2–10. https://doi.org/10.1016/j.cej.2009.09.013

Food Safety Institute. (2023, December 26). Key characteristics of heavy metals and their environmental impact. *Food Toxicology and Public Health.* https://foodsafety.institute/food-toxicology-public-health/key-characteristics-heavy-metals-environmental-impact/

Fouad, O. A., Adly, Y. M., Hosny, W. M., Mohamed, G. G., & Mostafa, M. R. (2024). Kinetics and process optimization studies for the effective removal of cresyl fast violet dye using reusable nanosized mullite. *Scientific Reports, 14,* 32164. https://doi.org/10.1038/s41598-024-81653-y

Gerke, T. L., Little, B. J., & Mayned, J. B. (2016). Manganese deposits in drinking water distribution systems. *Corrosion Reviews, 34*(3), 117–131. https://doi.org/10.1515/corrrev-2016-0010

Glossary. (2008). *The Brownfields and Land Revitalization Technology Support Center.* Archived February 18, 2008. Retrieved December 21, 2009.

Goher, M. E., Hassan, A. M., & Abdel-Moniem, I. A. (2015). Removal of aluminum, iron and manganese ions from industrial wastes using granular activated carbon and Amberlite IR-120H. *Egyptian Journal of Aquatic Research, 41*(2), 155–164. https://doi.org/10.1016/j.ejar.2015.04.002

Gupta, V. K., Carrott, P. J. M., Ribeiro Carrott, M. M. L., & Suhas. (2019). Low-cost adsorbents: Growing approach to wastewater treatment—a review. *Critical Reviews in Environmental Science and Technology, 39*(10), 783–842. https://doi.org/10.1080/10643380801977610

Guruge, A. R. (2021, February 17). Absorption vs adsorption. *Chemical and Process Engineering*. Retrieved November 26, 2023.

Hammal, A. (2025). Preparation of geopolymer membranes using clay and some industrial wastes to remove the organic load of pharmaceutical wastewater. *BMC Research Notes, 18*, 232. https://doi.org/10.1186/s13104-025-07299-9

Hazrat Ali, Khan, E., & Ilahi, I. (2019). Environmental chemistry and ecotoxicology of hazardous heavy metals: Environmental persistence, toxicity, and bioaccumulation. *Journal of Chemistry, 2019*, 6730305. https://doi.org/10.1155/2019/6730305

Hein, James R. (January 2016). Encyclopedia of Marine Geosciences - Manganese Nodules. Springer. pp. 408–412. Retrieved 2 February 2021.

Helmenstine, A. M., Ph.D. (2019). Manganese facts. ThoughtCo. Retrieved from https://www.thoughtco.com/manganese-facts-606557.

Hernroth, Bodil; Tassidis, Helena; Baden, Susanne P. (March 2020)."Immunosuppression of aquatic organisms exposed to elevated levels of manganese: From global to molecular perspective".Developmental&ComparativeImmunology.**104** 103536. doi:10.1016/j.dci.2019.103536. ISSN 0145-305X. PMID 31705914. S2CID 207935992.

International Manganese Institute. (n.d.). *Manganese in steel and non-ferrous applications*. Retrieved from https://manganese.org

International Seabed Authority. "Polymetallic Nodules" (PDF). isa.org. International Seabed Authority. Archived from the original (PDF) on 23 October 2021. Retrieved 2 February 2021.

InvestingNews. (2023). Manganese: Emerging battery metal. *Investing News Network (INN)*. Retrieved from https://investingnews.com

Irabor, E. E. I., & Emudiobagware, B. U. (2023). Physico-chemical and mineralogical properties of a clay mineral deposit in Aseni Site II, Kogi State, Nigeria. *FUNAAB Journal of Science and Technology.*

Kale, A. E., Mandake, M. B., & Chitodkar, V. D. (2017). Removal of heavy metals using adsorption process: A review. *International Journal of Advanced Engineering Research and Development, 4*(1), 1–4. (DOI not found)

Kilaru, H. V., Kumar, P. S., & Panda, R. C. (2019). A review on heavy metal pollution, toxicity and remedial measures: Current trends and future perspectives. *Journal of Molecular Liquids, 290*, 111197. https://doi.org/10.1016/j.molliq.2019.111197

Kneip Nina∗ , Dominik Studer , Tom Kieck , Jiri Ulrich , Rugard Dressler , Dorothea Schumann and Klaus Wendt (17 January 2022).Separation of manganese isotopes by resonance ionization mass spectrometry for 53Mn half-life determination. https://doi.org/10.1051/epjap/2022210270

Knopf, D. A., & Ammann, M. (2021). Technical note: Adsorption and desorption equilibria from statistical thermodynamics and rates from transition state theory. *Atmospheric Chemistry and Physics, 21*, 15725–15753. https://doi.org/10.5194/acp-21-15725-2021

Krstić, V. (2021). Role of zeolite adsorbent in water treatment. In *Handbook of Nanomaterials for Wastewater Treatment.* (no DOI found)

Lakherwal, D. (2014). Adsorption of heavy metals: A review. *International Journal of Environmental Research and Development, 4*(2), 41–48. (no DOI)

M. G. Nguemtchouin Mbouga, M. B. Ngassoum, R. Kamga, & M. Cretin. (2018). Characterization of acidic and alkali treated kaolinite and montmorillonite clay from Cameroon. *Journal of Applied Chemical Science International.*

Manganese Mining in South Africa – Overview". MBendi Information Services. Archived from the original on 5 February 2016. Retrieved 10 December 2022.

Maria Bibi, Samiullah, Behilil, F., Afzal, S., & Sahifa. (2023, June). Essential and nonessential heavy metal sources and impacts on human health and plants. *Pure and Applied Biology, 12*(2), 835–87. http://dx.doi.org/10.19045/bspab.2023

Memidex (Word Net) Dictionary/ Thesaurus. Absorption (chemistry). (n.d.). Archived October 5, 2018. Retrieved November 2, 2010.

Mohamed Nasser, S., Abbas, M., & Trari, M. (2025). Understanding the rate-limiting step adsorption kinetics onto biomaterials for mechanism adsorption control. *Progress in Reaction Kinetics and Mechanism, 49,* Article 14686783241226858. https://doi.org/10.1177/14686783241226858

Mohammad, A., Ali, A., Ahmad, S., & Al-Khalid, T. (2025). Anthropogenic sources of heavy metals and their environmental impacts: A global perspective. *Discover Environment.* Springer Nature. https://doi.org/10.1007/s43994-025-00241-6

Mou, D., Yao, Y., Yang, Y., Zhang, Y., Yian, C., & Achal, V. (2011). Plant high tolerance to excess manganese related with root growth, manganese distribution and antioxidative enzyme activity in three grape cultivars. *Plant Physiology and Biochemistry, 49*(5), 434–442. https://doi.org/10.1016/j.plaphy.2011.01.023

Mthombeni, N. H., Mbakop, S., & Onyango, M. S. (2016). Adsorptive removal of manganese from industrial and mining wastewater. *Annual Conference on Sustainable Research and Innovation, 2016,* 4–6. (no DOI)

Mustapha, S., Ndmitso, M. M., Abdulkareem, A. S., Tigani, J. O., Mohammed, A. K., & Shuaib, D. T. (2019, November 3). Potential of using kaolin as a natural adsorbent for the removal of pollutants from tannery wastewater. *Heliyon, 5*(11), e02923. https://doi.org/10.1016/j.heliyon.2019.e02923

Nguyen, C. H., Fu, C. C., & Juang, R. S. (2018). Removal of heavy metal ions from water by adsorption using zeolite, kaolin, and activated carbon. *Environmental Technology & Innovation, 12*, 91–102. https://doi.org/10.1016/j.eti.2018.08.005

Nurul Nadia, R., Mimi Suliza, M., Lee, T. C., Janifal, A., Suhair, O., Nuramidah, H., Nor Hazren, A. H., Norshuhaila, M. S., Roslinda, A., & Hasnida, H. (2020). Evolution of adsorption process for manganese removal in water via agricultural waste adsorbents. *Heliyon, 6*(9), e05049. https://doi.org/10.1016/j.heliyon.2020.e05049

O'Neal, S. L., Hong, L., Fu, S., Jiang, W., Jones, A., Nie, L. H., & Zheng, W. (2014). Manganese accumulation in bone following chronic exposure in rats: Steady-state concentration and half-life in bone. *Toxicology Letters, 229*(1), 93–100. https://doi.org/10.1016/j.toxlet.2014.06.031

Okon, E. E., Kudamnya, E. A., Oyeyemi, K. D., Omang, B. O., Ojo, O., & Metwaly, M. (2022). Field Observations and Geophysical Research Applied to the Detection of Manganese (Mn) Deposits in the Eastern Part of Oban Massif, South-Eastern Nigeria: An Integrated Approach. Minerals, 12(10), 1250. https://doi.org/10.3390/min12101250

Outram, J. G., Couperthwaite, S. J., & Millar, G. J. (2018). Enhanced removal of high Mn(II) and minor heavy metals from acid mine drainage using tunnelled manganese oxides. *Journal of Environmental Management, 223*, 1–9.

Patel, R., Sharma, M., & Singh, P. (2020). Kinetic modeling of adsorption processes for environmental applications. *Environmental Pollution, 263*, 114378. https://doi.org/10.1016/j.envpol.2019.114378

Paul, B. T., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J. (2014). Heavy metals toxicity and the environment. *EXS/Experientia Supplementum, 101,* 133–164. https://doi.org/10.1007/978-3-7643-8340-4

Pennsylvania Department of Health. (2025). *Understanding manganese exposure through drinking water*. Retrieved October 22, 2025, from https://www.pa.gov/content/dam/copapwp-pagov/en/health/documents/topics/documents/environmental-health/Understanding%20Manganese%20Exposure%20Through%20Drinking%20Water.pdf

Piwowarska, K. (2024). Heavy metals in the environment: Sources, pathways, and ecological risks. *Critical Reviews in Environmental Science and Technology.* https://doi.org/10.1080/10643389.2024.2317112

Porto Francesca , Sara Cisternino , Emiliano Cazzola , Giorgia Speltri , Liliana Mou , Alessandra Boschi , Lorenza Marvelli , Giovanni Di Domenico , Antonella Pagnoni , Lucia De Dominicis , Irene Calliari , Claudio Gennari , Licia Uccelli , Gaia

Pupillo , Giancarlo Gorgoni, Juan Esposito , Petra Martini (2024 Aug)Cyclotron production of manganese-52: a promising avenue for multimodal PET/MRI imaging. doi: 10.1186/s41181-024-00288-6

Qasem, N. A. A., Mohammed, R. H., & Lawal, D. U. (2021). Removal of heavy metal ions from wastewater: A comprehensive and critical review. *npj Clean Water, 4*(3), 3. https://doi.org/10.1038/s41545-021-00127-0

Qi, Y., Zhao, S., Shen, Y., Jiang, X., Lv, H., Han, C., Liu, W., & Zhao, Q. (2024, August 29). A critical review of clay mineral-based photocatalysts for wastewater treatment. *Catalysts, 14(9),* 575. https://doi.org/10.3390/catal14090575

Rashid, H., & Yaqub, G. (2017). Bioadsorbents and filters for removal of heavy metals in different environmental samples: A brief review. *Nature Environment and Pollution Technology, 16*(4), 1157–1164. (no DOI

Ravindra, K., *et al* . (2022). Atomic absorption spectrometry in trace metal analysis: Recent advances and applications. *Spectrochimica Acta Part B: Atomic Spectroscopy, 192,* 106414. https://doi.org/10.1016/j.sab.2022.106414

Rongrong Wu, Fangting Yao, Xiaoya Li, Chongjing Shi, Xue Zang, Xiao Shu, Hengwei Liu, Wenchao Zhang (2022). Manganese pollution and its remediation: A review of biological removal and promising combination strategies. Microorganisms 10 (12), 2411, 2022

ScienceMadness. (2020, August 11). Manganese – Sciencemadness Wiki. Retrieved from https://www.sciencemadness.org/smwiki/index.php/Manganese?oldid=13192

Shehzadi, Ramoona , Nabi, Jameel-Un, Farooq, Fakeha (2023) Beta decay and electron capture rates of manganese isotopes in astrophysical environments. New Astronomy, 98, 101937 (2023) 26 Pages doi:10.1016/j.newast.2022.101937

Silva. M Adarlene , Emanoelle C. Cunha, Flávia D.R. Silva, Versiane A. Leão (2012). Treatment of high-manganese mine water with limestone and sodium carbonate. *Journal of Hazardous Materials, 227-228*, 1–7. https://doi.org/10.1016/j.jclepro.2012.01.032

Sun, W.-J., Tang, Q.-T., Lu, T.-H., Fan, R.-D., Sun, G.-G., & Tan, Y.-Z. (2024, January 23). Adsorption performance of bentonite and clay for Zn(II) in landfill leachate.

Suresh Kumar, P., Korving, L., Keesman, K. J., van Loosdrecht, M. C. M., & Witkamp, G. J. (2019). Effect of pore size distribution and particle size of porous metal oxides on phosphate adsorption capacity and kinetics. *Chemical Engineering Journal, 358,* 160–169. https://doi.org/10.1016/j.cej.2018.09.202

Trevor J Henderson (Mar 6, 2025) LabManager: Atomic Absorption Spectroscopy (AAS) vs. Inductively Coupled Plasma (ICP) Spectroscopy: Which Elemental Analysis is right for your Lab.

U.S. Geological Survey.(USGS) 2009.Mineral Commodity Summaries 2009 . Water Resources Division doi:10.3133/mineral2009

Uddin M.K.(2016) A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. Chem. Eng. J. 2016;308:438–462.

Urbancl, D., Goricanec, D., & Simonic, M. (2023). Zero-waste approach for heavy metals' removal from water with an enhanced multi-stage hybrid treatment system. *Materials, 16*(5), 1816. https://doi.org/10.3390/ma16051816

Wang, Y., Chen, L., Zhang, J., Liu, Q., & Zhao, H. (2024). Comparative study of AAS and ICP-OES for trace metal analysis in environmental samples. *Analytical Methods, 16(2),* 288–298. https://doi.org/10.1039/d4ay00288c

Wasilewska, M., *et al.* (2024). Comprehensive studies of adsorption equilibrium and kinetics: Influence of pH, contact time, adsorbate concentration, and grain size on organic compound adsorption. *Molecules, 29(9),* 2038. https://doi.org/10.3390/molecules29092038

Wikipedia contributors. (2025a). *Aluminium–manganese alloys.* In *Wikipedia.* Retrieved October 25, 2025, from https://en.wikipedia.org/wiki/Aluminium–manganese_alloys Wikipedia contributors. (2025b). *Mangalloy.* In *Wikipedia.* Retrieved October 25, 2025, from https://en.wikipedia.org/wiki/Mangalloy Wikipedia contributors. (2025c). *Manganese.* In *Wikipedia.* Retrieved October 25, 2025, from https://en.wikipedia.org/wiki/Manganese

Wikipedia contributors. (2025d). *Manganese dioxide.* In *Wikipedia.* Retrieved October 25, 2025, from https://en.wikipedia.org/wiki/Manganese_dioxide

Williams, M., Todd, G. D., Roney, N., Crawford, J., Coles, C., McClure, P. R., Garey, J. D., Zaccaria, K., & Canda, E. R. (2012). Toxicological profile for manganese. U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR). https://stacks.cdc.gov/view/cdc/12399

Yongchao Li, Xu, Z., Ma, H., & Hursthouse, A. S. (2019, November 26). Removal of manganese(II) from acid mine wastewater: A review of the challenges and opportunities with special emphasis on Mn-oxidizing bacteria and microalgae. *Water, 11*(12), 2493. https://doi.org/10.3390/w11122493

Yusuf, A. A. (2024). Methylene Blue adsorption kinetics investigation by coconut shell activated carbon adsorbent using fractional power, Avrami, and Bangham models. *ENPES Journal.* Retrieved from https://enpesj.enp.edu.dz/index.php/enpesj/article/view/259