ADSORPTION OF Pb^{2+} FROM AQUEUOUS SOLUTION USING CLAY OBTAINED FROM DANGARA IN F.C.T, ABUJA.

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BENIN, BENIN CITY.**

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CERTIFICATION

This is to certify that this research project was carried out by Anita chinanu onyemesim with the Matriculation Number PSC2105279 under the supervision of Professor Emmanuel E. I Irabor in the Department of Chemistry, Faculty of Physical science, University of Benin, Benin City, Edo State, Nigeria.

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DEDICATION

This research project is wholly dedicated to God Almighty and to my beloved family Mr Henry and Mrs Favour Onyemesim whose steadfast love, encouragement and unwavering support gave me the strength and motivation to undertake and complete this research project.

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ABSTRACT

This study investigates the potential of Dangara middle layer clay**,** an abundant natural resource in Nigeria, as a low-cost and sustainable adsorbent for the removal of Pb^{2+} ions from aqueous solutions. Batch adsorption experiments were conducted to evaluate the effects of initial lead concentration (10– 50 mg/L), adsorbent dosage (0.2–1.0 g), agitation time (5–120 min), and pH (4–9) on removal efficiency. The Adsorption process was evaluated by different kinetic models such as pseudo-first-order and pseudo-second-order kinetic models. The Adsorption mechanism was determined by the use of adsorption isotherm such as Langmuir and Freundlich isotherms. Results obtained showed that adsorption efficiency decreased with increasing initial Pb^{2+} concentration due to active site saturation with values ranging from $99.80 \pm 0.01\% - 96.34 \pm 0.80\%$. Increasing adsorbent dosage enchaned removal, producing adsorption efficiency from $97.00 \pm 0.35\% - 98.57 \pm 0.31\%$. Agitation time markedly improved adsorption efficiency, yielding removal values from $94.00 \pm 0.03\% - 99.00 \pm 0.02\%$, while pH had the strongest effect, with adsorption efficiency increasing from 94.97 ± 0.91 % to 99.93 ± 0.06 %, with the maximum removal obtained at pH 9**.** Isotherm modelling revealed that the Freundlich model best described the equilibrium adsorption behaviour than the Langmuir model, indicating a heterogeneous multilayer adsorption, while Kinetic data fitted the pseudo-second-order model, suggesting chemisorption-controlled uptake. Overall, the findings reveal that Dangara middle layer clay demonstrates strong potential as an efficient, ecofriendly, and locally available material for the removal of lead ions from contaminated water, contributing valuable insight into sustainable water purification and environmental remediation strategies.

CHAPTER ONE

1.0 INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

Lead (Pb^{2+}) is an exceptionally toxic heavy metal that presents considerable environmental and public health risks when introduced into aquatic ecosystems. Industrial discharges originating from sectors such as battery production, electroplating, mining, and pigment manufacturing significantly contribute to the lead pollution in aquatic environments (Jaishankar *et al.,* 2014; Fu and Wang, 2011). Exposure to lead has been linked to a range of adverse health outcomes, including neurological deficits, renal dysfunction, anemia, developmental abnormalities in pediatric populations, and various other systemic toxicities (WHO, 2017). Given that lead is non-biodegradable and exhibits a propensity for bioaccumulation, the elimination of lead from contaminated aqueous systems constitutes an urgent global challenge.

Traditional remediation techniques, including chemical precipitation, membrane filtration, ion exchange, and electrochemical remediation, have been utilized for the extraction of lead. Nevertheless, these approaches frequently encounter significant drawbacks, such as elevated operational costs, incomplete removal of pollutants, generation of sludge, and diminished efficacy at low metal concentrations (Fu and Wang, 2011; Barakat, 2011). In contrast, adsorption presents a straightforward, cost-effective, and efficacious strategy characterized by high efficiency and the reusability of adsorbents (Foo and Hameed, 2010; Al-Ghouti and Da’ana, 2020).

Natural clays are particularly promising for the adsorption of heavy metals owing to their abundant availability, affordability, considerable cation exchange capacity, and layered aluminosilicate frameworks that contain reactive functional groups *(*Malamis and Katsou, 2013; Ghorbel-Abid and Trabelsi-Ayadi, 2011). Previous investigations have elucidated the efficacy of montmorillonite, bentonite, and kaolinite clays in the adsorption of Pb^{2+} (Awaad *et al.,* 2019; Al-Ghouti and Da’ana, 2020). Nonetheless, there exists a paucity of research on Dangara middle layer clay, a local deposit characterized by a potentially advantageous mineralogical composition and its capacity as an economically viable adsorbent. This study aims to address this research gap.

1.1.1 BACKGROUND OF STUDY

The contamination of water bodies with lead (Pb^{2+}) continues to represent a significant environmental and public health challenge due to its persistence, toxicity at minimal concentrations, and propensity for bioaccumulation. Conventional water treatment methodologies (e.g., chemical precipitation, ion exchange, and advanced filtration) frequently prove inadequate in terms of economic viability, operational efficiency at trace levels, and scalability particularly within low-resource contexts.

In contrast, adsorption emerges as a promising, cost-effective, and environmentally sustainable alternative for the removal of heavy metals from aqueous solutions (Raji *et al.,* 2023). Natural clays are particularly noteworthy as adsorbents due to their substantial surface area, cation exchange capacity, and stratified structure (Mao *et al.,* 2022). The mechanisms underlying adsorption, including ion exchange, complexation, electrostatic attraction, and precipitation, have been extensively recognized as pivotal factors influencing the uptake of heavy metals by clays (Raji *et al.*, 2023).

Within the Nigerian context, recent research highlights the potential of indigenous clays as low-cost and effective adsorbents. For example, clay sourced from Sokoto State (Goronyo) demonstrated maximum adsorption capacities of 49.72 mg/g for Pb(II), with efficiency contingent upon variables such as pH (optimal at approximately 5.5), contact duration (approximately 60 minutes) (Rabiu *et al.,* 2022), and adsorbent dosage (0.5 g/50 mL). Similarly, pulverized local clay from the Ondo State (Akoko region, Nigeria) exhibited adsorption behavior best described by the Freundlich isotherm, with optimal removal achieved at mildly alkaline pH and ambient temperature, although its maximum capacity (Olaremu, 2021) was comparatively lower (approximately 0.49 mg/g).

Particularly, preliminary studies on Dangara clay reveal remarkably elevated adsorption potentials, with removal efficiencies approaching 99% across a variety of tested parameters, including adsorbent mass, contact time, Concentration and pH.

1.1.2 STATEMENT OF PROBLEM

The pervasive contamination of aquatic ecosystems by heavy metals has emerged as a significant global challenge, attributable to the toxic, persistent, and non-biodegradable characteristics of these pollutants. Among the myriad heavy metals, lead (Pb^{2+}) poses particular hazards as it bioaccumulates in living organisms, leading to severe health implications, which encompass neurological disorders, renal impairment, anemia, and developmental anomalies in pediatric populations (Jaishankar *et al.*, 2014). Industrial operations, including battery production, mining, electroplating, pigment synthesis, and improper waste management, constitute the principal sources of heightened lead concentrations in aquatic systems. Traditional remediation techniques such as chemical precipitation, ion exchange, membrane filtration, and electrochemical methods, while effective, are frequently associated with high costs, significant energy demands, and the potential generation of secondary pollutants (Fu and Wang, 2011).

In recent times, adsorption has been recognized as one of the most effective, cost-efficient, and ecologically benign strategies for the remediation of heavy metals. Nonetheless, the efficacy of adsorption is significantly contingent upon the nature of the adsorbent material utilized. Commercial activated carbon, although highly efficient, remains prohibitively expensive for large-scale applications, particularly within developing regions. Consequently, the quest for low-cost, locally sourced, and environmentally sustainable adsorbents has become a pressing necessity. Clay minerals, owing to their natural prevalence, stratified structure, substantial surface area, and ion-exchange capabilities, represent a promising alternative for remediation efforts. The Dangara middle layer clay, in particular, has not been thoroughly investigated despite its advantageous physicochemical attributes and local availability. A comprehensive assessment of its lead adsorption capacity could yield a cost-effective and sustainable approach for water purification in affected locales. This study thus seeks to address the urgent demand for affordable remediation technologies by exploring the adsorption potential of Dangara middle layer clay for the removal of lead from aqueous solutions. Despite the increasing awareness surrounding heavy metal pollution, lead contamination continues to be widespread, particularly in rural and peri-urban communities where water treatment infrastructure is inadequate. Commercial adsorbents such as activated carbon remain excessively costly and present logistical challenges for extensive implementation in these contexts.

While the use of natural clays for adsorption demonstrates promise, the majority of existing studies are limited in their scope, primarily concentrating on raw performance metrics without an exhaustive evaluation of underlying mechanisms, regeneration potential, or practical applicability. For instance:

- Sokoto clay exhibited a promising adsorption capacity (~49.72 mg/g), however, investigations were restricted to laboratory batch experiments, failing to provide mechanistic insights beyond isotherm modeling (Langmuir/Freundlich) (Olaremu, 2021).

- The study on Akoko clay established its feasibility but reported a relatively low maximum adsorption capacity (~0.49 mg/g) (Rabiu *et al*., 2022).

- Although the results pertaining to Dangara clay are noteworthy, they remain confined to initial performance assessments without comprehensive analyses of kinetics, isotherms, or mechanistic elucidation.

Thus, there exists a compelling necessity to:

- Conduct a thorough characterization of the Dangara clay adsorbent regarding its surface chemistry, kinetics, isotherms, and adsorption mechanisms.

- Assess its potential for regeneration and reuse to ensure practical sustainability.

- Perform a comparative analysis against other local clays to establish contextual relevance.

In the absence of such investigations, the genuine applicability of Dangara clay in sustainable water treatment remains speculative, perpetuating risks for affected communities and overlooking the potential for an economical, locally sourced remediation solution.

1.1.3 JUSTIFICATION OF STUDY

The imperative need for sustainable and economically viable water purification technologies in developing regions substantiates the investigation of indigenous natural resources as potential adsorbents. Lead contamination persists as a significant water quality challenge in numerous communities where access to advanced water treatment facilities is constrained (WHO, 2017; Barakat, 2011). Clays, being readily accessible, cost-effective, and environmentally friendly, represent exemplary candidates for low-cost remediation strategies (Malamis and Katsou, 2013). Despite the abundance of Dangara middle layer clay, it remains inadequately investigated within the context of adsorption research. Assessing its efficacy in adsorbing Pb^{2+} could pave the way for a novel, locally sourced material for the treatment of contaminated water bodies. Furthermore, the implementation of adsorption isotherm and kinetic modeling will yield critical insights into the underlying adsorption mechanisms, thereby reinforcing its prospective application in practical water treatment systems. Consequently, this study is warranted by its potential contributions to environmental remediation, scientific advancement, and the safeguarding of community health.

1.1.4 SCOPE OF WORK

This investigation is centered on the assessment of Dangara middle layer clay as an adsorbent for the extraction of Pb^{2+} ions from aqueous matrices. The scope encompasses:

1. The collection and processing of Dangara middle layer clay.
2. Conducting batch adsorption experiments under rigorously controlled laboratory conditions.
3. Evaluation of critical operational parameters, including initial Pb^{2+} concentration, contact duration, adsorbent dosage, pH, and thermal conditions.
4. Modeling of adsorption equilibrium through the application of isotherm models, specifically Langmuir and Freundlich.
5. Kinetic investigations aimed at elucidating the mechanisms of adsorption.
6. Assessment of the practical viability of Dangara clay as a cost-effective solution for water purification.

1.1.5 LIMITATIONS

While this scholarly endeavor enhances the understanding of lead adsorption utilizing Dangara middle layer clay, several limitations warrant consideration:

1. **Focus on a Singular Metal**: This investigation is exclusively concerned with the adsorption of lead (Pb^{2+}) ions, neglecting the fact that real wastewater generally contains a multitude of heavy metals and other pollutants that may vie for adsorption sites.

2. **Laboratory Conditions versus Real-World Environments**: The adsorption experiments are executed under meticulously controlled laboratory settings. Factors such as variable pH, temperature fluctuations, dissolved organic substances, and complex ionic interactions present in actual wastewater may significantly impact the clay's true efficacy.

3. **Application Scale**: The adsorption assessments are conducted on a batch basis, which may not comprehensively reflect the challenges faced in continuous, large-scale, or industrial treatment systems.

4. **Regeneration and Reusability**: This study does not rigorously evaluate the regeneration, reusability, or potential leaching risks associated with the adsorbent, all of which are vital for ensuring long-term environmental sustainability.
5. **Site-Specific Material Variability**: The characteristics of Dangara clay may exhibit variability based on the extraction location and depth, which could influence the consistency of adsorption performance.

These limitations underscore the necessity for further research to substantiate the practical applicability of Dangara middle layer clay under field conditions, evaluate its capability for multi-metal adsorption, and enhance its performance for extensive wastewater treatment applications.

1.1.6 AIM AND OBJECTIVES

AIM

To Study the adsorption of lead (Pb^{2+}) from aqueous solution using Dangara middle layer clay as a low-cost natural adsorbent.

OBJECTIVES

1. To evaluate the effects of initial Pb^{2+} concentration, contact time, adsorbent dosage, pH, and temperature on adsorption efficiency.
2. To determine adsorption equilibrium and model it using different isotherms (Langmuir and Freundlich).
3. To study the kinetics of (Pb^{2+}) adsorption to elucidate the underlying adsorption mechanism.
4. To assess the feasibility of Dangara middle layer clay as an alternative, sustainable adsorbent for water purification.

1.2 LITERATURE REVIEW

The contamination of soil and water by heavy metals like lead (Pb), cadmium (Cd), chromium (Cr), and copper (Cu) is becoming an increasingly serious global issue. These metals are not only toxic but also tend to persist in the environment and accumulate in living organisms over time (Uddin, 2017). Among the many methods used to clean up such pollution, adsorption especially using affordable, natural materials has gained attention as a practical and eco-friendly solution. Clays, thanks to their large surface area, layered structure, and high cation exchange capacity (CEC), show great promise in this regard (Gu *et al.*, 2018; Wang *et al.*, 2024). However, to use clays effectively for environmental cleanup, it's essential to understand their mineral makeup and physical-chemical properties, as these directly influence how well they can absorb contaminants. Professor E. E. I. Irabor has played a key role in studying clay deposits across Nigeria. In a comprehensive analysis of Geheku clay from Kogi State, Irabor and Okunkpolor (2020) identified minerals such as montmorillonite, kaolinite, illite, and halloysite, along with quartz and other minor components. Montmorillonite, in particular, stands out for its high CEC and surface charge traits that make it especially effective at capturing metal ions through ion exchange and surface bonding. Geheku clay also showed moderate plasticity and swelling ability, both of which are indicators of good adsorption potential.

In a similar report, Irabor and Okeke (2018) examined Dangara clay from Kwali, Abuja, using mineralogical, chemical, and engineering tests. Their findings revealed a mineral profile dominated by kaolinite and montmorillonite. The clay's Atterberg limits and particle size distribution pointed to its suitability for both industrial use and pollutant adsorption. Later, Irabor *et al.* (2022) explored the chemical characteristics of Geheku clay for soil blending applications, analyzing factors like pH, exchangeable bases, and elemental composition all of which affect adsorption behaviour through surface charge and the point of zero charge (pHpzc). Collectively, these studies lay a solid foundation for future research into clay-based adsorption.

Looking beyond Nigeria, global studies show that clays rich in smectitic minerals like montmorillonite are particularly good at binding heavy metals such as Pb^{2+}, Cd^{2+}, and Cu^{2+} (Uddin, 2017; Gu *et al.*, 2018). Researchers typically evaluate adsorption performance through batch experiments that vary conditions like pH, metal concentration, clay dosage, and contact time. Results are often analyzed using Langmuir and Freundlich isotherm models, which help estimate how much metal the clay can hold and how uniform the adsorption surface is.

Kinetic models especially the pseudo-second-order type are used to understand how quickly and effectively adsorption occurs, often pointing to chemisorption as the dominant mechanism. Thermodynamic studies also shed light on whether the process is spontaneous and whether it absorbs or releases heat (Wang *et al*., 2024). Although Irabor's work has not yet included direct batch adsorption tests for heavy metals, the mineral and chemical profiles of Geheku and Dangara clays suggest they are strong contenders for low-cost remediation. Future research should focus on conducting controlled adsorption experiments using Pb^{2+} and Cd^{2+} solutions, applying isotherm and kinetic models, and analyzing the clays before and after adsorption using techniques like XRD, FTIR, and SEM-EDS. This would build on Irabor's foundational work and help unlock the full potential of locally sourced clays for cleaning up heavy-metal pollution.

1.2.1 LEAD

Lead is a chemical element symbolized by Pb (from the Latin word "plumbum"), with the atomic number 82 and atomic mass of 207.2(Encyclopedia Britannica, 2025). It is a heavy metal, denser than most common substances, and is known for being soft, malleable, and having a relatively low melting point. When newly cut, lead appears silvery-blue, but it quickly becomes a dull gray when exposed to air. Lead holds the highest atomic number among stable elements, and it concludes three primary decay chains of heavier elements. It is a relatively unreactive post-transition metal, showing weak metallic properties and amphoteric behavior it reacts with both acids and bases and often forms covalent bonds. Lead compounds most commonly exhibit a +2 oxidation state, rather than the +4 state seen in lighter elements of its group, except for some organolead compounds. Like its lighter counterparts, lead can bond to itself, creating chains, rings, and polyhedral forms. Extraction of lead from its ores is straightforward, and ancient Western Asia was aware of the element. Galena, a common lead ore, frequently contains silver, fueling early interest, especially in ancient Rome, in mining and utilizing lead. Following the fall of Rome, lead production decreased and did not rise again significantly until the Industrial Revolution. Lead's high density, low melting temperature, flexibility, and resistance to oxidation contributed to its widespread use in items such as construction materials, plumbing, batteries, ammunition, weights, solders, pewter, special alloys, paints, leaded gasoline, and radiation shields (Boldyrev, 2018).

1.2.1.0 GENERAL PROPERTIES OF LEAD

Property	Value
Name	Lead
Symbol	Pb
Atomic Number	82
Element Category	Post-transition metal
Group (Periodic Table)	14 (Carbon group)
Period	6
Block	p-block
Electron Configuration	$4f^{14}\,5d^{10}\,6s^{2}\,6p^{2}$
Electrons Per Shell	2, 8, 18, 32, 18, 4

1.2.1.1 PHYSICAL PROPERTIES OF LEAD

At standard temperature and pressure (STP), lead exists as a solid. It has a melting point of 600.61 K, which corresponds to 327.46 °C or 621.43 °F, and a boiling point of 2022 K, equivalent to 1749 °C or 3180 °F. The density of lead at 20 °C is 11.348 g/cm^3, while in its liquid state at the melting point, its density is slightly lower at 10.66 g/cm^3. In terms of thermal properties, lead has a heat of fusion of 4.77 kJ/mol, a heat of vaporization of 179.5 kJ/mol, and a molar heat capacity of 26.650 J/(mol·K) (Encyclopedia Britannica,2025).

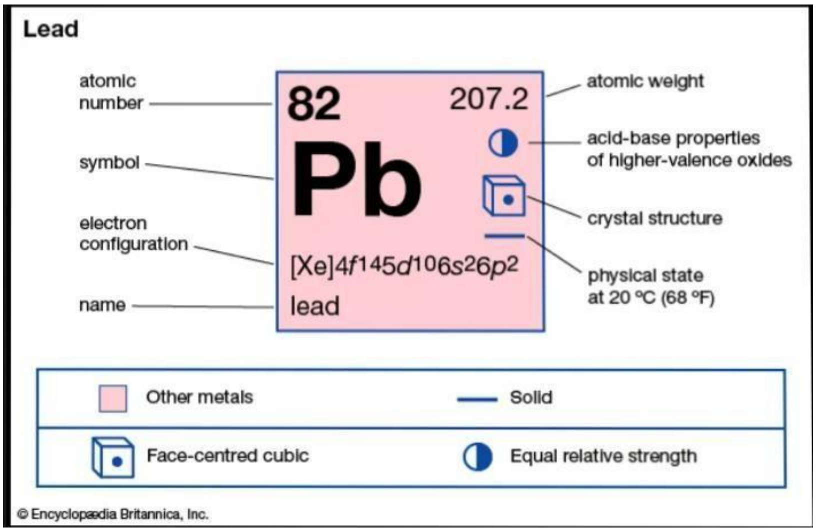

Fig 1: *Lead (Pb) properties;atomic number,mass and chemical information. Adapted from lead (chemical element). Encyclopaedia britannica (2025).*

1.2.1.2 CHEMICAL PROPERTIES OF LEAD

Lead exhibits two predominant oxidation states, namely +4 and +2. It exhibits a gradual decomposition in water and most cold acidic solutions. While lead metal demonstrates resistance to phosphoric and sulfuric acids, it is susceptible to nitric acid (HNO3) and hydrochloric acid. Lead shows limited reactivity with atmospheric oxygen and does not ignite readily. The reaction with chlorine necessitates elevated temperatures. When exposed to humid air, lead tends to tarnish relatively rapidly. Combustion of lead in its powdered form in the presence of air produces a bluish-white flame. Additionally, lead reacts promptly with fluorine at ambient temperature (Bashyal, 2025).

1.2.1.3 ISOTOPES OF LEAD

Natural lead comprises four stable isotopes characterized by mass numbers 204, 206, 207, and 208, along with traces of five short-lived radioisotopes. The primary isotopes of lead, alongside their percent abundance, half-life, decay mode, and products, are detailed in Table below. The significant variety of isotopes aligns with the even atomic number of lead. Lead possesses a magic number of protons (82), which enables the nuclear shell model to accurately predict a particularly stable nucleus. Lead-208 features 126 neutrons, another magic number, which may contribute to its remarkable stability (Bolydrev, 2018).

As the element with the highest atomic number that has natural isotopes considered stable, lead is noted for having lead-208 as the heaviest stable nucleus. This distinction was previously attributed to bismuth, which has an atomic number of 83, until the slow decay of its sole primordial isotope, bismuth-209, was established in 2003.Although lead's stable isotopes could theoretically decay, their predicted half-lives are so immense that they are considered stable. Finally, the isotopes lead-206, lead-207, and lead-208 are the final, stable products of major radioactive decay chains from uranium and thorium (Bolydrev, 2018).

Isotope	Abundance	Half-life ($t_1/_2$)	Decay Mode	Decay Product
^{202}Pb	syn	5.25(28)×10^4 y	ε	^{202}Tl
^{204}Pb	1.4%	stable	–	–
^{205}Pb	trace	1.53(7)×10^7 y	ε	^{205}Tl
^{206}Pb	24.1%	stable	–	–

^{207}Pb	22.1%	stable	–	–
^{208}Pb	52.4%	stable	–	–
^{209}Pb	trace	3.253(14) h	β^-	^{209}Bi
^{210}Pb	trace	22.3(22) y	β^-	^{210}Bi
^{211}Pb	trace	36.1(2) min	β^-	^{211}Bi
^{212}Pb	trace	10.64(1) h	β^-	^{212}Bi
^{214}Pb	trace	26.8(9) min	β^-	^{214}Bi

1.2.1.4 HISTORY OF LEAD

Preliminary evidence suggests that the ancient Egyptians were among the first to extract lead, utilizing it primarily for the creation of small sculptures. Additionally, lead compounds have been identified in the glazes of Egyptian pottery. By 2000 BC, lead was also employed in China for the production of coins (Bell, 2025). The ancient Greeks were pioneers in acknowledging the corrosion-resistant properties of lead, using it as a protective covering for ship hulls. This practice has persisted, with lead compounds still in use for similar applications today. Following this, the Romans ramped up lead extraction to support their extensive water systems. It is estimated that by the first century AD, Roman lead production reached around 80,000 tons annually. They utilized sheets of lead to line baths and crafted lead piping by wrapping these sheets around a rod and soldering the seams. Although lead piping was employed until the 20th century and offered protection against corrosion, it also led to significant incidences of lead poisoning (Bell, 2025). Lead's fire-resistant properties made it a valuable roofing material in parts of Europe during the Middle Ages; in fact, the lead roofs on London's Westminster Abbey and St. Paul's Cathedral are centuries old. The metal was also combined with tin to form an alloy called pewter, which was used to make tableware such as cutlery, plates, and mugs. Subsequently, the development of firearms created a new use for lead. Its high density was recognized as ideal for ammunition, and a method for producing lead shot was developed in the mid-17th century where droplets of molten lead were solidified into spheres by being dropped into water (Bell, 2025).

1.2.1.5 CHARACTERISTICS OF LEAD

The characteristics that contribute to the diverse applications of elemental lead encompass its ductility, favorable welding properties, low melting point, high density, and capability to absorb gamma and X-ray radiation. When in a molten state, lead serves as an exceptional solvent and collector for elemental silver and gold. Freshly exposed lead exhibits a silvery appearance with a hint of blue (Encyclopedia Britannica, 2025). Lead (Pb) possesses malleability, allowing it to be readily hammered into sheets without fracturing. Additionally, it is a ductile metal that can be drawn into fine wires without breaking. The manipulation of this metal, often referred to as "working," involves processes such as bending, cutting, shaping, and general alteration of its form. In terms of reactivity, lead tarnishes gradually in moist air, resulting in the formation of a dull gray surface. Furthermore, it demonstrates remarkable resistance to corrosion and is classified as a poor conductor of electricity, sound, and vibration (Bashyal, 2025).

1.2.1.6. OCCURRENCE OF LEAD

Lead is found in the Earth's crust at a concentration of approximately 0.0018%, but it is quite rare in its elemental form. As of 2017, there are around 200 known locations worldwide where solid lead can be found. These sites include countries such as Argentina, Ethiopia, Australia, Belgium, Brazil, China, Germany, Finland, France, Georgia, Greece, Greenland, Italy, Canada, Kazakhstan, Kyrgyzstan, Mexico, Mongolia, Namibia, Norway, Austria, Poland, Russia, Sweden, Slovenia, the Czech Republic, the US Virgin Islands, the United Kingdom, and the United States (Geoscience Australia, 2025).

Elemental lead occurs naturally in limited quantities, it is seldom found in its natural, unbound form. It is associated with various ores, including galena (lead sulfide, PbS), anglesite (lead sulfate, $PbSO4$), minim (a lead oxide, $Pb3O4$), cerussite (lead carbonate, $PbCO3$), and several other minerals. Among these, galena scientifically known as PbS is recognized as the primary source of lead (Geologyscience, 2023). By the early 2000s, the leading producers of lead concentrate included countries such as China, Australia, the United States, Peru, Mexico, and India (Encyclopedia Britannica,2025). To extract lead, the ore is typically roasted and then subjected to smelting in a blast furnace, although it can also be smelted directly without the roasting step. Afterward, refining processes are applied to eliminate any impurities from the lead bullion. Produced by either method. Notably, nearly half of all refined lead comes from recycled Scrap materials (Encyclopedia Britannica, 2025).

Fig 2: *Galena (lead sulfide) sample. From lead; Definition, uses, properties and facts, Encyclopaedia Britannica.(2025,september 24).*

1.2.1.7. EXPOSURE ROUTES/SOURCES OF LEAD

Lead enters water systems mainly through anthropogenic activities such as battery recycling, mining, smelting, metal plating, paints, ceramics, and effluents from industries (Jaishankar *et al*., 2014). Natural sources such as rock weathering also contribute, though at a smaller scale (Jarup, 2003). Individuals encounter lead from both workplace and environmental sources. The main routes of exposure include:

1. INHALATION: Breathing in lead particles that are released during the burning of materials such as lead-containing substances when processes like smelting, recycling, and the removal of lead-based paint and plastic wires take place (WHO, 2024).

2. INGESTION: it involves consuming dust, soil, water, or food that has been contaminated with lead (WHO, 2024).In the general population, including children, ingestion is the primary way people are exposed to lead, often leading to increased blood lead levels (BLLs). This can also happen when someone accidentally swallows objects containing lead, like jewelry. Research indicates that between 20% and 70% of the lead ingested can be absorbed into the body, with children typically absorbing a higher percentage than adults. In the United States, lead-based paint is a significant source of lead exposure for children. As paint with high lead content deteriorates peeling, chipping, being removed during renovations, or crumbling from wear in areas like window sills, steps, and doors it can create lead-laden dust and contaminate nearby soil (WHO, 2021).

3. DERMAL ABSORPTION: Dermal exposure to lead can happen in workplaces or from using cosmetic products that contain lead, although this is generally seen as a minor exposure route (WHO, 2021). For workers, skin exposure can contribute to organic lead absorption, but it's not viewed as a major concern for the general public. Organic lead, such as tetraethyl lead, is more readily absorbed through the skin compared to inorganic lead. Individuals who work with lead or products that include lead are the most likely to experience dermal exposure(ATSDR,2019).It's important to note that lead dust on skin, clothing, shoes, or hair can be subtle and difficult to detect (CDC,2024).

4. ENDOGENOUS OR RETAINED FRAGMENT EXPOSURE: Retained lead fragments, such as those from gunshots or bullets, can lead to lead absorption in the body. This risk increases when these fragments come into prolonged contact with bodily fluids like synovial, pleural, or cerebrospinal fluid. Additionally, if the bullet is located near a bone or joint, or if there is a related bone fracture especially in the tarsal region the likelihood of absorption rises. The absorption process is further amplified when the bullet is broken into smaller pieces or if there are multiple pellets, as both scenarios enhance the surface area available for lead absorption *(*Apte *et al*., 2019; WHO, 2021*).* In one specific case, bullet fragments were discovered in the left lower leg of a patient who had suffered a gunshot wound a decade earlier. Analysis of the excised bullet fragment revealed that the lead composition matched the elevated blood lead levels of the patient, as determined through isotope ratio analysis. This case represents an uncommon instance of significantly high blood lead levels that were linked directly to bullet fragments lodged in soft tissue (Weiss *et al.,* 2017).

1.2.1.8 HEALTH EFFECTS OF LEAD

Even at very low levels, lead exposure can negatively affect multiple systems in the human body. Among these, the nervous system is the most sensitive, especially in children (WHO, 2024).

- **IN CHILDREN**:

Severe Lead Poisoning:

- Ataxia (loss of control of bodily movements)

- Coma

- Death

- Hyperirritability
- Seizures
- Stupor (CDC, 2024; ATSDR, 2020)

Mild Lead Poisoning:

- Cognitive difficulties (such as learning issues, memory problems, and reduced attention span)
- Intellectual disability and developmental delays
- Attention Deficit Hyperactivity Disorder (ADHD)
- Hearing loss
- Balance issues
- Impaired functioning of peripheral nerves (WHO, 2021)
- Behavioral challenges
- Decreased coordination and balance (Lanphear *et al*., 2005)

- **IN ADULTS:**

Severe Lead Poisoning:

- Lead encephalopathy (brain dysfunction caused by lead) (ATSDR,2020)

Mild Lead Poisoning:

- Reduced libido
- Depression and mood alterations
- Headaches
- Lower cognitive performance and reduced IQ
- Decreased manual dexterity
- Slower reaction times
- Impaired visual-motor skills
- Dizziness

- Fatigue and lethargy

- Forgetfulness

- Difficulty concentrating

- Impotence

- Heightened nervousness

- Irritability

- General malaise

- Paresthesia (tingling sensation)

- Weakness (EPA, 204; WHO, 2021).

- **SYSTEMS AFFECTED BY LEAD EXPOSURE:**

1. **Nervous System**: The brain and nerves are most vulnerable. Lead can interfere with brain development in children and cause lasting neurological damage in adults (WHO, 2021).
2. **Cardiovascular System**: Exposure can raise blood pressure and contribute to heart conditions such as coronary artery disease, hardening of the arteries (atherosclerosis), irregular heart rhythms (arrhythmias), stroke, and heart attack (NTP, 2012).
3. **Renal System (Kidneys)**: Lead can impair kidney function and increase the risk of chronic kidney disease and failure (ATSDR, 2020; Ekong *et al*., 2006).
4. **Endocrine System**: It disrupts hormonal function, particularly by blocking the conversion of vitamin D to its active form (CDC, 2024).
5. **Reproductive System**: Lead may harm fertility by affecting sperm quality and sexual development. In women, it can cause miscarriages, premature births, and stillbirths (CDC, 2022; WHO, 2021).

1.2.1.9 PREVENTION MEASURES OF LEAD POISONING

- Hand and Toy Hygiene: To mitigate the transfer of potentially contaminated dust or soil to the mouth, it is advisable to wash children's hands following outdoor activities, prior to meals, and before bedtime. Regular washing of their toys is also recommended (Mayo Clinic, 2025). Additionally, it is important to clean your home at least once a week using a clean, damp cloth, sponge, or mop to reduce the accumulation of dust, which may contain lead (EPA, 2025).

- Primary prevention entails the elimination of lead hazards from the environment prior to any exposure occurring in children. This approach is recognized as the most effective strategy to prevent the deleterious long-term effects associated with lead exposure (CDC, 2024).
- It is essential to thoroughly wash all food with safe water sources before consumption to eliminate any dirt or lead dust present on the surface (CDC, 2024).
- Engage in renovations with caution. Home improvement tasks, such as sanding or removing paint in residences constructed prior to 1978, may result in the release of lead dust. When undertaking such renovations, it is imperative to utilize only approved techniques for the removal of lead hazards from your dwelling (EPA, 2025).

- Exercise caution in the kitchen. Certain imported or vintage ceramic and pottery dishes may feature a glaze containing lead. This glaze has the potential to contaminate food during storage or preparation in these vessels (EPA, 2025).

- Assess your drinking water quality. Inquire with your water provider to determine whether your home is linked to a lead service line. If lead is present in your tap water, it is crucial to implement measures aimed at reducing or eliminating exposure *(*EPA, 2025).

1.2.1.10 APPLICATIONS OF LEAD

- Lead finds various applications, with its most significant use being in the production of storage batteries.
- It is utilized in ammunition, specifically in shot and bullets, as well as serving as a component in solder, type metal, bearing alloys, fusible alloys, and pewter.
- In heavy and industrial machinery, lead compounds are often incorporated into sheets and other components to mitigate noise and vibration.
- Due to its effective capacity to absorb electromagnetic radiation of short wavelengths, lead is employed as protective shielding in nuclear reactors, particle accelerators, X-ray equipment, and in containers for transporting and storing radioactive materials.
- Additionally, lead is used in conjunction with lead oxide (PbO2) and lead-antimony or lead-calcium alloys in common storage battery applications (Encyclopedia Britannica, 2025).

1.2.2 CLAY MINERALS AND THEIR CHARACTERISTIC PROPERTIES

Georgius Agricola (1494–1555), recognized as the progenitor of geology, appeared to be the first individual to define clay in the year 1546. This definition has undergone numerous modifications over time, leading to important inquiries regarding the constituents of clay. The most recent endeavor to address these complexities was undertaken by the Joint Nomenclature Committees (JNCs) of the Association Internationale pour l'Étude des Argiles (AIPEA) and the Clay Minerals Society (CMS). These organizations affirm that clay is a naturally occurring substance primarily comprised of fine-grained minerals, which exhibits plasticity upon the addition of water and hardens upon drying or firing. Consequently, this definition allows for the differentiation of engineered clays and clay-like materials as those substances that contain fine-grained minerals and demonstrate plastic properties when wet, solidifying when dried or fired (Kumari *et al.*, 2021).

Clay minerals are distinctive geological materials located near the planetary surface specifically, the interface where the outer crust interacts with the atmosphere. It is composed of hydrous aluminum phyllosilicates, such as koalin (Al2Si2O5(OH)4). These minerals exhibit variable concentrations of ions, including but not limited to iron, magnesium, alkali metals, alkaline earth metals, and other cations (Kumari *et al.*, 2021). The formation of these minerals requires the presence of water and they have played a significant role in the development of life, with numerous abiogenesis theories referencing their importance. Historically, clay minerals have constituted essential soil components and have been utilized by humans for agricultural and manufacturing purposes since ancient times (Wikipedia, 2025).

1.2.2.1 CLASSIFICATION/ STRUCTURE OF CLAY MINERALS

The aluminosilicate layers are comprised of essential structural units inherent to phyllosilicates, which arise from the amalgamation of tetrahedral and octahedral sheets, interconnected through the sharing of oxygen atoms. Both tetrahedral and octahedral sheets constitute critical components of phyllosilicates and are designated as such due to their distinctive leaf-like or plate-like morphologies. According to Kumari *et al.* (2021), these sheets are interconnected via the sharing of oxygen atoms, leading to the formation of diverse layers. Phyllosilicates, which represent the predominant category of clay minerals, are defined by a silicon-centric tetrahedral unit and an aluminum or magnesium-centric octahedral unit, arranged in a sheet-like architecture. The classification of phyllosilicates is predicated upon the number and configuration of tetrahedral and octahedral sheets, encompassing categories such as layer silicates, chain silicates, sesquioxides, and other inorganic minerals. Furthermore, clay may be classified based on the spatial arrangement of the tetrahedral and octahedral sheets (Kumari *et al.*, 2021).

Phyllosilicates are systematically categorized according to their structural characteristics, specifically:

- The type of sheets (either trioctahedral or dioctahedral) and
- The arrangement of layers (1:1 or 2:1). The 1:1 configuration, also designated as TO, comprises a solitary tetrahedral sheet coupled with a single octahedral sheet. Conversely, the 2:1 arrangement, referred to as TOT, consists of two tetrahedral sheets encasing one octahedral sheet. The crystalline chemical properties of phyllosilicates have been the focus of extensive scrutiny over recent decades, frequently employing X-ray or neutron diffraction methodologies. Micas and clay minerals, denoted as hydrous phyllosilicates, exhibit two-dimensional tetrahedral polymerization articulated as T2O5 (where T may signify Si, Al, Fe3+, etc.) (Elmi, 2023).

1.2.2.1.1 CLASSIFICATION BASED ON LAYER STRUCTURE

- **Kaolinite**: The minerals classified as 1:1 layer types are exemplified by the kaolinite group, which demonstrates significant thermal stability and minimal flexibility. It serves as a valuable material employed in the production of paper coatings, ceramics, and refractory materials (Ombaka, 2016).
- **Montmorillonite**: Recognized as a 2:1 layer mineral, it contains one octahedral sheet interposed between two tetrahedral sheets (Nadziakiewieza *et al.*, 2019). According to Uddin, (2021), montmorillonite exhibits an elevated capacity for cation exchange (CEC) and swelling, rendering it advantageous for applications in drilling muds, environmental remediation, and geotechnical engineering. Each of these minerals possesses unique properties that can influence their potential applications. In smectites, exchangeable cations are located between water molecules within the interlayer space. Upon saturation with water, the interlayer distance, known as basal spacing, may augment; conversely, in arid conditions, this spacing may contract. This attribute of smectites is frequently referred to as shrink-swell potential. In contrast, vermiculites display a robust bonding of the interlayer cations, which effectively stabilizes the 2:1 layers, thereby constraining any considerable expansion of the basal spacing.

The surface chemistry of clays renders them optimal adsorbents. Permanent negative charges arise from isomorphic substitution (e.g., Al^{3+} substituted by Mg^{2+}), while variable charges originate from the deprotonation of hydroxyl groups (Bhattacharyya and Gupta, 2012).

The contamination of water by heavy metals represents one of the most critical environmental challenges currently faced. Among heavy metals, lead (Pb^{2+}) raises significant concerns due to its pervasive application in various industrial sectors and its pronounced toxicity, even at minimal concentrations. Traditional treatment methodologies, including chemical precipitation, ion exchange, and reverse osmosis, frequently demonstrate prohibitive costs and inefficiencies when applied to trace levels (Fu and Wang, 2011). Adsorption has surfaced as one of the most efficacious and cost-effective strategies for the remediation of heavy metals, with natural clays receiving considerable attention owing to their widespread availability, economic feasibility, and advantageous surface chemistry (Bhattacharyya and Gupta, 2012). The current investigation centers on Dangara middle-layer clay, a Nigerian clay deposit that exhibits notable adsorptive capabilities. While there has been extensive research conducted on Nigerian clays, there remains a paucity of studies specifically addressing Dangara clays, thereby necessitating a thorough review of existing literature and the identification of pertinent research gaps.

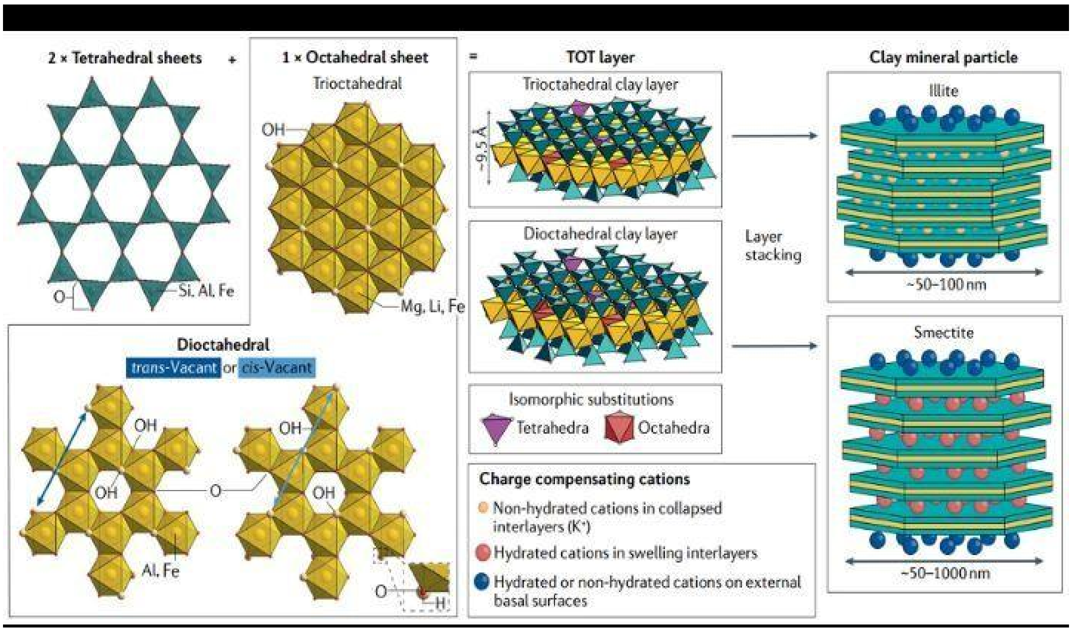

Fig 3:*Trioctahedral and dioctahedral clay sheet structures. Reprinted from clay-based materials for heavy metal adsorption: Mechanisms, advancements and future prospects in environmental remediation by wang et al (2024)*

1.2.2.2 ADVANTAGE OF CLAY OVER OTHER ADSORBENT

- **Abundance & Low Cost**

  Clay represents one of the most economically advantageous adsorbent materials accessible in contemporary research. For instance, a comparative cost evaluation revealed that the price of clay ranges from \$0.04 to \$0.12 per kilogram, in stark contrast to activated carbon, which is priced between \$20 and \$22 per kilogram, thereby rendering clay significantly more feasible for extensive applications (Bailey *et al.*, 1999).

- **High Surface Area & Porosity (Post-Modification)**

  While unprocessed clay exhibits a moderate surface area, the processes of acid activation and surfactant modification substantially augment its porosity and adsorption efficacy.

- **High Cation Exchange Capacity (CEC) & Effective Heavy Metal Uptake:**

  Clay minerals possess substantial cation exchange capacities, which facilitate their ability to effectively capture and immobilize heavy metals. For instance, hybrid clay composites demonstrated a CEC of approximately 75 meq/100 g and successfully removed heavy metals such as Cd^{2+}, Ni^{2+}, and Pb^{2+} to concentrations compliant with World Health Organization guidelines (Unuabonah *et al.*, 2013).

- **Tailorable Surface Properties via Modification**

  The surface characteristics of clays can be readily altered through the application of acids, bases, or surfactants to enhance selectivity and optimize the adsorption of organic pollutants and heavy metals.

- **Strong Adsorption Capacity (especially for heavy metals)**

  Literature reviews corroborate that clay minerals and clay-derived composites exhibit a pronounced efficacy in the removal of metals and dyes, while also presenting significant potential for regeneration (Edebali, 2019).

- **Low Environmental Impact and Sustainable Regeneration**

  Clay is characterized by its non-toxic nature, abundance, and stability across a broad spectrum of pH levels and temperatures. This inherent stability facilitates regeneration and reuse through uncomplicated chemical or thermal treatments, in contrast to biosorbents, which are more susceptible to degradation (Edebali, 2019).

- **Versatility for Diverse Contaminants**

  Clays demonstrate the capacity to effectively remove a wide array of contaminants, including heavy metals, radionuclides, dyes, pesticides, and pharmaceuticals, thereby offering a broader range of applicability compared to numerous alternative adsorbents (Bailey *et al.*, 1999).

1.2.3 ATOMIC ABSORPTION SPECTROSCOPY (AAS)

Atomic Absorption Spectrometry (AAS) is an analytical technique that measures the absorption of optical radiation by free atoms in the gaseous state (Lagalante, 2004). In practice, a sample is atomized into a vapor, and a beam of light from a source lamp passes through it. The extent to which atoms absorb light at their element-specific wavelengths indicates their concentration in the sample (Resano *et al.*, 2013*).* This principle, rooted in the Beer–Lambert law, has made AAS one of the most widely applied methods for trace metal analysis across environmental, clinical, and industrial fields (Borges, 2022)

1.2.3.1 FUNCTIONAL PARTS OF AN AAS INSTRUMENT

- **Radiation Source (Lamp)**

  Traditional AAS relies on hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs), each designed for a specific element (Lagalante, 2004). The emission line produced by the lamp matches the absorption line of the analyte, ensuring high selectivity (Zehr and VanKuren, 1994). More recently, high-resolution continuum source (HR-CS) AAS uses a xenon short-arc lamp as a universal source, enabling simultaneous multi-element detection and more robust interference correction (Resano *et al.*, 2014).

- **Atomizer**

  The atomizer converts analytes into free atoms. Flame atomizers (FAAS) use a nebulizer and spray chamber to mix the sample aerosol with fuel and oxidant before introduction into a flame. Commonly, air–acetylene or N_2O acetylene flames are employed, making FAAS rapid and robust for routine analysis (Zehr and VanKuren, 1994). Graphite furnace atomizers (GFAAS/ETAAS) heat a small sample in a graphite tube through sequential stages (drying, pyrolysis, atomization), offering superior detection limits down to the sub-ppb level (Resano *et al.*, 2014; Borges, 2022).

  Specialized atomizers include hydride generation AAS (HG-AAS) for As, Se, and Sb, and cold vapor AAS (CV-AAS) for Hg, enabling ultra-trace detection in environmental samples (Chirita *et al.*, 2023).

- **Monochromator / Spectrometer**

  In line-source AAS, a monochromator isolates the analytical line and reduces background interference (Slavin *et al.,* 2008). By contrast, HR-CS AAS employs an echelle spectrometer and CCD detector to capture the entire spectral environment around the absorption line, enabling improved correction of overlapping signals (Resano *et al*., 2013).

- **Detector**

  Most LS-AAS instruments use a photomultiplier tube (PMT) to measure transmitted light (Slavin *et al.,* 2008). In HR-CS AAS, CCD or CMOS array detectors provide pixel-resolved absorption spectra, enhancing precision in spectral correction (Resano *et al*., 2013).

- **Background Correction**

  Accurate analysis requires compensating for non-specific absorption from the matrix. Classic approaches include deuterium lamp correction and Zeeman Effect correction (Slavin *et al*., 2008). Zeeman correction, in particular, remains vital for graphite furnace analysis where background interferences are strongest (Resano *et al*., 2014).

- **Electronics & Data Processing**

  Modern AAS systems include programmable lamp power supplies, temperature controllers (for furnaces), and software algorithms for calibration, baseline correction, and quality assurance (Borges, 2022). In HR-CS AAS, sophisticated fitting routines analyze spectral structures pixel by pixel, enabling detection of multiple elements from a single spectrum (Resano *et al*., 2013).

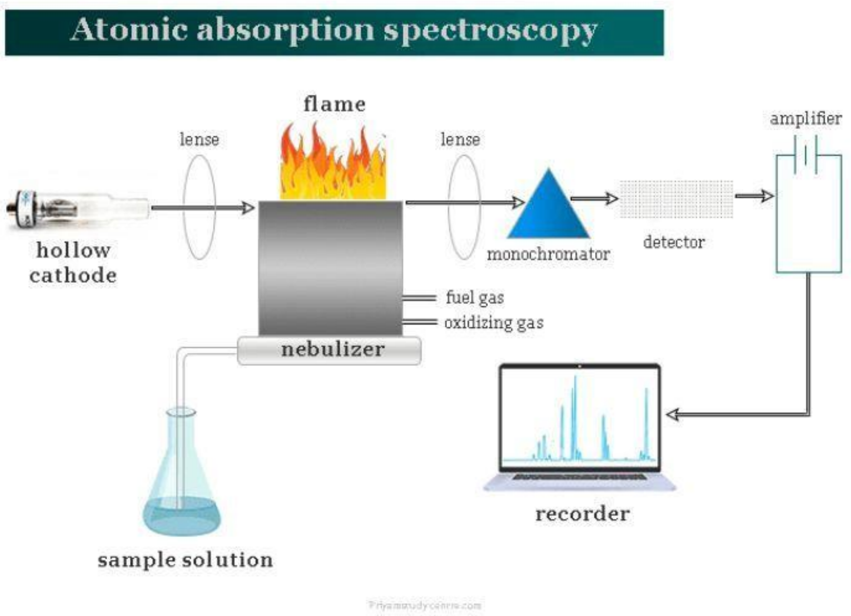

Fig 4: *Priyam study centre. (November, 2021).Atomic absorption spectroscopy instrumentation.*

1.2.4 ADSORPTION

1.2.4.1 DEFINITION OF ADSORPTION

Adsorption is the accumulation of molecules (the adsorbate) at the surface of a solid or liquid (the adsorbent) in preference to the bulk phase, distinguished from absorption, which is the uptake into the bulk material (IUPAC Technical Report,) (Thommes *et al.*, 2015). Adsorption behavior at equilibrium i.e., the relationship between amount adsorbed and pressure (for gases) or concentration (for solutes) at a constant temperature is described by the adsorption isotherm, which encodes critical information about surface energetics, porosity, and sorption mechanisms (Langmuir,1918;Brunauer *et al.*, 1938; IUPAC Technical Report, 2015).Adsorption in Water Treatment offers advantages over other methods such as low operational cost, ease of design, effectiveness at low concentrations, and potential for regeneration of adsorbents (Crini and Lichtfouse, 2019).Clays, due to their high cation exchange capacity (CEC), negative surface charges, and layered structure, are highly efficient for adsorption of heavy metals, including lead (Uddin, 2017).

1.2.4.2 TYPES OF ADSORPTION

❖ **Based on Interaction Mechanism**

1. **Physisorption:** dominated by weak van der Waals interactions, is typically reversible, low in enthalpy, and capable of multilayer formation; it forms the basis for surface area and porosity measurements via gas adsorption (IUPAC Technical Report, Thommes *et al.*, 2015).
2. **Chemisorption**: involving specific chemical bonding, is typically stronger, often irreversible, limited to monolayer coverage, and central to catalysis and reactive surface studies (IUPAC Technical Report, Thommes *et al.*, 2015; Langmuir, 1918).

❖ **Based on Layer Structure**

1. Monolayer adsorption describes a single layer of adsorbate molecules on available uniform sites idealized by the Langmuir model (Langmuir, 1918).
2. Multilayer adsorption occurs when additional layers build up on the first adsorbate layer, as modeled by the BET theory (Brunauer *et al.*, 1938).

- **By Isotherm Shape (IUPAC Types I–VI)**

  According to IUPAC, Type I isotherms show monolayer adsorption typical of microporous materials; Type II and Type III denote nonporous or macroporous solids with multilayer formation; Types IV and V exhibit capillary condensation and hysteresis typical of mesoporous structures; Type VI shows stepwise multilayer adsorption on uniform surfaces (IUPAC Technical Report, Thommes *et al.*, 2015).

1.2.4.3 FACTORS AFFECTING ADSORPTION

- **pH**: pH significantly influences adsorption processes. As the pH of the solution increases, the concentration of hydrogen ions (H^+) decreases. These H^+ ions can compete with the target adsorbate for binding sites on the adsorbent material. When H^+ ion concentration is lower, there is less competition, allowing the target adsorbate to bind more effectively to the active sites. This explains why adsorption often increases at higher pH values (Adom *et al.*, 2020).
- **Adsorbent dosage**: The amount of adsorbent used is another critical factor. Increasing the adsorbent dose directly correlates with a greater number of available active sites. A higher surface area and a larger quantity of the adsorbent material provide more locations for the adsorbate molecules to attach. This relationship is well-documented in research, with studies like Crini and Lichtfouse (2019) highlighting this positive correlation. More adsorbent means more capacity for removal.
- **Concentration**: Solution concentration plays a vital role as well. The concentration of the adsorbate in the solution acts as the driving force for the adsorption process. A higher concentration creates a steeper concentration gradient between the bulk solution and the adsorbent surface. This greater gradient pushes more adsorbate molecules towards the adsorbent, promoting faster and more extensive uptake (Li *et al.*, 2022).
- **Agitation time**: Contact time is essential for allowing the adsorption reaction to reach completion. Adsorption is a kinetic process that takes time. Typically, equilibrium, where the rate of adsorption equals the rate of desorption, is achieved within a specific timeframe. For many systems, this equilibrium is observed to occur between 60 and 180 minutes, meaning the majority of the adsorbate has bound to the adsorbent by this point.
- **Ionic strength**: Ionic strength within the solution can negatively impact adsorption. When the solution contains a high concentration of other ions, these competing ions

can occupy the active sites on the adsorbent. This phenomenon reduces the availability of sites for the target adsorbate. Therefore, higher ionic strength generally leads to decreased adsorption efficiency (Aranda-Garcia *et al*., 2020).

- **Temperature**: can have a variable effect, depending on the nature of the adsorption process. If the adsorption is an endothermic process, meaning it absorbs heat from the surroundings, increasing the temperature will favor the reaction. Higher temperatures provide more kinetic energy, assisting the adsorbate molecules in overcoming any energy barriers to adsorption. Conversely, if adsorption is exothermic (releases heat), higher temperatures would inhibit it (Ali *et al.*, 2020).

1.2.4.4 ADSORPTION ISOTHERM MODELS

Adsorption isotherms represent mathematical frameworks that elucidate the correlation between the quantity of a substance adsorbed per unit mass of adsorbent (q_e) and its equilibrium concentration in a solution or pressure in the gas phase (C_e or p) at a constant temperature. These models are crucial for comprehending surface phenomena and for the design of adsorption systems applicable in water treatment, catalysis, gas separation, and environmental remediation (Foo and Hameed, 2010).

Investigating adsorption isotherms aids in discerning the adsorption mechanism whether it is governed by physical forces (physisorption), chemical bonding (chemisorption), or a combination of both and offers insights into surface characteristics such as heterogeneity, energy distribution, and maximum adsorption capacity (Moussavi and Khosravi, 2011).

Numerous classical models have been formulated to characterize adsorption equilibrium. The **Langmuir** isotherm posits a uniform surface with a limited number of identical sites and monolayer coverage (Langmuir, 1918). The **Freundlich** isotherm accounts for adsorption on heterogeneous surfaces with multilayer formation (Freundlich, 1906). The BET model (Brunauer *et al*., 1938) builds upon Langmuir's theory to encompass multilayer adsorption and is extensively utilized for surface area assessment. Additional models such as Temkin (Temkin and Pyzhev, 1940), Sips (Sips, 1948), Redlich–Peterson (Redlich and Peterson, 1959), Tóth (Tóth, 2001), and Dubinin–Radushkevich (Dubinin, 1960) offer versatility in depicting adsorption on heterogeneous surfaces, at elevated concentrations, or within microporous materials. Adsorption isotherms are vital instruments in surface chemistry and environmental science, enabling researchers to design, refine, and forecast adsorption processes for practical applications.

- **Langmuir Isotherm (Monolayer, Uniform Sites)**

Langmuir (1918) proposed that a fixed number of identical surface sites bind single adsorbate molecules without interactions, yielding saturation at high pressure or concentration. Although widely used, contemporary reviews advise nonlinear regression fitting and caution against over interpretation when surface heterogeneity or multilayer adsorption is significant (Foo and Hameed, 2010; Murphy *et al.*, 2023).

Formula:

$$Q_e = \frac{(q_{max}\, x\, K^l\, x\, C_e)}{(1 + K^l x\, C_e)}$$

Where:

Q_e = amount adsorbed at equilibrium (mg/g)

q_{max} = maximum adsorption capacity (mg/g)

K^L = Langmuir constant (L/mg)

C_e = equilibrium concentration (mg/L)

- **Freundlich Isotherm (Multilayer, Heterogeneity)**

Freundlich's multilayer model captures adsorption onto heterogeneous surfaces by a power-law relation, useful across limited concentration ranges, but it lacks a defined saturation limit and remains phenomenological rather than mechanistic (Foo and Hameed, 2010).

Formula:

$$Q_e = K\; X\; Ce^{\frac{1}{n}}$$

Where:

Q_e = amount of substance adsorbed per unit mass of adsorbent at equilibrium (mg/g)

C_e = equilibrium concentration of the substance (mg/L)

K= Freundlich constant related to adsorption capacity

1/n = Freundlich exponent related to adsorption intensity

1.2.5 ADSORPTION KINETICS

Adsorption kinetics describes the rate at which a solute (adsorbate) transfers from a fluid phase to the surface/pores of a solid (adsorbent), and how that rate depends on time, concentration, temperature, mass transfer, and the availability/reactivity of surface sites (external film diffusion, intraparticle diffusion, and surface reaction) (Wang and Guo, 2020).

Kinetic models are used to

(i) Extract quantitative rate constants,

(ii) Infer rate-limiting steps (film diffusion vs. pore diffusion vs. surface reaction),

(iii) Estimate characteristic times to reach equilibrium, and

(iv) Compare materials process conditions fairly (Wang and Guo, 2020). Good practice is to fit models with nonlinear regression (avoiding linearization bias) and to compare goodness-of-fit with multiple metrics (R^2/adj-R^2, RMSE, χ^2, AIC) rather than one statistic (Wang and Guo, 2020).

1.2.5.1 PSEUDO – FIRST -ORDER KINETICS

The earliest formal adsorption rate equation is due to Lagergren, who proposed a first-order rate law with respect to the number of unoccupied sites (originally for solute uptake onto solids) (Lagergren, 1898). In differential form:

1st equation:

$$\frac{dq}{dt} = K_{1\,(q_{e-}\,q_t})$$

Where:

q_t = Amount of substance adsorbed at time t

q_e = Amount of substance adsorbed at equilibrium

K_1 = Pseudo first order rate constant

Integrated Form:

$$I(q_e \;- q_t) = In(q_e) - K_1 t$$

Pseudo first order kinetics often fits early-time data when the rate is controlled by surface availability or by external mass transfer, but it can be underestimated if fit in linearized coordinates (leading to biased slopes and intercepts) (Wang and Guo, 2020). According to wang and Guo, (2020) it is historically important and still used as a benchmark model in comparative kinetics.

1.2.5.2 PSEUDO – SECOND – ORDER KINETICS

Ho and McKay systematically analyzed diverse sorption systems and showed that many datasets are well described by a second-order dependence on the fraction of unoccupied sites (Ho and McKay, 1999). The rate law is:

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

Where:

q_t = Amount of substance adsorbed at time t

q_e = Amount of substance adsorbed at equilibrium

K_2 =Pseudo second order rate constant

T= time

Integrated Form:

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

Pseudo second order frequently provides excellent fits for metal-ion and dye adsorption where the overall rate is dominated by surface reaction/chemisorption or where site heterogeneity gives an apparent second-order time dependence (Ho and McKay, 1999; Wang and Guo, 2020). But "good fit ≠ mechanism": PSO's popularity has sometimes led to over-interpretation fit quality alone cannot prove chemisorption without complementary diagnostics (e.g., activation energies, diffusion tests, spectroscopic evidence) (Wang and Guo, 2020). Linear vs. nonlinear fitting. Because both PFO and PSO have exact nonlinear solutions, parameter estimation is more reliable via nonlinear least squares. Linearization can distort error structure and bias (Wang and Guo, 2020).

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 CHEMICAL USED

- Lead nitrate (Pb(NO3)2)
- Clay Sample
- 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 metre
- Fume Cupboard
- Atomic Absorption spectroscopy
- Thermometer

2.2 METHODS

2.2.1 PREPARATION OF ADSORBENT (DANGARA MIDDLE LAYER CLAY)

The Dangara middle layer clay was sourced and meticulously washed. Subsequently, the sample was dried and then ground using a mortar and pestle, and then sieved to achieve a particle size. These preparatory measures align with established protocols in clay adsorption research, wherein natural clays are subjected to washing, drying, and grinding to enhance both homogeneity and surface activity (Mao *et al.*, 2022).

2.2.2 PREPARATION OF ADSORBATE (LEAD NITRATE SOLUTION)

Standard solutions of 1000mg/L of the needed absorbates were prepared by dissolving the calculated mass in grams of salt that contains 1g of the metal ion based on stoichiometric analysis. Analytical grade lead (II) nitrate [$Pb(NO_3)_2$] served as the source of lead ions. A stock solution of 1000 mg/L was prepared by dissolving 1.6g of $Pb(NO_3)_2$ in 1000ml distilled water, and working solutions ranging from 10 to 100 mg/L were produced via serial dilution. The solutions' pH was modified to fall between 2–8 utilizing 0.1 M HNO3 and 0.1 M NaOH, as the adsorption effectiveness is significantly affected by pH and ionic strength (Wang *et al.*, 2024). Comparable methods for adsorbate preparation have been utilized in both kinetic and thermodynamic analyses of Pb^{2+} adsorption onto natural clay (Abbou *et al.*, 2021).

Plate 1*: Preparation of stock solution in the chemistry laboratory*

2.2.3 BATCH ADSORPTION TESTING

Batch adsorption tests were performed in 250 mL Erlenmeyer flasks, each holding 100 mL of Pb^{2+} solution with a specified concentration. Specified quantities of clay adsorbent (0.1–1.0 g) were introduced, and the flasks were positioned on a mechanical shaker for contact durations between 5 and 120 minutes. The influences of adsorbent amount, initial Pb^{2+} concentration, contact duration and pH were examined systematically, in line with methods described in the clay adsorption research (Mao *et al*., 2022; Abbou *et al.,* 2021). Following equilibration, the suspensions underwent centrifugation and filtration. The Pb^{2+} concentration remaining was examined using Atomic Absorption Spectrophotometry (AAS). The capacity for adsorption (Q_e) and the efficiency of removal (%) were calculated using the equations below:

$$Q_e = (\frac{C_{o-}C_e}{M} X\ V)$$

Where:

Q_e =Amount of substance adsorbed per unit mass of adsorbent (mg/L)

C_o =Initial concentration of the substance (mg/L)

C_e = Equilibrium concentration of the substance (mg/L)

V = volume of the solution (L)

M = mass of the adsorbent (g)

2.2.3.1 EFFECT OF CONCENTRATION

Five conical flasks with 1.0 g of untreated dangara middle layer clay had 100 mL of $Pb(NO_3)_2$ solutions with different concentrations (10, 20, 30, 40, and 50 mg·L^{-1}) added to them. The suspensions were stirred on a mechanical shaker for 30 minutes at a steady speed at room temperature. Following shaking using a mechanical shaker, the mixtures were filtered, and the supernatants were gathered individually. The remaining Pb (II) levels in every filtrate were measured with Atomic Absorption Spectroscopy (AAS), and the adsorption capacities were assessed, the initial concentration of each sample was also taken to the AAS before the aliquot solution came in contact with the adsorbent. This procedure was repeated thrice under the same conditions to get an average multiple reading in order to obtain a more precise estimate of the true value. This method adhered to conventional adsorption research that assesses how initial solute concentration affects adsorption dynamics, as increased Pb(II) levels generate a stronger driving force for mass transfer until the adsorption sites on the clay surface reach saturation (Hussain and Ali, 2021; Uygun *et al.,* 2023; Bourliva *et al.,* 2015).

Plate 2*: A representative sample bottle used to store the aliquot solution prior to analysis using AAS.*

2.2.3.2 EFFECT OF ADSORBENT DOSAGE

A systematic batch adsorption investigation was executed utilizing five conical flasks, each containing 0.2 g, 0.4 g, 0.6 g, 0.8 g, and 1.0 g of dangara middle layer clay, respectively. Each container was administered an equivalent volume of 100 ml of a 30 ppm lead nitrate solution. The resulting suspensions were subjected to mechanical agitation for a duration of 30 minutes at a steady room temperature to ensure optimal interaction between the clay adsorbent and the lead ions. Subsequently, the mixtures were filtered, and the resultant filtrates were examined through Atomic Absorption Spectroscopy (AAS) to quantify the residual dissolved lead, thus facilitating the assessment of adsorption efficiency. This procedure was repeated thrice under the same conditions to get an average multiple reading in order to obtain a more precise estimate of the true value.

This methodological framework is grounded in established batch adsorption research; for instance, Khan *et al.* (2017) optimized parameters such as agitation time, clay dosage, and initial concentration within bentonite systems, achieving a maximum uptake of 26.3mg/g under similar conditions.

2.2.3.3 EFFECT OF AGITATION TIME

A fixed mass of 1.0 g of clay was added to 100 mL of 30 ppm $Pb(NO_3)_2$ solution in six conical flasks. The suspensions were positioned on a mechanical shaker and stirred at a constant speed for various time periods (5, 15, 30, 60, 90, and 120 minutes). Following each specified duration, the mixtures were promptly filtered, and the filtrates were examined via Atomic Absorption Spectroscopy (AAS) to ascertain the remaining Pb (II) concentration. This procedure was repeated thrice under the same conditions to get an average multiple reading in order to obtain a more precise estimate of the true value. The removal efficiency (%) and adsorption capacity (qt) were determined based on the concentration changes before and after treatment. The time intervals were chosen based on earlier research that indicated a quick initial absorption of Pb(II) during the first 15–30 minutes, with equilibrium reached at 60–120 minutes for clay-based adsorbents (Hussain and Ali, 2021; Uygun *et al.,* 2023; Bourliva *et al.,* 2015).

2.2.3.4 EFFECT OF pH

To determine how pH influences the amount of Pb(II) ion adsorbed to the clay, six conical flasks were filled with 100 mL of a 100 ppm $Pb(NO_3)_2$ solution at initial pH values of 4, 5, 6, 7, 8, and 9 (determined by using diluted HNO3 or NaOH as needed to adjust the pH). Each flask was charged with an equal mass of 1 g clay. The mixtures were shaken on a mechanical shaker for 45 minutes to ensure adequate contact between the clay and lead solution. The supernatants were analyzed after filtration, and Pb (II) concentrations remaining in solution were measured by AAS. This procedure was repeated thrice under the same conditions to get an average multiple reading in order to obtain a more precise estimate of the true value. As pH influences both the ionization state of adsorbates and the surface charge of clay minerals, it has a strong impact on the efficiency of Pb (II) adsorption (Hussain and Ali 2021; Olaremu 2021).

Plate 3: *Batch adsorption testing in the lab*

CHAPTER THREE

3.0 RESULTS AND DISCUSSION

The tables below were produced from results obtained from Atomic Adsorption Spectrophotometric analysis carried out on the various filtrates obtained from the experiment using Dangara Middle Layer Clay in heavy metals solutions.

All the equilibrium concentration are calculated from the triplicate values obtained from Atomic Adsorption Spectroscopy (AAS)

3.1 RESULTS

TABLE 3.1.0: EFFECT OF CONCENTRATION ON ADSORPTION– pb^{2+}

S/N	INITIAL CONC(mg/L)	EQUILIBRIUM CONC(mg/L)	AMOUNT ADSORBED± SD (mg/L)	PERCENTAGE ADSORPTION (%)
1	10	0.02	9.98±0.01	99.80
2	20	0.50	19.50±0.58	97.50
3	30	0.67	29.33±0.26	97.77
4	40	1.03	38.97±0.80	97.43
5	50	1.83	48.17±0.80	96.34

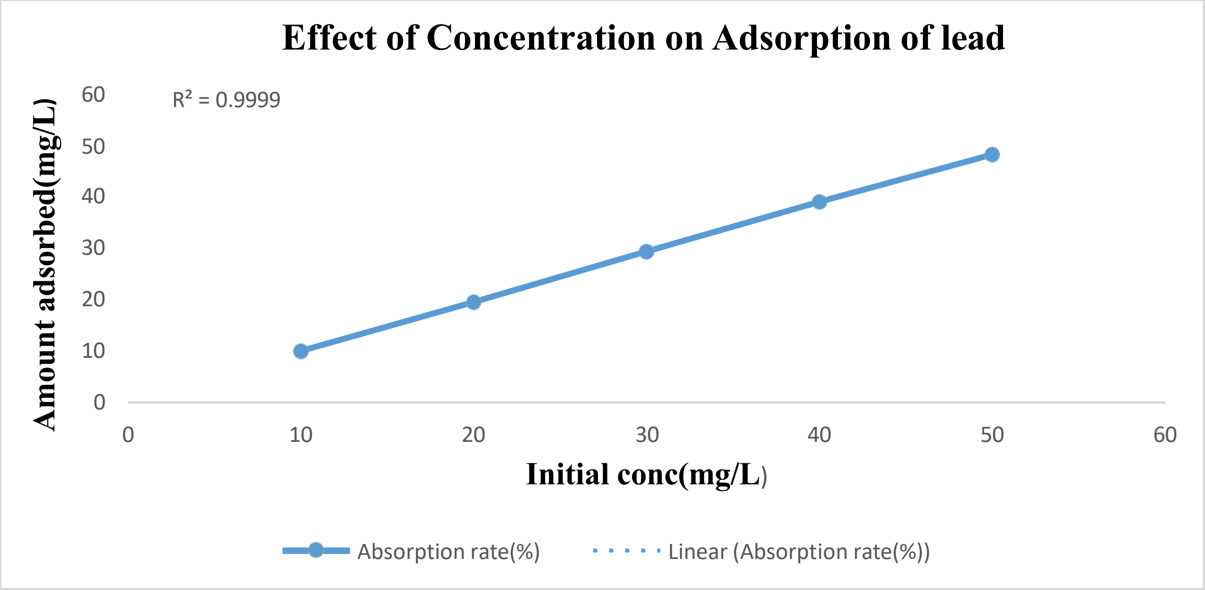

***Fig 5**: Effect of Concentration on Adsorption of pb*$^{2+}$

DISCUSSION: EFFECT OF CONCENTRATION

When initial concentration (C_o) was enhanced from 10 to 50 mg/L, the resultant equilibrium concentration (C_e) also enhanced from 0.02 to 1.83 mg/L. This enhanced the adsorption of the total volume of lead, and the percentage of lead removal decreased slightly, from 99.80% to 96.34%.

It can be accounted for based on the fact that as the initial lead ion concentration increases, there has been a growth in the force that pushes for the movement of mass among the aqueous phase and the adsorbent surface, thus adsorption uptake increases in absolute value (Kouadio *et al*., 2024). But since the amount of vacant adsorption sites available for the untreated clay does not change, percentage removal decreases when the concentrations are high, as the adsorption sites become saturated.

This characteristic is consistent with the classical adsorption theory that, for a constant adsorbent dose, the elimination efficiency will lower gradually as the increasing concentration has limited adsorption surface sites (Foo and Hameed, 2010). High elimination at low concentrations also shows high affinity of natural clay towards lead ions, which must be due to the high number of exchangeable cations as well as hydroxyl functional groups present on the clay surface

TABLE 3.1.1: EFFECT OF ADSORBENT DOSAGE ON ADSORPTION –Pb^{2+}

S/N	ADSORBENT DOSAGE(g)	INITIAL CONC(mg/L)	EQUILIBRIUM CONC(mg/L)	AMOUNT ADSORBED ±SD (mg/L)	PERCENTAGE ADSORPTION (%)
1	0.2	30	0.90	29.10±0.35	97.00
2	0.4	30	0.73	29.27±0.29	97.57
3	0.6	30	0.63	29.37±0.31	97.90
4	0.8	30	0.53	29.47±0.31	98.23
5	1.0	30	0.43	29.57±0.31	98.57

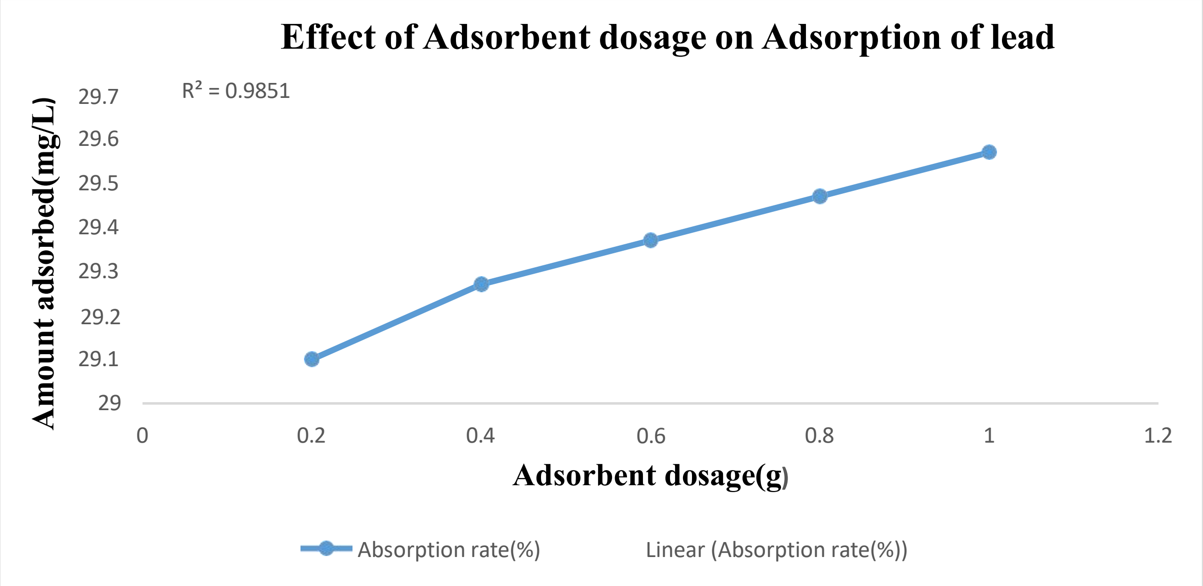

Fig 6: Effect of Adsorbent dosage on Adsorption of Pb^{2+}

DISCUSSION: EFFECT OF ADSORBENT DOSAGE

The mass of adsorbent was adjusted between 0.20 to 1.00 g, and initial lead concentrations remained constant at 30 mg/L. With increasing dosage, the equilibrium adsorption (C_e) diminished from 0.90 to 0.43 mg/L, and percentage removal enhanced from 97.00% to 98.57%.

This enhanced removal efficiency resulting from higher adsorption sites and surface area with higher amounts of clay. But the overall lead removed (mg/L) stayed almost the same, which implies that there was the same level of lead being distributed against a larger adsorbent mass. Therefore, the adsorption capacity per gram of clay (q_e) tends to lower when there are larger dosages. This reverse tendency implies that there could be a tendency towards agglomeration of particles or overlapping of adsorption sites when there are higher concentrations of clay and lower surface area that is actually used to absorb the lead.

Therefore, there is an optimum dosage of adsorbent that lies beyond which addition gives little increment in removal efficiency. This kind of behavior characterizes adsorption systems of natural compound, as in the case of clay (Raji *et al.*, 2023).

TABLE 3.1.2: EFFECT OF AGITATION TIME ON ADSORPTION−Pb^{2+}

S/N	AGITATION TIME(MINS)	INITIAL CONC(mg/L)	EQUILIBRIUM CONC (mg/L)	AMOUNT ADSORBED ±SD (mg/L)	PERCENTAGE ADSORPTION (mg/L)
1	5	30	1.80	28.20±0.03	94.00
2	15	30	1.50	28.50±0.02	95.00
3	30	30	1.00	29.00±0.04	96.67
4	60	30	1.11	28.89±0.02	96.33
5	90	30	0.30	29.70±0.01	99.00
6	120	30	0.30	29.70±0.02	99.00

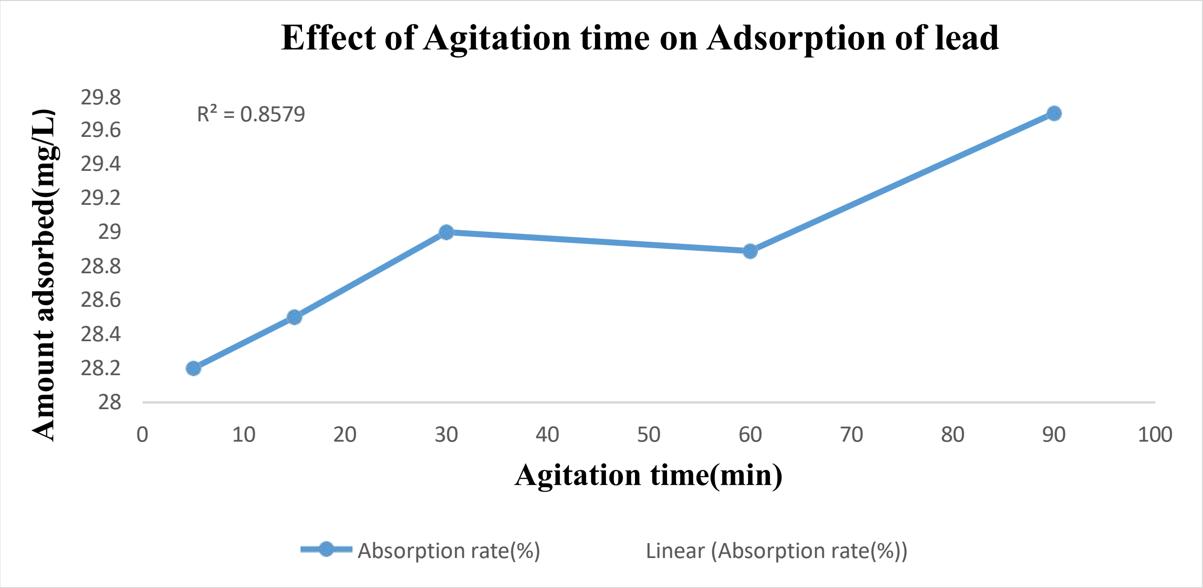

Fig 7: Effect of Agitation time on Adsorption of Pb^{2+}

DISCUSSION: EFFECT OF AGITATION TIME

Results of adsorption as a function of time of contact are as indicated in Table 3.1.2 For the initial concentration of 30 mg/L, adsorption of lead rose steeply in the first 30 minutes and slowly attained an equilibrium value after about 90 minutes, after which a maximum percentage adsorption of 99.00% was attained.

It can be described as consisting of an initial fast adsorption phase. It can be explained as due to the existing huge number of vacant surface sites of the clay that have an easy diffusion as well as lead ion binding. When these sites become increasingly filled, the adsorption rate slows further and finally comes to equilibrium when no further adsorption will take place. This two-stage pattern initial fast stage followed slowly by an equilibrium stage is typical of first film diffusion and intraparticle diffusion-controlled adsorption.

Equilibrium time of 90 minutes obtained in this paper conforms to reports in the literature on lead adsorption from natural clay minerals, verifying that natural clay has a huge potential as a good low-cost adsorbent for heavy metals (Kouadio *et al.*, 2024).

TABLE 3.1.3: EFFECT OF pH ON ADSORPTION –Pb^{2+}

S/N	pH	INITIAL CONC (mg/L)	EQUILIBRIUM CONC (mg/L)	AMOUNT ADSORBED±SD (mg/L)	PERCENTAGE ADSORPTION (%)
1	4	100	5.03	94.97±0.91	94.97
2	5	100	5.43	94.57±0.58	94.57
3	6	100	1.53	98.47±0.61	98.47
4	7	100	0.10	99.90±0.00	99.90
5	8	100	0.10	99.90±0.00	99.90
6	9	100	0.07	99.93±0.06	99.93

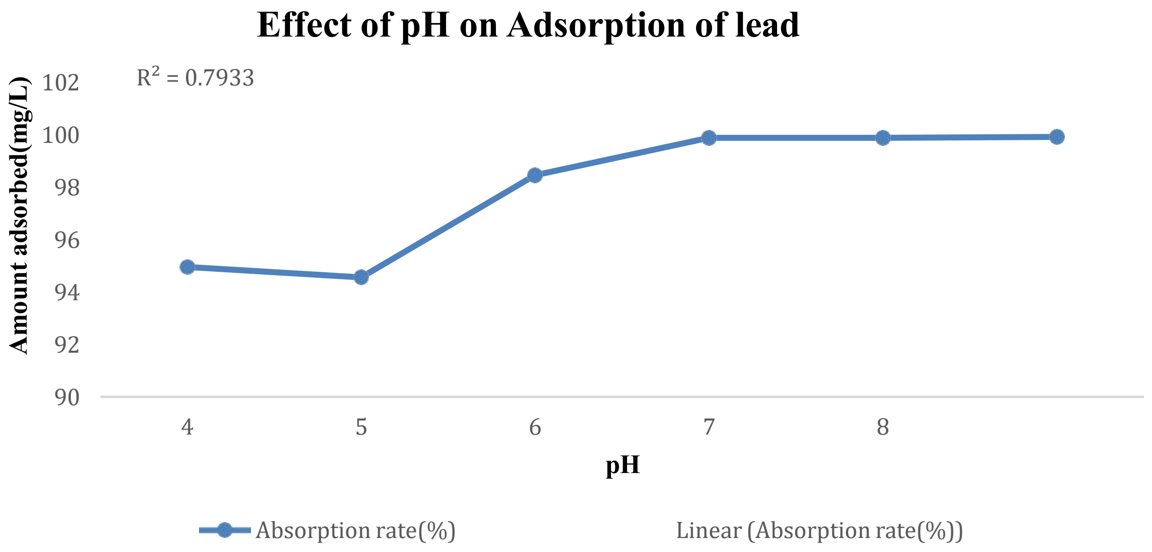

Fig 8: Effect of pH on Adsorption of Pb^{2+}

DISCUSSION: EFFECT OF pH

Removal efficiency ranged from 94.97% efficiency at a pH of 4 to a maximum efficiency of 99.93% at a pH of 9. This high increase in adsorption efficiency when the pH increases can be accounted for based on the ionization characteristic of surface functional groups of the clay and lead ion speciation in solution.

Lowering further the already excess hydrogen ions, which are competing against lead cations for the adsorption sites. With increasing pH, the surface of the clay gets less protonated due to the deprotonation of surface hydroxyl groups, and thus, there is a higher electrostatic attraction to Pb^{2+} ions. Above pH 7, we have to account for the lead hydroxide precipitation ($Pb(OH)_2$) as a possibility since it can spuriously increase the apparent adsorption efficiency. Hence, a range between a pH of 7–8 is taken as optimum for efficient lead elimination as a function of surface adsorption as opposed to precipitation. This behaviour also agrees with Raji *et al.* (2023) and Xie *et al.* (2024), who found increased adsorption of cationic metals at near-neutral to weakly alkaline pH by reason of increased surface negativity.

TABLE 3.1.4: LANGMUIR ADSORPTION ISOTHERM RELATIONSHIP FOR Pb^{2+}

S/N	**Co(mg/L)**	**Ce(mg/L)**	**Ca(mg/L)**	**V(L)**	$q_e\ (\frac{mg}{g})$	$\frac{C_e}{q_e}\ (\frac{g}{L})$
1	10	0.02	9.98	0.1	0.99	0.02
2	20	0.50	19.50	0.1	1.95	0.26
3	30	0.67	29.33	0.1	2.93	0.23
4	40	1.03	38.97	0.1	3.90	0.26
5	50	1.83	48.17	0.1	4.82	0.38

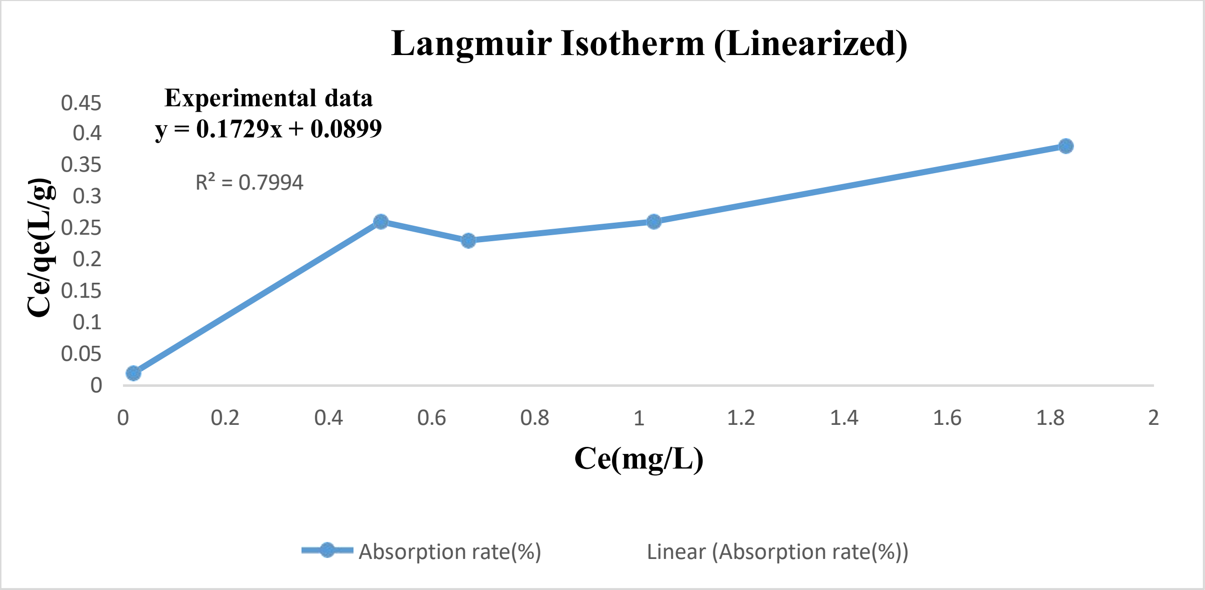

Fig 9: *Langmuir Adsorption isotherm curve for* Pb^{2+}

DISCUSSION: LANGMUIR ADSORPTION ISOTHERM FOR Pb^{2+}

Data on adsorption equilibrium were treated with the isotherm expression for the Langmuir equation, with assumptions for a monolayer adsorption at a surface that is homogeneous with finite identical sites and no interaction with adsorbed ion. The linear form expression is given as:

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

Where Ce is the equilibrium concentration (mg/L), qe is the amount that gets adsorbed per unit mass unit of adsorbent (mg/g), Qmax is the maximum monocritical layer adsorption ability (mg/g), and b is the Langmuir constant that is relevant to the linking energy of the adsorption loci (L/mg).

The graph of Ce/qe versus Ce (Figure 9) provided the following regression equation:

$$\frac{C_e}{q_e} = 0.1729\text{Ce} + 0.0899\ (\text{R}^2 = 0.7994)$$

From the intercept and slope, the Langmuir parameters were then calculated as follows:

Qmax = 1/slope = 1/0.1729 = 5.79mg/g

B = slope/intercept = 0.1729/0.0899 = 1.92L/mg

Correlation coefficient is 0.7994 that shows fairly good agreement between the experimental data and the Langmuir ISO fit. A maximum adsorption capacity of 5.79mg/g was calculated that tells that native clay has significant potential for lead ion removal. But that the correlation coefficient value is below 0.9 shows that surface is not completely uniform and that adsorption might not strictly be ideal monolayer adsorption.

Hence, though the Langmuir isotherm accounts for extensive lead uptake and surface affinity (b value is high), a complete explanation for the system is not given, suggesting that a surface interaction other than simple adsorption at a monolayer level exists (Khamwichit *et al.*, 2022).

TABLE 3.1.5: FREUNDLICH ADSORPTION ISOTHERM RELATIONSHIP FOR Pb^{2+}

S/N	$q_e \frac{(mg)}{(g)}$	Log q_e	Ce(mg/L)	Log C_e
1	0.99	-0.00	0.02	-1.70
2	1.95	0.29	0.50	-0.30
3	2.93	0.47	0.67	-0.17
4	3.90	0.59	1.03	0.01
5	4.82	0.68	1.83	0.26

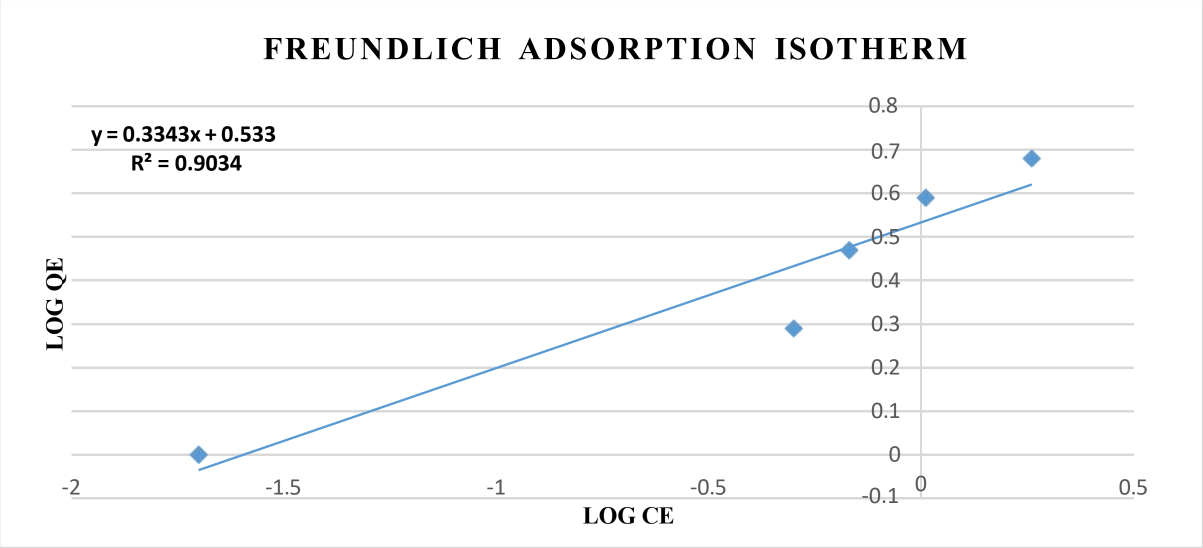

Fig 10: Freundlich Adsorption isotherm curve for Pb^{2+}

DISCUSSION: FREUNDLICH ADSORPTION ISOTHERM FOR Pb^{2+}

The adsorption data at equilibrium were also correlated with the Freundlich isotherm equation, which accounts for adsorption at a heterogeneous surface with sites with different energies and is not limited to adsorption to form a monolayer. In logarithmic form, this is:

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

Where Kf is Freundlich constant related to adsorption capability, and 1/n is intensity of adsorption.

The linear graph of log qe against log Ce (Figure 10) provided the following regression equation:

Log qe = 0.3343 log Ce + 0.5330($R^2 = 0.9034$)

From the slope and intercept:

1/n = 0.3343 → n = 2.99

Kf = $10^{0.5330}$= 3.41

Correlation coefficient ($R^2 = 0.9034$) is a good fit, which means that the Freundlich isotherm is a better fit than the Langmuir isotherm for the adsorption of Pb^{2+} onto untreated clay. The fact that n > 1 also proves that the process was favorable. The relatively high value of Kf proves that there is a strong affinity between lead ion and clay surface. This implies that adsorption is taking place mostly on a heterogeneous surface via multilayer forming, so the Freundlich model is the best description of Pb^{2+} adsorption across untreated clay. A similar conclusion was also reached by Wang and Guo (2020) during their analysis of their work on adsorption isotherms of heavy metals.

TABLE 3.1.6: PSEUDO-FIRST ORDER KINETICS FOR Pb^{2+}

S/N	TIME(min)	Ct(mg/L)	qe(mg/g)	qt(mg/g)	qe-qt (mg/g)	In(qe-qt)
1	5	1.80	3.05	2.82	0.23	-1.47
2	15	1.50	3.05	2.85	0.20	-1.61
3	30	1.00	3.05	2.90	0.15	-1.90

4	60	1.11	3.05	2.89	0.16	-1.83
5	90	0.30	3.05	2.97	0.08	-2.53
6	120	0.30	3.05	2.97	0.08	-2.53

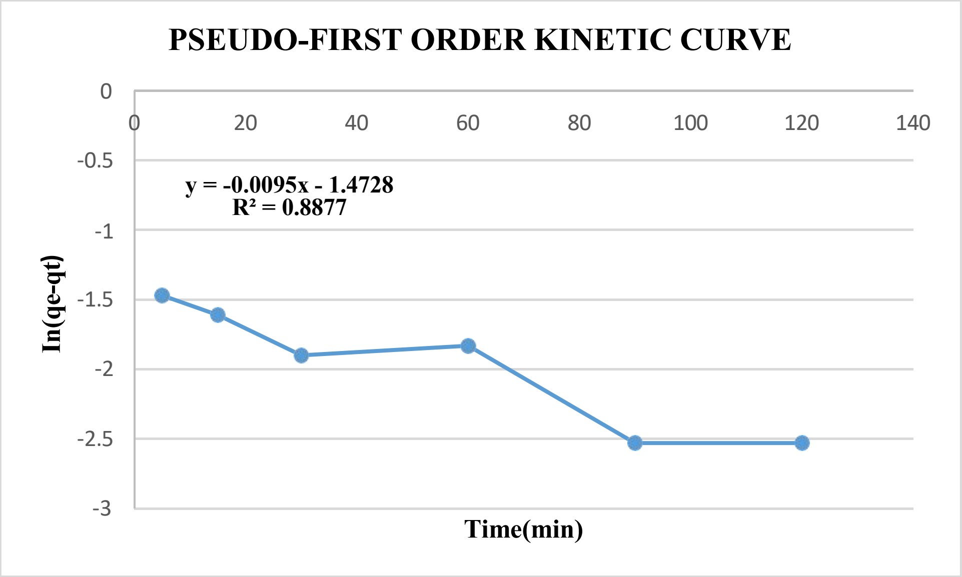

Fig 11: Pseudo-first order kinetic relationship **-Pb^{2+}**

DISCUSSION: PSEUDO FIRST ORDER KINETICS

Data for adsorption have been solved under the pseudo-first-order kinetics assumption that the occupation rate is directly proportional to the unoccupied sites. In the linear version, we have:

In $(q_e - q_t)$ = In $q_e - k1t$

Where qt and qe are the quantities of Pb^{2+} adsorbed at t and equilibrium time (mg/g), and k1 is the constant rate (min^{-1}).

The linear graph of ln (qe – qt) vs t (Figure 11) produced the following regression equation:

In (qe – qt) = -0.0095t – 1.4728 (R^2 = 0.8877)

From the slope and intercept:

K1 = 0.0095 min^{-1}

Qe (calculated) = $e^{-1.4728}$ = 0.23mg/g

The theoretical qe (0.23 mg/g) was significantly less than the experimental value (3.05 mg/g), showing that the pseudo-first-order theory is not fit for Pb^{2+} adsorption on untreated clay.

The relatively low R^2 value (0.8877) verifies that the pseudo-first-order model does not adequately fit experimental data. The divergence indicates physical adsorption alone (which is typical in first-order systems) is not the major process controlling lead adsorption on untreated clay. It is perceivable in observations that the adsorption of heavy metals is generally more than a mere interaction and might involve chemisorption and ion exchange processes (Azanfire *et al.*, 2025).

TABLE 3.1.7: PSEUDO-SECOND ORDER KINETICS FOR Pb^{2+}

S/N	**TIME(min)**	**Ct(mg/L)**	**qt(mg/g)**	$\frac{t}{qt}(\mathrm{min}.\frac{g}{mg})$
1	5	1.00	2.82	1.77
2	15	0.70	2.85	5.26
3	30	0.40	2.90	10.34
4	60	0.40	2.89	20.76
5	90	0.40	2.97	30.30
6	120	0.30	2.97	40.40

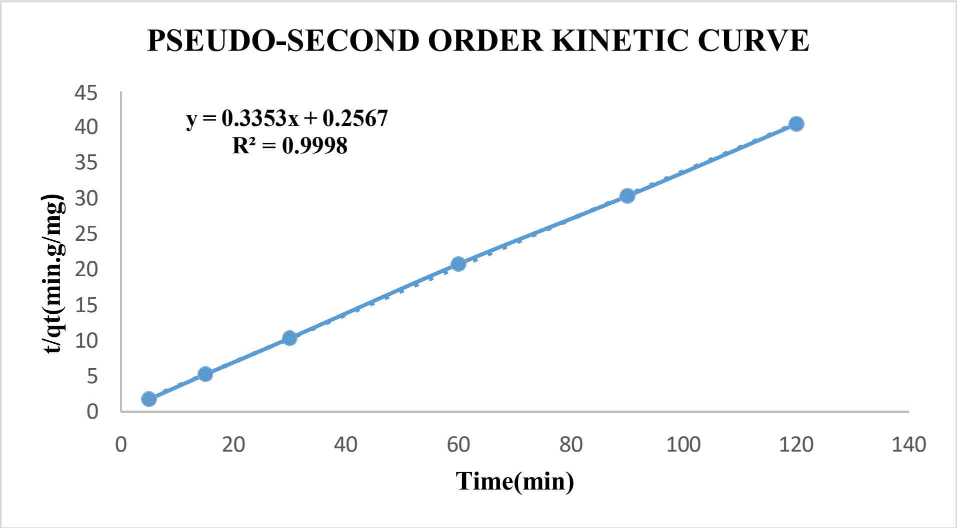

Fig 12: Pseudo-second order kinetic relationship -Pb^{2+}

DISCUSSION: PSEUDO SECOND ORDER KINETICS

The adsorption kinetics was again discussed based on the pseudo-second-order equation that considers that the rate is directly proportional to the square of the vacant sites. The linear form is:

$$\frac{t}{q_t} = \frac{1}{q_{e2}\, k_2} t + \frac{1}{q_e}$$

Where qt and qe are quantities absorbed at time t and equilibrium (mg/g) and K2 is a constant about rates (g/mg·min).

The linear plot of t/qt against t (Figure 12) provided the following regression equation:

$\frac{t}{q_t}$ = 0.3353t + 0.2567 (R^2 = 0.9998)

From the slope and intercept:

The y-intercept

Qe = 1/slope = 1/0.3353=2.98 mg

K2 = 1/ (intercept × qe^2) = 0.44g/mg·min

High value of R^2 (0.9998) suggests good fit, indicating that the pseudo-second-order equation effectively portrays Pb^{2+} adsorption on untreated clay well. The calculated qe (2.98) is very close to the experimental qe value (3.05 mg/g), verifying chemisorption as the preponderant mechanism with electron exchange between Pb^{2+} cations and the surface of the clay.

The almost perfect linear correlation ($R^2 \approx 1.0$) proves that the pseudo-second-order equation efficiently depicts the kinetics of lead adsorption unto untreated clay. This indicates that the chemisorption is the rate-limiting process that can comprise the sharing or exchanging of electrons between the lead ions and the adsorbent surface.

The good matching between the experimental q_e value and the predicted by the model q_e also supports this conclusion. The same findings have been found in literature for metal adsorption experiments on natural adsorbents (Tenea *et al.*, 2024).

3.2 COMPARISON WITH PREVIOUS STUDY

Equilibrium concentrations and kinetics found for Pb^{2+} adsorption on native clay here (Freundlich; Langmuir; pseudo- first and second-order) are typical for wide ranges adsorption documented in the literature, with rather significant variations in capacity and isotherm preference. The key points of agreement and contrast are as follows:

- Many studies document that heavy-metal adsorption on clay minerals and cheap adsorbents is optimally characterized by the pseudo-second-order (PSO) kinetic equation, construed as chemisorption is a function-controlling molecule (Chen and Wang, 2007). For Pb^{2+} alone, various experimental works on kaolinite, palygorskite and functionalized clays concluded that PSO was a significantly better fit than pseudo-first-order (PFO) (Unuabonah *et al*., 2007; Jiang *et al*., 2009). The data gotten corroborate this commonly found behavior: the fit for PSO is very good ($R^2 = 0.9998$) and predicted value concurs with experimental value, favoring chemisorption (sharing of electrons/complexation or ion exchange) as the preponderant kinetic mechanism.

- Isotherm Models (Freundlich vs. Langmuir) Reports in the literature are inconsistent: some researchers achieve improved Langmuir fits (monolayer, uniform sites), whereas others find the best Freundlich behaviour (heterogeneous/multilayer adsorption) occurs. As an example, Jiang et al. (2009) found equilibrium data for their unmodified and modified kaolinite fit well to the Langmuir isotherm (modified kaolin $q_m \backsim 20$ mg/g; unmodified $\backsim 4.2$ mg/g), whereas a series of comparative studies involving minerals in the past found Freundlich often yielded the best fit under specific pH values (Mao *et al*., 2022). Reviews that compile numerous studies also report that both are standard fare with Freundlich favored frequently when the adsorbent surface is a heterogeneous surface (Bayuo *et al*., 2022). Freundlich fit ($R^2 = 0.9034$) is then in agreement with such studies that stress surface heterogeneity for natural clays; the Langmuir fit in this data is less good ($R^2 = 0.7994$), suggesting restricted usability of simple monolayer assumptions for the untreated clay. Listed maximum reported Pb^{2+} capacities on clay minerals cover a wide range depending upon clay type, modification and experimental conditions. Mao et al. (2022) reported common minerality values for common minerals that span many orders of magnitude (montmorillonite ~69.2 mg/g; kaolinite ~18.6 mg/g under specific conditions) significantly higher than the q_m= 5.79mg/g found for the untreated clay.

Jiang et al. (2009) demonstrated that chemical modification works greatly to increase kaolinite capacity ((modified ≈ 20 mg/g vs unmodified ≈ 4.2 mg/g). The literature findings are consistent with the relatively modest q_m in this work:

(i) Lower specific surface area and cation exchange capability for untreated clay compared with montmorillonite or chemically treated clays, and

(ii) A wide variety in experimental parameters ((pH, ionic strength, initial concentration range and adsorbent dosage) significantly impacts measured value for q_m. Therefore, a value for q_m= 5.79mg/g is in no way inconsistent with a raw, untreated clay and falls comfortably between values we see in the literature for typical unmodified kaolin =~4 mg/g) and higher-modified materials =~>10 mg/g).

The Freundlich isotherm model having higher quality indicates energy heterogeneity at adsorption sites and potential multilayer uptake at untreated clay. Mechanistically, untreated clays have a combination of edge sites, basal planes, structural OH groups and exchangeable cations; these provide a series of binding energies so a proportion of Pb^{2+} sites bind tightly (complexation/inner-sphere) while others bind less tightly (outer-sphere or electrostatic).

A number of mechanistic investigations at lead and clay interplay (spectroscopy and selective extract) verify mixed mechanisms (ion exchange, complexation and precipitation at higher pH), that bodes well with a Freundlich description when datasets fall across a series of concentrations/pH values (Mao *et al.*, 2022).

Pseudo-first-order commonly represents physisorption/diffusion-limited uptake. For clay metal compositions in which chemical complexation and ion exchange are significant uptake processes, PFO characteristically provides a less satisfactory fit (poorer R^2 and unrealistically calculated q_e). That pattern is found in the literature (PFO R^2 less than PSO) and is consistent with the result. The variability between PFO and PSO fits is typically assigned to preeminence by chemically controlled steps and to the dependence on the adopted q_e value inherent in linearizing the PFO transform (Chen and Wang, 2007).

3.3 SUMMARY OF RESULTS

The experimental study examined the adsorption behavior of lead (Pb^{2+}) ions on untreated clay to evaluate its potential as a low-cost natural adsorbent. Batch adsorption experiments were carried out to investigate the effects of equilibrium concentration and contact time, and the resulting data were fitted to both isotherm and kinetic models.

The adsorption ability (qe) also rose with the rising Pb^{2+} ion initial focus, 0.99 mg/g at 10 mg/L to 4.82 mg/g at 50 mg/L, showing that active sites at the surface of the clay became more exploited with a rise in focus.

Isotherm analysis determined that both the Freundlich and the Langmuir isotherms had acceptable data fits, although the Freundlich isotherm ($R^2 = 0.9034$) had a higher correlation than that for the Langmuir isotherm ($R^2 = 0.7994$). The maximum adsorption at the Langmuir maximum monolayer was 5.79 mg/g, and the Freundlich constants were 3.41 and 2.99 for Kf and n, respectively, showed that adsorption was favorable and that adsorption was taking place at a heterogenic surface.

Kinetic modeling showed that the pseudo-second-order (PSO) model fitted very well ($R^2 = 0.9998$), correctly predicting the experimental equilibrium capacity (qe = 2.98mg/g). The pseudo-first-order (PFO) model gave a worse correlation ($R^2 = 0.8877$) and underestimated qe, indicating that the rate-controlling process was not physical adsorption but chemisorption, involving valence forces via electron sharing or exchange.

Overall, the results indicated that lead ions were efficiently adsorbed on untreated clay through chemisorption on a heterogeneous surface with various functional sites such as hydroxyl and oxygen groups. The study sheds light on untreated clay's viability in environmental remediation of heavy metals in polluted water systems.

CONCLUSION

Adsorption of Pb^{2+} ions onto untreated clay followed an inclined, spontaneous, and surface-dependent process regulated predominantly by chemisorption. The strong correlation of the pseudo-second-order kinetic model ($R^2 = 0.9998$) ensures that chemical interactions between the lead ions and the active functional groups on the clay surface regulate predominantly the adsorption rate.

The Freundlich Isotherm represented the equilibrium data more accurately than Langmuir model, suggesting that the surface of clay is heterogeneous and multilayer adsorbable. The relatively higher value of n (2.99) and Freundlich constant $Kf = 3.41$ reflects a strong tendency of Pb^{2+} ions toward the untreated clay surface sites.

The moderate Langmuir capacity (qmax =5.79mg/g) suggests that although untreated clay is less efficient than chemically modified clays, it remains a promising, low-cost, and eco-friendly material for lead removal. These results align well with previously reported studies on natural adsorbents and support the potential of untreated clays for wastewater purification applications.

RECOMMENDATIONS

- Surface modification of clay using acids, bases, or organic functional groups is recommended to enhance adsorption capacity and selectivity toward Pb^{2+} and other heavy metals.

- The influence of key parameters such as pH, temperature, concentration, contact time, and ionic strength should be studied in detail to optimize the adsorption process and improve efficiency.

- Continuous-flow column studies and adsorbent regeneration tests should be conducted to evaluate reusability and long-term performance.

- The adsorption efficiency of untreated clay should be tested on industrial effluents and multi-metal systems to assess its real-world applicability.

- Comparative studies between untreated, thermally treated, and chemically modified clays would help identify the most cost-effective and efficient adsorbent for large-scale environmental cleanup.

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